Produção de policristais sintéticos de CaSiO\(_3\) e seu estudo como novos detectores de radiação gama, nêutrons térmicos e íons acelerados

Carlos David Gonzales Lorenzo

Orientador: Prof. Dr. Shigueo Watanabe
Coorientador: Prof. Dr. Nilo Cano Mamani

Tese de doutorado apresentada ao Instituto de Física da Universidade de São Paulo, como requisito parcial para a obtenção do título de Doutor em Ciências.

Banca Examinadora:
Prof. Dr. Shigueo Watanabe (Orientador/IFUSP)
Profa. Dra. Sonia Hatsue Tatumi (EPUSP)
Profa. Dra. Márcia de Almeida Rizzutto (IFUSP)
Profa. Dra. Susana de Souza Lalic (UFS)
Prof. Dr. René Rojas Rocca (UNIFESP)

São Paulo
2019
Gonzales Lorenzo, Carlos David

Produção de policristais sintéticos de CaSiO3 e seu estudo como novos detectores de radiação gama, nêutrons térmicos e íons pesados. São Paulo, 2019.

Tese (Doutorado) – Universidade de São Paulo. Instituto de Física, Depto. de Física Nuclear.

Orientador: Prof. Dr. Shigueo Watanabe
Área de Concentração: Física das radiações

Unitermos: 1. Dosimetria termoluminescente; 2. Radiação gama; 3. Nêutrons; 4. Íons pesados; 5. Medicina nuclear.

USP/IF/SBI-096/2019
Production of synthetic polycrystals of CaSiO$_3$ and their study as new detectors of gamma radiation, thermal neutrons and accelerated ions

Carlos David Gonzales Lorenzo

Supervisor: Prof. Dr. Shigueo Watanabe
Co-supervisor: Prof. Dr. Nilo Cano Mamani

Thesis submitted to the Physics Institute of the University of São Paulo in partial fulfillment of the requirements for the degree of Doctor of Science.

Examiner Committee:
Prof. Dr. Shigueo Watanabe (Supervisor/IFUSP)
Prof. Dr. Sonia Hatsue Tatumi (EPUSP)
Prof. Dr. Márcia de Almeida Rizzotto (IFUSP)
Prof. Dr. Susana de Souza Lalic (UFS)
Prof. Dr. René Rojas Rocca (UNIFESP)

São Paulo
2019
Dedico este trabalho para toda minha família,
em especial para minha mãe quem foi o meu
suporte ao longo da minha vida pessoal e
acadêmica. Muito obrigado, família querida.
Agradecimentos

Em especial ao prof. Shigueo Watanabe pela sua orientação, paciência, disposição e apoio no desenvolvimento deste trabalho, incentivando a maioria das minhas decisões, agradeço muito.

Ao Conselho Nacional de desenvolvimento Científico e Tecnológico (CNPq) pelo apoio financeiro.

À Eng. Elizabeth Ribeiro Somessari, ao Eng. Carlos Gaia da Silveira do CTR-IPEN-SP; ao Aldo Oliveira e Vicente de Paulo Campos do GMR-IPEN-SP pelas inúmeras vezes que nos atenderam gentilmente para as irradiações gama realizadas neste trabalho.

À Professora Carmen Cecilia Bueno do Centro de Tecnologia das Radiações - IPEN pela ajuda nas irradiações com nêutrons no reator nuclear de pesquisa IEA-R1 do IPEN.

Ao Prof. Gundu Rao pela análise das medidas de EPR as quais ajudaram muito no aprimoramento do presente trabalho, e pela ajuda na revisão do inglês.

Ao prof. Satoshi Kodaira do Instituto Nacional de Ciências Radiológicas (NIRS) em Chiba-Japão e à Dra. Luana Nascimento do Centro Belga de Pesquisa Nuclear (SCK-CEN) pela ajuda nas irradiações das nossas amostras com prótons e íons de carbono no NIRS.

Ao Prof. Sergey Nikiforov e à colega Daria Ananchenko do Instituto de Física e Tecnologia da Universidade Federal dos Urais em Ecaterimburgo - Rússia por me aceitar no seu laboratório como parte de um estágio de pesquisa.
Ao Dr. Tássio A. Cavalieri do Centro de Engenharia Nuclear do Instituto de Pesquisas Energéticas e Nucleares (CEN-IPEN-SP) pela importante colaboração e ajuda com as simulações de Monte Carlo.

À Nancy Kuniko Umisedo do Laboratório de Dosimetria do IFUSP pelas irradiações com raios X.

Aos Professores Nilo Cano, René Rojas e Fernando Chubaci pela paciência, compreensão e pela sua disponibilidade para responder às minhas dúvidas no desenvolvimento deste trabalho.

À Dra. Roseli Gennari pela ajuda na mistura das amostras e pelas sugestões na produção dos policristais usados neste trabalho.

À Edna Toledo pela ajuda e disposição nos processos burocráticos e os muitos momentos agradáveis na hora do café no LACIFID.

Aos colegas do LACIFID, Bruno, Antônio, Edy, Monise, Noemi, Lucas, Rogerio, Bruna, Leticia, Rafaela, Ellen, Juanito e Luis por ter me acompanhado nesta viagem de formação acadêmica.

Aos amigos do IF-USP, Heyner, Naupa, Victor, Fernando, Jose, Dianita, Gustavo, Rodrigo, Erik, Causha, Martin, Rene, Héctor, Tania, Lindber, e Julio, por me acompanhar nas muitas atividades tanto acadêmicas como pessoais nestes anos de estudo.

Aos meus grandes amigos de longa data, Judith Huaranca Aliaga, Simone Palmeiras, Nilo Barrantes Melgar e Elizabeth Pastrana Alta pelo grande apoio tanto no aspecto profissional quanto pessoal.

Agardo também a todas as pessoas que estiveram ao meu lado me apoiando, direta ou indiretamente, muito obrigado.
“Com sabedoria se constrói a casa, e com discernimento se consolida. Pelo conhecimento os seus cômodos se enchem do que é precioso e agradável.” Provérbios 24:3-4
Resumo

Neste trabalho, policristais sintéticos de silicato de cálcio (CaSiO₃) foram preparados. O objetivo é ampliar o conhecimento atual dos detectores termoluminescentes de baixo custo e fácil produção para doses de radiação gama, nêutrons térmicos e feixe de íons acelerados e suas possíveis aplicações em medicina nuclear e radioterapia. Por essa razão o silicato de cálcio dopado com boro, cádmio, disprósio e európio foram produzidos tendo em mente a detecção de radiação gama e de nêutrons. Para a produção de policristais de silicato de cálcio sintético, foi utilizado o método de devitrificação. Nesse processo, foram identificados dois polítipos de CaSiO₃ não dopados, α- e β- CaSiO₃. O α-CaSiO₃ é um detector de radiação gama muito sensível, com o pico principal de termoluminescência (TL) ocorrendo em 250-270 °C e um pico de baixa temperatura a 120 °C utilizando uma taxa de aquecimento de 4 °C/s. A resposta TL do α-CaSiO₃ é linear para a dose < 10 Gy e, em seguida, apresenta um comportamento supralinear até 7 kGy, depois disso entra em saturação. O comportamento de TL muda muito pouco dopando com B, Cd e Dy, enquanto o dopado com o Eu traz mudanças. Além disso, o polycrystal β-CaSiO₃ exibe três picos TL em 124, 250 e 306 °C. Todos estes picos têm um comportamento linear no intervalo de doses de cGy a 1 Gy. Depois disso, as respostas de TL são supralineares até cerca de 3 kGy e depois são saturadas.

Policristais sintéticos de CaSiO₃ (aqueles dopados e não dopados) foram também irradiados com nêutrons de um reator de pesquisa nuclear. Os nêutrons térmicos reagem com o Ca, Si e O através do processo (n, γ), toda ou parte da radiação gama emitida nessa reação é absorvida pela amostra e é responsável pela indução de TL. A energia total emitida pela reação (n, γ) na amostra de CaSiO₃ não dopado foi calculada analiticamente. Além disso, simulações de Monte Carlo usando o código de transporte de radiação MCNP5 foram realizadas no Centro de Engenharia Nuclear no IPEN para calcular a dose depositada na amostra de CaSiO₃ pela interação com os nêutrons do reator, encontrando doses variando de 42 Gy até 21 kGy. As curvas de TL do CaSiO₃,
após a exposição à radiação do reator, exibem o principal pico proeminente de TL em torno de 234 - 259 °C.

A Ressonância Paramagnética Eletrônica (RPE) foi usada para estudar os centros de defeitos induzidos nos policristais de α- e β-CaSiO₃ por irradiação gama e para identificar os centros responsáveis pelo processo de TL. Para β-CaSiO₃, três centros de defeitos contribuem para o espectro observado à temperatura ambiente. O centro I com os principais valores g = 2.0135, 2.0094 e 2.0038 é atribuído ao íon O⁻ e o centro parece ser o centro de recombinação para os picos de TL em 124 °C, 147°C e 306 °C. O Centro II que exibe um valor g isotrópico de 2.00025 é identificado como um centro F⁺. Também é observado que o centro F⁺ é um centro de recombinação para vários picos de TL. O centro III é atribuído a um centro de Ti³⁺ exibindo um tensor g ortorrômbico com valores principais de g₁ = 1.9830, g₂ = 1.9741 e g₃ = 1.9046. Este centro está associado aos picos de TL em 124 e 147 °C. O espectro de emissão TL de β-CaSiO₃ mostra duas bandas de emissão em 370 e 520 nm.

Além disso, pastilhas de CaSiO₃ foram irradiadas com um feixe de prótons de 160 MeV e com um feixe de íons de carbono de 290 MeV/n no sincrotron HIMAC no Instituto Nacional de Ciências Radiológicas (NIRS) em Chiba, Japão. As pastilhas de silicato de cálcio apresentaram um pico de TL em 120 °C e um pico proeminente em 270 °C quando irradiados com próton e feixe de íons de carbono. A dose lida no leitor Harshaw TL apresentou boa concordância com as doses encontradas na câmara de ionização no caso de feixes de prótons e um pouco menos no caso de feixes de carbono devido à dependência da transferência linear de energia (LET).

**Palavras-chave:** Policristais sintéticos, Silicato de Cálcio, Devitrificação, Termoluminescência, Dosimetria Gama, Nêutrons Térmicos, Dosimetria de Nêutrons, Ressonância Paramagnética Eletrônica, Centros de Defeitos, Irradiação de prótons e íons de carbono, Dosimetria de íons acelerados, Pastilhas de CaSiO₃.
Abstract

In this work, synthetic polycrystals of calcium silicate (CaSiO$_3$) are prepared. The objective is to expand the current knowledge of low cost and easy production thermoluminescent detectors for doses of gamma radiation, thermal neutrons and accelerated ions beam, as well as, the possible applications in nuclear medicine or monitoring actual radiotherapy treatment. For that reason, calcium silicate doped with Boron, Cadmium, Dysprosium, and Europium were produced keeping in mind gamma and neutron detection. For the production of synthetic calcium silicate polycrystals, the devitrification method was used. In this process, two polytypes of undoped CaSiO$_3$ were identified, $\alpha$- and $\beta$- polytypes. $\alpha$-CaSiO$_3$ is a very sensitive gamma radiation detector with main prominent thermoluminescence (TL) peak occurring at about 250-270 °C and a low-temperature peak at 120 °C, using 4 °C/s heating rate. The TL response of $\alpha$-CaSiO$_3$ is linear for dose < 10 Gy and then has a supralinear behavior up to about 7 kGy and saturating beyond. The TL behavior changes very little by doping with B, Cd, and Dy while Eu doping brings changes. Additionally, $\beta$-CaSiO$_3$ polycrystal exhibits three TL peaks at 124 °C, 250 °C, and 306 °C. All peaks at 124, 250 and 306 °C for $\beta$-CaSiO$_3$ have a linear behavior in the dose range from cGy to 1 Gy. After that, the TL responses are supralinear up to about 3 kGy and then they are saturated.

Synthetic polycrystals of CaSiO$_3$ (doped or not) were also irradiated with neutrons from a nuclear research reactor. This thermal neutron reacts with Ca, Si and O through (n, $\gamma$) process, all or part of the gamma emitted in this reaction is absorbed by the sample and is responsible for the induction of TL. The total energy emitted by the (n, $\gamma$) reaction on the sample of CaSiO$_3$ was calculated analytically. Furthermore, Monte Carlo simulations using the MCNP5 radiation transport code was carried out at the Nuclear Engineering Center in IPEN to calculate the deposited dose on CaSiO$_3$ by the neutron interaction finding doses ranging from 42 Gy to 21 kGy. CaSiO$_3$ TL
glow curves, after radiation exposure from the reactor, display the main prominent TL peak around 234 - 259 °C.

Electron paramagnetic resonance (EPR) spectroscopy was used to study the defect centers induced in the polycrystals of α- and β-CaSiO₃ by gamma irradiation and to identify the centers responsible for the TL process. For β-CaSiO₃, three defect centers contribute to the observed spectrum at room temperature. Center I with principal g-values = 2.0135, 2.0094 and 2.0038 is attributed to O⁻ ion and the center appears to be the recombination center for 124, 147, and 306 °C TL peaks. Center II exhibiting an isotropic g-value of 2.00025 is identified as an F⁺-center. F⁺-center is also observed to be a recombination center for several TL peaks. Center III is assigned to a Ti³⁺ center displaying an orthorhombic g-tensor with principal values g₁ = 1.9830, g₂ = 1.9741 and g₃ = 1.9046. This center is associated with 124 °C and 147 °C TL peaks. TL emission spectrum of β-CaSiO₃ shows two emission bands at 370 and 520 nm.

In addition, pellets of CaSiO₃ were irradiated at 160 MeV proton beam and at 290 MeV/n carbon ion beam from an upper synchrotron of HIMAC (Heavy Ion Medical Accelerator in Chiba, Japan) at NIRS (National Institute of Radiological Sciences). These pellets of calcium silicate presented a prominent TL peak at 120 °C and at 270 °C when irradiated with proton and carbon ion beam. The dose read out in Harshaw TL reader presented a good agreement with doses found using ion chamber in the case of proton beams and slightly less in the case of carbon beam due to the linear energy transference (LET).

**Keywords:** Polycrystal, Calcium Silicate, Devitrification Method, Thermoluminescence, Gamma dosimetry, Thermal Neutrons, Neutron dosimetry, Electron Spin Resonance, Defect center, Proton and Carbon beam irradiation, Ion beam dosimetry, Pellets of CaSiO₃.
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Chapter 1

Introduction

1.1 Ionizing radiation: history

The history of radiation has its beginnings since the discovery of X-ray by Roentgen in 1895. He found using a Crookes tube, or cathode ray tube, that besides the cathode rays there was another type of radiation that could go through the glass tube, which he called X-rays. These X-rays could easily pass through the human body and in front of a photographic plate displayed the shade left by the bones; it led to numerous applications in medicine. Radioactivity was found by Becquerel in 1896 when he observed emission of radiation from salts of uranium that could pass through the metal foil and darkened a photographic plate. Moreover, the discovery of radium and polonium by Marie and Pierre Curie in 1898 was an important addition [1].

The use of X-rays and of radiation from radioactivity grew rapidly, accompanied by an increase in the negative effect of these radiations on human health. In 1897, the first cases of the X-rays overexposure effect on the human body like skin burns, hair loss, and cancer was reported. These events led the researchers, in those years, to the important necessity to discover the origin and nature of X-rays.

J.J. Thomson, in 1897, with cathode ray tubes, showed that all atoms contain small subatomic particles with a negative charge, called electrons. These cathode ray tubes
are sealed glass tubes from which most of the air has been evacuated. Then a high voltage was applied across two electrodes (cathode and anode) inside the cathode ray tubes both located at one end of the tube. The cathode is the negatively charged electrode and anode being the positively charged electrode. This high voltage between the electrodes produces a particle beam from the anode towards the cathode. After that, Thomson placed two oppositely charged electrical plates around the cathode ray on the other end of the tube. Thomson observed the cathode ray was deflected away from the negatively charged electric plate and towards the positively charged plate. Thomson also placed two magnets between the cathode ray in which the magnetic field produced deflected this cathode ray in the same way that the charged electrical plates. This indicated that the cathode ray was composed of negatively charged particles. Additionally, Thomson knew that atoms had an overall neutral charge and proposed in 1904 the first atomic model also known as the plum pudding model of the atom. This model could be described as negative particles floating within a soup of diffuse positive charge.

Another important experiment was performed by Ernest Rutherford in 1911. Rutherford based on Thomson’s plum pudding model bombarded a high energy stream of $\alpha$-particles from a radium source on a thin gold foil. The main purpose in this experiment was the deflection produced in the trajectory of $\alpha$-particles after interaction with the thin gold foil. For this reason, Rutherford placed a screen made up of zinc sulfide that would flash when hit with an $\alpha$-particle. He observed that almost all of the $\alpha$-particle passed through the foil but a few of these particles (about 1 in 20,000 particles) were deflected more than 90° from their trajectory. These results led Rutherford to conclude that the positive charge in the atom is concentrated in a small region of space at its center containing most of the atom’s mass. In addition, he concluded that the atom must be formed mostly by empty space since most of the $\alpha$-particle passed straight through the gold foil. After that, other important discoveries were found giving place to the modern physics that we currently know, between them, the Planck’s radiation law, the photoelectric effect, and the Bohr’s theory of the atom in 1913.

All these discoveries helped scientists to explain X-rays. It turns out that two different
mechanisms are present in the production of X-rays. The first process occurs when the fast electrons that come out from the cathode collide with the metal atoms of the anode. If these electrons have enough energy, they can remove the electrons from the inner layers of the atom leaving a free vacancy. This vacancy is then filled by an electron of higher layers releasing an X-ray photon. In the second place, the emission of X-rays is given by electrons from the cathode when they are dispersed by the strong electric field of the high-Z atomic nucleus in the anode. This type of emission is also known as braking radiation or bremsstrahlung. In both cases, a high-energy photon is emitted that allows these X-rays to pass through solid matter. A clear example is shown in the human body, where x-rays are not blocked by human tissue cells but partially blocked by the high density of bone tissue. Thus, if an X-ray or any gamma radiation hits a molecule while traveling within the body, it can divide it and break the chemical bonds that hold it together. These interactions, if are present in large quantities, can cause real damage to living tissue. In this sense, the radiation is named ionizing radiation.

## 1.2 Ionizing radiation in human activities

As was briefly explained earlier, after the discovery of X-rays soon followed by interests in applying in medicine such as radiography of bones or other organs of a man. Currently, sophisticated electronic devices are used for diagnostic as well for treatment of patients such as X-rays radiography, fluoroscopy, computed tomography (3D images), nuclear medicine scintigraphy, linac accelerators for radiotherapy [2].

The use of ionizing radiation in the industry has increased substantially during the 1950s and radiation sources as cobalt-60 and cesium-137 became available for industrial utilization. One of the most known industrial applications is for radiation processing of polymeric materials which is a practical and economical method for modifying the chemical and physical properties of polymers. Among this type of application, we found the cross-linking of polymers to improve heat tolerance and the resistance to abrasion.
and solvents [3]. In addition, the use of ionizing radiation in industry alimentary as such food preservation is one the most known application used in the past. Mobile irradiation facilities were also used, such as, for inhibiting sprouting of potatoes and in fisheries research vessel carrying an X-ray facility able to treat quantities of fish [4, 5].

The decontamination process is another important ionizing radiation application. For example, in the radiation processing of sewage and sludge for the elimination of microorganisms in São Paulo, Brazil, an electron beam accelerator is used instead of a gamma source because this type of accelerators are more suitable due to versatility and lower costs, and with the advantage that these types of equipment can be turned on and off instantaneously thus facilitating control, contrary to gamma sources [6].

Currently, the IAEA has developed several programs of ionizing radiation applications in order to help developing countries. The flagship publication of the IAEA in March 2018 named “Atoms for Peace and Development: working towards the Sustainable Development Goals” [7] shows different kinds of applications. Among them, Nuclear technique to eradicate insect pests and resumed fruit and vegetable exports in the Dominican Republic and the use of nuclear techniques of saving fertile land and preserving water quality in Morocco.

Another important application nowadays and with the IAEA’s support involves the transfer of technology for virus detection based on Reverse Transcription Polymerase Chain Reaction (RT-PCR) to assist Latin American and Caribbean countries. This equipment uses an efficient nuclear-derived technique in early detection of Zika virus, which has affected many countries in the region. Additionally, the IAEA has developed a new technical cooperation project named Sterile Insect Technique (SIT) to complement other efforts aimed at suppressing the Aedes aegypti mosquito population, which transmits viruses such as Zika [7]. In this way, as has been shown in this section, there are many ways to ionizing radiation application keeping in mind the benefits in humanity. All of this application, of course, must have a radiation protection system to safeguard the health of operators.
Chapter 2

Radiation dosimetry

Radiation dosimetry is the determination of the deposited energy by the ionizing radiation (directly or indirectly) in a given matter of unit mass. During the 1920s, it was suggested to establish quantitative measurements of radiation. Consequently, the First International Congress of Radiology in 1920, created the International Commission on Radiation Units and Measurements (ICRU) in order to establish international standards for radiation units & measurement.

In 1937 the ICRU (ICRU 1938) has established: “The international units of ‘quantity’ or ‘dose’ of X-rays shall be called roentgen and expressed as $r$. That roentgen shall be the quantity of X or $\gamma$ radiation such that the associated corpuscular emission per 0.001293 gram of air produces, in air, ions carrying 1 e.s.u. of quantity of electricity of either sign.” This expression was confusing among the scientists because expressions of ‘quantity’ and ‘dose’ were unclear.

The ICRU did not make any recommendations during the Second World War but the use of nuclear reactors, high-energy accelerators and unfortunately the use of atomic weapons were becoming more common. That is why there was a need to establish new quantities in dosimetry that not only include X-rays or gamma rays but also new and more energetic types of radiation such as neutrons, mixed neutron - $\gamma$, $\beta$ and $\alpha$ particles.
It was also important to define a physical quantity that quantifies the amount of radiation absorbed in materials and in the human body. Thus, in 1953, the ICRU established a quantity called absorbed dose, which meant a great advance in the improvement of dosimetry terminology [8]. The ICRU (ICRU 1954) established that the absorbed dose of any ionizing radiation is the amount of energy imparted by this ionizing radiation per unit mass of the material irradiated at the place of interest. This amount is expressed in rad and it is equal to 100 erg per gram.

2.1 Importance of radiation dosimetry for humanity

In recent years, the use of different types of radiation is becoming increasingly widespread in various human activities such as the intensive development of radiation technologies, testing, sterilizing and processing materials. In nuclear facilities with high-energy accelerators for research (e.g. Large Hadron Collider LHC); in cancer radiotherapy treatments, and in fission and fusion energy facilities, Obryk et al. (2014) ionizing radiation is involved. Therefore, the use of ionizing radiation, which is carcinogenic, must always be associated with an efficient radiological protection system as a means of safety. For instance, it is very common to use of dosimeters as radiation detectors to monitor people who often work with radiation sources in medical centers or nuclear facilities.

Currently, the International Atomic Energy Agency (IAEA) has established the International Standard in Radiation Protection that involves safe and effective use of radiation in medicine. The IAEA was created in 1957 in order to bring the use of nuclear technology for non-military purposes but for peaceful purposes (“Atoms for Peace”) within the United Nations family. The IAEA is a government agency, with 170 member states (as of 30 April 2018). It is the official organization for establishing international safety standards. For this purpose, the IAEA has published several scientific and technical works related to the radiation protection and safety of radiation
sources; radioactive waste management; transport of radioactive material; government-
mental, legal and regulatory - framework in safety infrastructure; nuclear power plants; among others [9].

On the other hand, the International Commission on Radiological Protection (ICRP) is another important non-government entity. The ICRP was created in 1928 in order to respond and give recommendations to the constant concerns where the ionizing radiation was involved. Periodically the ICRP publishes its scientific publications in order to give recommendations in the area of radiological protection. For this purpose, the ICRP periodically edits its recommendations and advice in its own series of publications called “Annal of the ICRP”. In 2007, the ICRP published “The 2007 Recommendations of the International Commission on Radiological”[10], in which, the recommendations for the radiological protection system of 1990 are updated and consolidated. In this new edition, an additional guide in the control of exposure from radiation sources was issued from 1990.

Among the quantities used in radiological protection in this publication [10] we have,

(1) The *Absorbed dose* ($D$): this is the basic physical dose quantity, which is used for all types of ionizing radiation and any irradiation geometry [10]. It is defined as $\frac{dE_m}{dm}$, where $dE_m$ is the mean energy imparted to matter of mass $dm$ by ionizing radiation. The SI unit of absorbed dose is J·kg$^{-1}$ also known as gray (Gy).

(2) *Equivalent dose* ($H_T$) and *radiation weighting factors* ($w_R$): the equivalent dose in an organ or tissue (whose unit is the sievert (Sv): J·kg$^{-1}$) ($H_T$) is defined by equation 2.1,

$$H_T = \sum_R w_R \cdot D_{T,R}$$  \hspace{1cm} (2.1)$$

where $w_R$ is the radiation weighting factor for radiation R and the average absorbed dose ($D_{T,R}$) in the volume of a specified organ or tissue T due to radiation of type R [10]. $H_T$ is considered over all types of radiations involved.
Table 2.1: Recommended tissue weighting factors. After [10].

| Tissue                                      | $w_T$ | $\sum w_T$ |
|---------------------------------------------|-------|------------|
| Bone-marrow, Colon, Lung, Stomach, Breast, Remainder tissues | 0.12  | 0.72       |
| Gonads                                      | 0.08  | 0.08       |
| Bladder, Oesophagus, Liver, Thyroid         | 0.04  | 0.16       |
| Bone surface, Brain, Salivary glands, Skin  | 0.01  | 0.04       |
| **Total**                                   | 1.00  |            |

(3) Effective dose and tissue weighting factors: the effective dose ($E$) is defined by a weighted sum of tissue equivalent doses by equation 2.2,

$$E = \sum_T w_T \cdot H_T = \sum_T w_T \sum_R w_R \cdot D_{T,R}$$  \hspace{1cm} (2.2)

where $w_T$ is the tissue weighting factor for tissue $T$ and $\sum w_T = 1$ as shown in Table 2.1. The sum is performed over all tissues and organs of the human body. The unit of effective dose is the sievert (Sv).

All medical procedures where radiation exposure is involved usually have a dose measurement system for professionals, patients, and the public for radiological protection purposes [11]. In radiotherapy, for example, the most used techniques for dosimetric quality assurance are (1) the ionization chamber, (2) thermoluminescence (TL) and optically stimulated luminescence (OSL) dosimeters, (3) diodes and (4) metal-oxide-semiconductor field-effect transistors (MOSFETs). Diodes, for instance, give an instantaneous readout, for this reason, it is commonly used for in vivo dosimetry, however, their calibration factor is temperature-dependent and they have a non-uniform angular response to radiation. MOSFET dosimeters are free of the above drawbacks, but their lifetime is limited. On the other hand, the use of TL and OSL dosimeters implies different processes, such as heating, light exposure, and annealing, before to obtain a final result. In this case, an instantaneous or near-instantaneous dose readout is not possible [12].


2.2 Radiation dosimeters

Besides TL dosimeters (TLD), a radiation dosimeter is an instrument or system whose purpose is to measure, either directly or indirectly, different dosimetric quantities, such as, the quantity exposure, kerma, absorbed dose or equivalent dose. Thus, the measurements process means of finding a value to express an experimental quantity using a dosimetric system [13].

The most popular usable dosimeters are polymeric-alanine, radio-photoluminescent glass detectors, optical absorption dosimeters (individual LiF crystals), liquid chemical dosimeters such as Fricke’s dosimeters and calorimeters. In addition, the photographic emulsion was one of the first to be used as radiation dosimeters. This emulsion consists of microscopic grains of silver bromide (AgBr) which is dispersed in a gelatin layer on a supporting film. After irradiation with charged particles, ion pairs are produced and Ag\(^+\) ions are converted to Ag atoms leaving behind an opaque microscopic grain of silver. Scintillator and semiconductor detectors are solid-state detectors. Scintillator detectors are based on scintillation, that is, light emission after absorption of radiation and also known as phosphors. Semiconductor detectors are formed by intrinsic semiconductors with very high bulk resistivity such as CdS or CdSe [13].

Among the solid-state detectors, there are luminescence dosimeters (which are generally ionic crystals but can also be semiconductors and glasses), characterized by the fact that after being irradiated the solid absorbs part of the radiation energy and this energy is used to promote an electron from ground states to metastable states. With heating, the electrons in metastable states are brought back to ground states, emitting light. This is the emission of light by thermal stimulation, known as thermoluminescence (TL). We can use light to stimulate the emission of light by light. This is optically stimulated luminescence - OSL. Furthermore, thermoluminescence detectors or TLDs are those in which they are previously excited by heating, and optically stimulated luminescence (OSL) detectors are those in which they are previously excited by light.
On the other hand, there are other types of radiation instruments used as survey monitors; these are the gas-filled detectors. For instance, the ionization chamber, Geiger-Müller and proportional counter are types of gas-filled detectors. According to the design and the voltage applied between the two electrodes on these detectors, these can work in three different regions called the ionization region, proportional region or Geiger-Müller (GM) region. In addition, thermal neutron detectors are commonly coated with a boron compound inside of the wall of the counter, or also is filled with a BF$_3$ gas. In this way, when a thermal neutron interacts with a $^{10}$B nucleus it causes a reaction (n, $\alpha$), and the $\alpha$ particles can be detected by their ionizing interaction [13].

The IAEA book entitled “Radiation oncology physics: a handbook for teachers and students” [13] shows the main advantages and disadvantages of the most commonly used dosimetric systems. Table 2.2 shows three of them, ions chambers, films and TLDs.

2.3 Thermoluminescence (TL): history and current status

Thermoluminescence as an experimental technique gained much popularity in the second half of the last century due to its great versatility and its possible applications in different branches of science such as archeology, geology, medicine, solid-state physics, biology among others [14].

Thermoluminescence is a phenomenon observed in ionic crystals (sometimes semiconductors and glasses) that have been previously irradiated and the crystals emit visible light when heated. That is, thermoluminescence is a thermally stimulated emission of light from this ionic crystal after absorption of energy when it was exposed to ionizing radiation (X-rays; gamma, neutron or ions radiation). The study of thermoluminescence and its applications in several different fields of application began in the University of Wisconsin, USA, during the 1950s by Farrington Daniels and his research
Table 2.2: Main advantages and disadvantages of the most commonly used dosimetric systems [13].

| Dosimeter       | Advantages                                                                 | Disadvantages                                                                 |
|-----------------|---------------------------------------------------------------------------|-------------------------------------------------------------------------------|
| Ionization chamber | - Accurate and precise                                                  | - Connecting cables required                                                   |
|                  | - Recommended for beam calibration                                       | - High voltage supply required                                                 |
|                  | - Necessary corrections well understood                                   | - Many corrections required for high energy beam dosimetry                    |
|                  | - Instant readout                                                         |                                                                               |
| Film             | - 2-D spatial resolution                                                  | - Darkroom and processing facilities required                                  |
|                  | - Very thin: does not perturb the beam                                     | - Processing difficult to control                                              |
|                  |                                                                         |                                                                                |
| TLD              | - Small in size: point dose measurements possible                         | - Signal erased during readout                                                 |
|                  | - Many TLDs can be exposed in a single exposure                           | - Easy to lose reading                                                         |
|                  | - Available in various forms                                              | - No instant readout                                                           |
|                  | - Some are reasonably tissue equivalent                                   | - Accurate results require care                                                |
|                  | - Not expensive                                                           | - Readout and calibration time                                                 |
|                  |                                                                         | - Not recommended for beam calibration                                         |

group. Furthermore, they were the first to propose the use of thermoluminescence as a mean of radiation dosimetry [14].

There are several books that explain the theory regarding thermoluminescence as well as the use and properties of dosimetric materials [14, 15]. We will go into more detail about the thermoluminescence phenomenon and their characteristics later, in the theoretical revision chapter. Now, we will introduce some details about the characteristics of dosimetric materials as well as the most known and currently used dosimeters and classify them according to their component elements and properties.
2.3.1 TL dosimeters: characteristics

Dosimetric materials must satisfy certain important characteristics to be considered as a suitable TL dosimeter. Among the main requirements imposed on these materials are the following [14, 16]:

1. **Linearity.** A wide range of linearity in which the intensity of the thermoluminescent signal is linear with the absorbed dose is an important condition. Several materials used as TL dosimeters have a linear behavior over certain doses range usually at low doses (µGy-Gy) and limited by superlinearity and saturation (decay) of the TL intensity at high and ultra-high doses (kGy-MGy) as shown by curve P in Figure 2.1. Other materials, however, after showing linearity with the absorbed dose, go into the saturation region, as shown by curve Q in Figure 2.1. The interval at which the dosimeter will be used is determined by the dependence of the linear dose. Figure 2.1 shows the response characteristics of two dosimetric materials, P and Q.

2. **High sensitivity.** A high TL response per unit of absorbed dose is another important condition. High sensitivity is essential for use in personal and medical...
dosimetry, as well as in the monitoring of environmental radiation. That is, TL dosimeters should be able to detect very low radiation doses of the order of uGy - mGy.

3. **Energy dependence.** Low dependence of the TL response on the energy of the incident radiation. TL detectors are usually calibrated for a type of radiation and a certain energy. Nevertheless, in practice, TL dosimeters are used in a wider range of radiation energy, and a TL response correction system must be taken into account for the dose calculation. Ideally, TL materials should be independent of the energy but often the energy dependence is present in different types of TL materials, thus the energy correction has to be included in the determination of the absorbed dose.

4. **Low fading and stability.** Besides having a low dependence on the TL response with the energy and high sensitivity, TLD’s detectors must present good stability in the TL signal. That is, it is necessary to evaluate the loss or not of the trapped charge within the material when they are exposed to light, thermal treatments or other means. Mckeever has mentioned that for dosimetry purposes it is suitable for the detector to work with a peak at around 200 - 250 °C of the TL glow curve. Thus, this temperature ensures that the trap depth is large enough (E > kT) and then the emptying of the traps is not significant. But at the same time, this trap is low enough so that the interference from the black-body background signal is negligible [17, 18].

5. **TL glow curve characteristics.** It is convenience to obtain a TL glow curve with an isolated peak because a large number of peaks in the TL curve complicates the heating of dosimeters. V. Kortov [16] has mentioned that a heating process of TLDs dosimeters should include preheating for the depletion of shallow traps and additional high-temperature annealing for the depletion of deep traps. In addition, TLDs must be mechanically strong, chemically inert and resistant to high radiation. Figure 2.2 shows a typical glow curve of the LiF:Mg,Ti detector composed by 5 peaks with the prominent peak around 215 °C.
2.4 Materials for thermoluminescent dosimetry

The development and study of new radiation dosimeters have been published in the past [20–26]. In fact, sensitivity of a large number of materials has been investigated for them to be considered as suitable thermoluminescent phosphors. Of course, other physical properties have also been investigated to be used for radiation dosimetry, such as electron spin resonance, optically stimulated luminescence, etc. [17, 27, 28]. Concerning TL dosimeters, it is desirable that they detect not only electromagnetic radiation but also charged accelerated particles as well as neutrons. Neutrons are detected through nuclear reactions with atoms in the detector. While very low energy neutrons with energy smaller than few keV interact with any element through \((n, \gamma)\) reaction [29], higher energy neutrons can have reactions involving protons or even larger particles. When the \((n, \gamma)\) reaction takes place, the nucleus of the element absorbs a neutron and the isotope formed drops to the ground state by gamma emission. The detector absorbs all or part of this emitted gamma radiation which induces TL in the dosimeter.

V. Kortov in his work “Materials for thermoluminescent dosimetry: current status and future trends” [16] has distinguished several groups of materials whose properties
are studied with respect to the TL dosimetry requirements. These materials include the most known alkali and alkali-earth haloids, whose typical representatives are LiF (LiF:Mg, Ti and LiF:Mg,Cu,P) and CaF₂ (CaF₂:Mn and CaF₂:Dy). The other group are sulfates (MgSO₄, CaSO₄), AS sulfides (A = Mg, Sr, Ca, Ba), and oxides, such as, Al₂O₃, BeO and also SiO₂. Additionally, it is possible to mention the group silicates, i.e., natural and synthetic minerals based on SiO₂.

2.4.1 Lithium Fluoride: LiF

Commercial TL dosimeters, today, have been designed using LiF, CaF₂ and Al₂O₃. Historically, the main crystal used was the LiF, which was found by F. Daniels (University of Wisconsin, USA) to be good material in radiation dosimetry because of its high sensitivity to radiation. LiF had its first applications in 1953. However, in 1957 Daniels had difficulties using pure LiF crystal and suggested the use of Al₂O₃ as a better dosimeter material. LiF would not emerge again as an excellent radiation dosimeter until after the studies carried out by Cameron and his collaborators in the 1960s. Cameron based his work on Wiedemann & Schmidt (1895) results, who showed that a crystal’s thermoluminescence response will increase in the presence of impurities. Thus, it was found that the sensitivity of LiF was improved when doped with other elements such as Mg and Ti.

The use of Mg-doped LiF first, and then with Mg and Ti provided a significant progression of the TLDs. Success in clinical applications made the importance of TLDs even greater especially that based on LiF:Mg,Ti. LiF:Mg,Ti was called TLD-100 in where Li found in nature is used. Then LiF:Mg,Ti was produced using enriched Li-6 or Li-7 and received the names of TLD-600, and TLD-700 respectively. The highest sensitivity of this material (LiF:Mg,Ti) as far as their dopants are concerned was obtained using approximately 180 ppm Mg²⁺ and 10 ppm Ti⁴⁺ [19, 30]. Table 2.3 gives the isotopic composition of the TLD-100, TLD-600, and TLD-700.

Despite the appearance over time of other good quality dosimetric materials such as calcium sulfate doped with thulium or dysprosium [31] and carbon-doped aluminium
Table 2.3: Isotopic composition of LiF dosimeters. After [17].

| Isotope | TLD-100 | TLD-600 | TLD-700 |
|---------|---------|---------|---------|
| Li-6    | 7.5%    | 95.6%   | 0.01%   |
| Li-7    | 92.5%   | 4.4%    | 99.99%  |

oxide [32], TLD-100 has maintained its outstanding position in the TLD field by some reasons as it comes in the form of a compact tablet of small size, high sensitivity, low cost, re-usability, etc. In 1978, Nakajima et al. introduced LiF doped with Mg, Cu, P, with a sensitivity almost 20-fold that of the TLD-100. Therefore, although it has not completely replaced the TLD-100, it has come to be used extensively. Today, lithium fluoride doped with magnesium and titanium (TLD-100) are mainly sold as pressed pellets of approximately 3x3x0.9 mm³ or 1x1x1 mm³, both available from Thermo Electron (formerly Harshaw Chemical Company). Those proposed by Nakajima (LiF: Mg, Cu, P) are distributed in several ways: GR-200 (Beijing Radiation Detector Works, People’s Republic of China), MH-N (Henry Niewodniczanski Institute of Nuclear Physics, Poland) and in the form of TLD-100H, TLD-600H and TLD-700H by Thermo Electron, USA (formerly Harshaw). The LiF: Mg, Cu, P is also known as MCP, whereas LiF: Mg, Ti as MTS. As in MTS’s, we also have MCP-N (with Li natural), MCP-6 (Li-6 enriched) and MCP-7 (Li-7 enriched).

M. Moscovitch and Y.S. Horowitz have proved the optimum concentration of dopants in the MCP is in the next range: Mg ~ 0.2 mol%, P = 1.0 - 3.0 mol%, and Cu = 0.02 - 0.05 mol% [30]. The main characteristics of TLD dosimeters include the wide useful range of detection doses (1 μGy - 10³ kGy), sensitivity to small doses, and limited fading. Both LiF:Mg, Ti and LiF:Mg, Cu, P have the same effective atomic number (8.20) which is an important factor for personal dosimetry and for medical applications [30, 33]. The effective atomic number for human tissue is between 7.35 and 7.65 [34].
2.4.2 Aluminum oxide: $\text{Al}_2\text{O}_3$

Another important dosimeter material to be mentioned is aluminum oxide. It was considered as the most sensitive material in TL dosimetry after Kortov and his colleagues proposed a technology to increase the anion deficiency in the crystals by growing or treating them under strongly reducing conditions [16, 21, 35]. In addition, the dopant version of aluminum oxide, the $\alpha$-$\text{Al}_2\text{O}_3$:C (TLD-500K) has been another important material for research purposes in the 1990s. $\alpha$-$\text{Al}_2\text{O}_3$:C was first developed at the Urals Polytechnic Institute (Ekaterinburg, Russia) in the form of a single crystal [32]. This material showed high TL sensitivity to ionizing radiation, simple TL glow curve, low background, low fading when stored in the dark, good reproducibility and reusability with annealing, wide useful range ($10^{-7}$ - $10$ Gy) of dose-response and relatively low effective atomic number (10.2) [32, 36].

2.4.3 Silicate minerals

On the other hand, wide variety of silicate minerals are produced by nature through rock-forming for thousands of years. In addition, in the laboratory, many of these silicate minerals are produced mainly for research purposes. The natural ones during their formation incorporate several strange elements in their crystal structure, the so-called impurities. These impurities are important because many properties of the minerals depend on them, especially, thermoluminescence. Whilst in synthetic materials, the impurities are placed according to the purpose of the study, after that, their effects are analyzed by different experimental techniques. These minerals have been widely studied keeping in mind their use as dosimetric materials from low dose of the order of mGy up to high dose of the order of kGy. Among them, Brazilian natural colorless topaz [37]; Brazilian natural pink tourmaline, morganite, aquamarine, etc. [38]; natural and synthetic diopside [39]; lapis lazuli [24]; wollastonite [40]; synthetic undoped and doped CaSiO$_3$ polycrystals [41]; and synthetic spodumene polycrystals [42].
Table 2.4: Examples of TL materials for low and high radiation doses.

| Materials                        | Type of irradiation | Dose (fluence) range | References               |
|----------------------------------|---------------------|----------------------|--------------------------|
| LiF:Mg, Cu, P, polycrystalline   | γ(Co-60)            | 1 µGy - 1 MGy        | Obryk et al., 2011a      |
| detectors                        |                     |                      |                          |
| LiF:Mg, Cu, P, polycrystalline   | Thermal neutron     | 3x10^{11} - 3x10^{15} n/cm^2 | Obryk et al., 2011b      |
| detectors                        |                     |                      |                          |
| α-Al_2O_3:C single crystals      | γ(Co-60)            | 1 µGy - 10 Gy        | Akselrod et al., 1990    |
|                                  | γ(Co-60)            | 1.5 kGy - 100 kGy    | Kortov et al., 2013      |
| CaF_2:Dy crystal chips           | γ(Co-60)            | 10^2 - 10^7 rad      | Hasan et al., 1983       |
| Brazilian natural topaz,         | γ(Co-60)-(Cs-137)   | 10^{-4} - 10^5 Gy    | Souza et al., 2002       |
| Al_2(SiO_4)(F,OH)_2              |                     |                      |                          |
| Brazilian natural aquamarine,    | γ(Co-60)            | 1 kGy - 3 MGy        | Watanabe et al., 2015    |
| tourmaline, morganite, etc        |                     |                      |                          |
| Brazilian Fluorite               | γ(Cs-137)           | 2 Gy - 1 kGy         | Watanabe et al., 1971    |

V. Kortov and Y. Ustyantsev [16, 43] have mentioned some examples of the most sensitive dosimeters for low doses as well as various luminescence materials which can be used for high-dose detector creation. Table 2.4 shows some of these dosimeters mentioned by Kortov and his colleague, among them, the polycrystalline LiF:Mg,Cu,P detectors, CaF_2, α-Al_2O_3:C, and Brazilian minerals.

2.5 TL and EPR in silicates

Natural minerals based on silica have been formed with many impurities located in specific points in the crystal structure, which produced optical absorption, defect center, luminescence, and dosimetric properties. In addition these natural and synthetic minerals based on silica have been widely studied in the last years and investigations such as Electron Paramagnetic Resonance (EPR) studies have been carried out to identify defects centers in the crystal structure responsible for the TL peaks [44–53]. For instance, Gundu Rao and collaborators [25] have analyzed the EPR centers responsible for the TL peaks of the willemite mineral. They found two ions center O_1^- and O_2^- correlates with the 160 °C TL peak (4 °C/s heating rate), and F^+ center appear to act as a recombination center for the 160, 225, 260, and 310 °C TL peaks.
Furthermore, synthetical material undoped and doped with different elements such as Cr, Eu, Gd, etc., were produced by different methods and EPR center on the crystal structure as well as their luminescence properties analyzed [39, 48–53].

2.6 High and very-high radiation dose

Different kinds of TL dosimeters were also exposed to high and very-high radiation doses of the order of kGy up to MGy with the purpose of studying the behavior of TL response, resistance and damage effects on the detectors. These materials were exposed to either gamma, neutron or electron beam irradiation and their use as dosimeters for high and very high radiation dose analyzed [37, 38, 43, 54–57].

For instance, LiF:Mg,Cu,P and LiF:Mg,Ti detector under high-dose gamma radiation and electron doses up to 1 MGy were studied for the first time by researches from the Institute of Nuclear Physics (IFJ) in Kraków, Poland [54–56]. They found that the main dosimetric peak at about 220 °C in LiF:Mg,Cu,P glow curves shifts toward high temperatures after radiation doses (from $^{60}$Co source) higher than about 30 kGy displaying significant changes of their shape. $\alpha$-$\text{Al}_2\text{O}_3$:C detectors irradiated by nanosecond pulse electron beam were studied by Kortov and Ustyantsev [43]. They found the dose-response of the high peak at 700 k, of the characteristic glow curve, changes linearly in the range doses from 1.5 kGy to 100 kGy.

Brazilian naturals mineral of colorless topaz and amethyst were studied by the first time by D. Souza et al. (2002) [37] and F. Rocha et al. (2003) [57] respectively. The dose-response of colorless topaz pellets after gamma irradiation (from Co-60 source) of the main dosimetric peak shown a sub-linear behaviour for low doses from $10^{-4}$ to $10^{-2}$ Gy, linear from $10^{-2}$ up to 20 Gy, followed by a supralinear and again a sublinear region, and finally reaching saturation for doses of about 2 - 3 kGy. On the other hand, the TL response of sintered amethyst pellets as a function of gamma dose (from Co-60 source) shows a tendency to saturation at 10 kGy. Furthermore, S. Watanabe and collaborators (2015) [38] have studied several other kinds of Brazilian minerals
like aquamarine, morganite, pink tourmaline, white and green jadeite by using the thermoluminescence technique to evaluate their potential for use as high & very-high dose dosimeters. This study has shown that even though all silicates minerals analyzed exhibit dose-dependent TL response up to 2 MGy, green jadeite and pink tourmaline have an extended behavior up to 3 MGy, that is, these can be used for very-high-dose dosimetry.

2.7 Neutron and ion beam dosimetry

2.7.1 Neutron dosimetry

Different important reasons have led to the neutron detection investigation, among them, the complexity involved in the neutron interaction with the matter. This interaction makes a difficult task to determine the dose deposited due to neutrons on detectors because there are many direct and indirect energy transfer processes involved and the variation of the reaction cross-sections with energy [58, 59]. In a biological or nonbiological system, the response to neutron cannot be related directly to the absorbed dose without considering the neutron energy. For this reason, the study of neutron interactions with the matter is dealt with separately in thermal, intermediate and fast neutrons [59, 60]. Neutron radiation protection related to neutron sources, radioactivity ion facilities and nuclear reactors become important for human health and a system of neutron detection safety must take into account the Neutron Relative Biological Effectiveness (RBE) [61–63].

Neutron detection from a nuclear reactor or neutron sources (such as Am-Be or $^{252}$Cf) using thermoluminescence detectors has been a great challenge in radiation dosimetry, and several works have been devoted to investigating this process in the past [58, 63–69]. Particularly, interaction of thermal and epithermal neutron with matter has awakened special interest in some authors because a larger effective neutron capture cross-section than fast neutrons is found for some nuclides like $^{10}$B and $^{6}$Li [70–72]. In
addition, the low energy of thermal neutrons makes that an interesting system to be used in medical and industrial purposes [60].

In medical application, boron neutron capture therapy (BNCT) is a method for the treatment of brain tumors in which TLDs detectors can be used to determinate the gamma dose and evaluate the dose due to the charged particles generated in the thermal neutron interaction using consistent kerma factor [62, 73]. On the other hand, Obryk et al. [69] have mentioned that during the research of radiation damage to electronic components at the Maria research fission reactor, Poland, TL dosimetry using different kinds of MCP and MTS has been performed in order to evaluate the neutron and gamma components of the radiation field during exposure.

### 2.7.2 Ion beam dosimetry

On the other hand, in the last few years, the increased demand for dosimetry of charged particle beams has taken great importance due to its utility in cancer diagnosis and therapy [74–76]. The use of ion beam in cancer therapy, for instance, is based on the phenomenon of dose deposition at Bragg’s peak [77]. Heavy charged particles, such as carbon ions and proton, ensure a well-defined penetration at the location of the final treatment inside the body, displaying a minimum scattering and stiffer particle trajectories, low straggling effects, and sharper field edges [77, 78].

Proton and carbon ions beam have better dose-depth distribution than photons and heavy ions like carbon ion provides a larger mean energy per unit length in the trajectory [79]. For bone and soft-tissue tumors diagnostics usually a surgical procedure is performed because they are radiological resistant, and the effect of photon radiation is not enough for long-term control. For this reason, radiotherapy is taken into account as a sole treatment [77].

Literature describing the effect of the accelerated ion beam on phosphor material as TL dosimeters are very limited. For this reason, in this work, pellets of calcium silicate
are produced as TL ion beam dosimeters in an attempt to obtain useful data regarding the TL response of proton and carbon ion beam-irradiated highly sensitive phosphors.

2.7.3 Detection of neutrons in a nuclear research reactor

In a nuclear reactor the neutron field comes accompanied mostly by gamma radiation, however, other different types of particles such as electrons, photons, protons and also heavy-charged particles can be also emitted [67, 69]. For instance, LiF TLDs enriched with $^6$Li ($^6$LiF, with 95.6 % $^6$Li) is sensitive to both neutron and gamma, whilst $^7$LiF (with 0.07 % $^6$Li) has no response to thermal neutrons [17, 29, 67, 69, 80]. Thus, in a mixed radiation field of gamma and thermal neutron field both TLDs can be used, $^7$LiF gives the gamma component and can be used to calculate the thermal neutron response on the other detector [17]. Furthermore, computational tools using the Monte Carlo method were used by some authors to estimate the deposited dose on TL detectors [64, 81, 82].

The response of various types of lithium fluoride MCP detectors under high thermal neutrons was studied for the first time by researches from the Institute of Nuclear Physics (IFJ) in Kraków, Poland [23]. They found that the main dosimetric peak at about 220 °C in LiF:Mg, Cu, P glow curves shifts toward high temperatures after high radiation neutron doses displaying significant changes of their shape, which results in the formation of the high temperature peak B. Figure 2.3 shows the emission curves of irradiated MCP-N with thermal neutrons fluences ranging from $3 \times 10^{11}$ to $3 \times 10^{15}$ n/cm$^2$. It is interesting to note that peak “B” decreases in intensity from $3 \times 10^{14}$ n/cm$^2$ to $3 \times 10^{15}$ n/cm$^2$. Peak “B” grows to reach the maximum intensity at 420 °C.

One of the purposes of this work is to extend the current knowledge of interesting materials as radiation dosimeters. For this reason, it is proposed the production of synthetic calcium silicate polycrystals (pure or doped) at the Laboratory of Ionic Crystals, Thin Films and Dating (LACIFID), aiming at not only X-ray and gamma radiation dosimetry, but also of neutrons produced in the research reactor, and accelerated ions from an
Figure 2.3: Glow-curves of MCP-N detectors for different thermal neutron fluences displaying the peak B. After [23]

synchrotron. In addition, the effects of europium, dysprosium, boron, and cadmium doped on the synthetic calcium silicate have been studied keeping in mind the thermal neutron capture.
Chapter 3

Silicate minerals

The eight most abundant elements in Earth’s crust by weight percent are oxygen (47%), silicon (28 %), aluminium (8.1 %), iron (5.0 %), calcium (3.6 %), sodium (2.8 %), potassium (2.6 %), magnesium (2.1 %), others (0.8 %) [83]. These eight elements constitute the 99.2 % by weight and almost 100 % by volume, being O and Si the two most abundant elements which are linked together to form SiO$_2$ the most abundant component of the Earth’ crust. With the above mentioned, the presence of silicates is predominant being $\sim$ 92% of the earth’s crust consists of silicate minerals [83, 84].

The ratio of tetravalent silicon radius (0.42 Å) to oxygen ion radius (1.40 Å) is 0.30. The bonding of this tetrahedron is originated, in part, from the ionic attraction due to opposing charges, and partly from the overlapping of electronic clouds (covalence). In the Si-O bond, the total energy of Si is distributed among the neighboring oxygen. As a consequence, the energy of any isolated Si-O bond is less than the total available energy in the oxygen ion. Thus, each oxygen can still bind to another silicon, forming another tetrahedral structure. Then, groups of tetrahedra can be strongly bound and since the four oxygenates are equivalent, there exists in nature, a large number of possible structural configurations.
Liebau, F. [85] shows that chemical formula of a complex silicate can be expressed in general form as $M'_{r'}M''_{r''}M'''_{r'''}...Si_sO_t$. where $M'_{r'}$, $M''_{r''}$, $M'''_{r'''}$ are the cation from monovalent, divalent up to heptavalent and $r'$, $r''$, $r'''$, and $s$, $t$ which satisfy the null total charge rule. Alternatively other form to indicate a complex silicate is expressing the component oxides $q'M'_{r'}O$, $q''M''_{r''}O...sSiO_2$. In the two forms of the chemical formula of silicates can be seen Si - O - M bonds.

Commonly metal ions are larger and have a lower valence than silicon (e.g., valence (Ca, Mg, Cd) = 2; valence (Si) = 4) for this reason the M - O bonds are weaker than the Si - O bonds (by valence bond theory). Then the silicon attracts oxygen ions more strongly than M, consequently the silicon forms the $[\text{SiO}_4]$ tetrahedron with a mean bond length (Si - O) = 16.2 nm, and coordination number 4. In addition, if M is a metalloid the M - O bond is comparable with the Si - O bond and the silicon atoms attracts oxygen ions with a mean bond length (Si - O) = 17.7 nm and promoting the formation of $[\text{SiO}_6]$ octahedron with six oxygen ions around each silicon atom with a coordination number 6. Figure 3.1 shows the $[\text{SiO}_4]$ tetrahedron and $[\text{SiO}_6]$ octahedron form.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{silicate_minerals.png}
\caption{(a) $[\text{SiO}_4]$ tetrahedron with a mean bond length (Si-O) = 1.62 Å and (O-O) = 2.64 Å. Ionic radius $\text{Si}^{+4} = 0.4$ Å and $\text{O}^{-2} = 1.40$ Å. (b) $[\text{SiO}_6]$ octahedron with mean bond length (Si-O) = 1.77 Å and (O-O) = 2.50 Å. Image obtained from [85], p. 15.}
\end{figure}
3.0.1 SiO$_4$ tetrahedron

The basic molecule that builds a silicate crystal structure is the tetrahedron SiO$_4$ as shown in Figure 3.2. Oxygen atoms occupy the vertices and Si sits in the center. Since each oxygen ion is in the -2 state and Si in the +4 state, an isolated tetrahedron is [SiO$_4$]; however, in a silicate mineral each oxygen share one negative charge with a neighboring tetrahedron or with a cation present, therefore each tetrahedron [SiO$_4$] is a negative ion (charge -4).

![Figure 3.2: (a) [SiO$_4$] tetrahedron. The Si cation with charge +4 is bonded to each oxygen of charge -2 resulting in a (SiO$_4$)$^{-4}$ tetrahedron. After [85].](image)

3.0.2 Classification of silicates

The arrangement of the SiO$_4$ tetrahedron and the Si:O ratio in the chemical formula of the silicate mineral give rise to the classification criterion used in Mineralogy [83]. In this classification, there are silicates with rings, chains, sheets, and three-dimensional structures.

3.0.2.1 Nesosilicates (orthosilicates)

Nesosilicates, also known as orthosilicates are characterized by the presence of isolated silica tetrahedra that are not linked through shared oxygen ions to other silica tetrahedra in the structure. Then, SiO$_4$ tetrahedron is connected by another divalent cation
that may include Fe$^{+2}$, Ca$^{+2}$, Mg$^{+2}$, and Mn$^{+2}$, among others, as shown in Figure 3.3. The Si:O ratio of such mineral is 1:4 which indicates the existence of a (SiO$_4$)$^{-4}$ component and implies the isolated tetrahedron. Olivine group, for example, crystallizes with an orthorhombic symmetry and the independent SiO$_4$ tetrahedron linked by divalent atoms in six-fold coordination. Olivine group has the formula (Mg,Fe)$_2$SiO$_4$ and is known as Mg$_2$SiO$_4$ (forsterite) and Fe$_2$SiO$_4$ (fayalite).

3.0.2.2 Sorosilicates (disilicates)

Sorosilicates, also known as disilicates, are characterized by pairs of silica tetrahedra bonded together by a single shared oxygen (O$^{-2}$) ion as shown in Figure 3.4. In this case, the basic structural unit is (Si$_2$O$_7$)$^{-6}$ and the Si:O ratio of such mineral is 2:7. The mineral hemimorphite has the formula Zn$_4$(Si$_2$O$_7$)(OH)$_2$H$_2$O indicating the presence of (Si$_2$O$_7$) with paired silica tetrahedra property which is typical of Sorosilicates mineral.

3.0.2.3 Cyclosilicates

Cyclosilicates structure is characterized by the silica tetrahedra forming closed rings linked by shared oxygen and forming groups (Si$_6$O$_{18}$)$^{-2}$ and the Si:O ratio of such mineral is 1:3. Three closed rings, (Si$_3$O$_9$)$^{-6}$, four closed rings, (Si$_4$O$_{12}$)$^{-8}$, and five
closed rings \((\text{Si}_5\text{O}_{15})^{-10}\) are also possible. An example of this type of silicate is the mineral Beryl - \(\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}\).

3.0.2.4 Inosilicates

Inosilicate is a type of silicate mineral where silica tetrahedra, which are bonded together by oxygen ion, form one-dimensional chains of a long-range extent. According to the formation of these minerals, they can be found as single-chain and double-chain inosilicate structures.
a) Single-chain inosilicates: In single-chain inosilicates structure, as in the cyclosilicates case, an oxygen ion is shared in a way to make long single chains of joined SiO$_4$ as shown in Figure 3.6(a). The Si:O ratio is 1:3 and the basic structure unit is (Si$_2$O$_6$)$^{-4}$ or (SiO$_3$)$^{-2}$. This type of silicates is the basis for the pyroxene group, the most abundant group of single-chain inosilicate minerals. Among the most known pyroxenes are the orthopyroxenes (enstatite Mg$_2$Si$_2$O$_6$, ferrosilite Fe$_2$Si$_2$O$_6$), diopside CaMgSi$_2$O$_6$, wollastonite CaSiO$_3$, and rhodonite MnSiO$_3$, among others.

b) Double-chain inosilicates: In the double-chain inosilicates structure, two single chains are bonded together by an additionally shared oxygen ion to form a double chain as shown in Figure 3.6(b), with the basic structure group (Si$_4$O$_{11}$)$^{-6}$ and Si:O ratio of 4:11. The amphibole group is the most abundant group of double-chain inosilicate mineral, for example the tremolite-ferroactinolite series - Ca$_2$(Mg,Fe)$_5$Si$_8$O$_2$(OH)$_2$. 

Figure 3.6: (a) Single-chain inosilicate structure in pyroxene. (b) Double-chain silicate structure in amphiboles. Image obtained from [83].
3.0.3 Pyroxene group

The members of the pyroxene group are the most important of rock-forming minerals. Pyroxenes usually are based on silicates of calcium, magnesium, iron, aluminum, sodium, and lithium, corresponding to the general formula $M''^2Si_2O_6$ and $M'M'''Si_2O_6$. Pyroxenes included both orthorhombic and monoclinic minerals. The orthopyroxenes consist essentially of a simple chemical series of $(Mg, Fe)SiO_3$ minerals, contrastively with the larger group of monoclinic pyroxenes which have a very wide range of chemical composition such as the four-component system $CaMgSi_2O_6$ - $CaFeSi_2O_6$ - $Mg_2Si_2O_6$ - $Fe_2Si_2O_6$ [87, 88]. The following important pyroxenes are described:

- Enstatite; $Mg_2Si_2O_6$; orthorhombic.
- Ferrosilite; $Fe_2Si_2O_6$; orthorhombic.
- Diopside; $CaMgSi_2O_6$; monoclinic.
- Aegirite; $NaFeSi_2O_6$; monoclinic.

Furthermore, the following minerals were formerly classified as pyroxenes (also known as pyroxenoid), however, they differ from the pyroxenes in optical and crystallographic properties as well as in structure.

- Wollastonite, $CaSiO_3$; triclinic.
- Rhodonite; $MnSiO_3$; triclinic.
- Pectolite; $HNaCa_2(SiO_3)_3$; triclinic.

A. Putnis [89] has shown the periodicity both in the pyroxenes and pyroxenoids mineral groups. In the pyroxenes, the periodicity of the chain is 2, that is, after every two tetrahedra the chain repeats. On the other hand, in the pyroxenoids, longer chain periodicities occur, such as in wollastonite $CaSiO_3$, where the periodicity is 3 (the chains repeats after every three tetrahedra). The Si:O ratio in these single-chain
silicates is 1:3 with a net charge of \((\text{SiO}_3)^{2n-}\). These chains are cross-linked by cations, usually in octahedral sites [89]. Figure 3.7 shows the comparison of the single SiO$_4$ chains in pyroxenes and pyroxenoids.

The cation positions in pyroxenes are of two types, the M1 and M2 sites. The M1 sites are located between the apices of opposing tetrahedra; the M2 sites lie between their bases. M1 sites are smaller and are almost regular octahedra, M2 are more distorted and when containing a smaller cation can be octahedra or 8-fold sites when a larger cation is accommodated. These M sites (M1 and M2) form edge-sharing chains that run parallel to the silicate chains. At this stage, it is important to know how the silicate chain links to the cation polyhedra and its response to changes in composition, temperature, and pressure. The way in which a straight silicate chain is linked, by its apices, to an edge-shared octahedral chain is displayed in Figure 3.8(a). This figure shows the fully extended situation. However, if the octahedra were larger, the pyroxene chain disposition could be accommodated them in a different way. When M1 and M2 sites expand and contract the tetrahedral chain changes its length to accommodate it by a rotation of the individual [SiO$_4$] tetrahedra which shortens the chain length as shown by A. Putnis [89].

Figure 3.7: A comparison of the single SiO$_4$ chains in (a) pyroxenes with periodicity of 2 (tetrahedra), and (b) pyroxenoids with periodicity 3. After [89].
Figure 3.8: (a) Pyroxenes case: the linkage between a single SiO$_4$ chain and a chain of octahedra in a fully extended chain, and (b) pyroxenoids case: the linkage between a chain of tetrahedra and an octahedral chain in wollastonite CaSiO$_3$. The relative size of the SiO$_4$ tetrahedra and CaO$_6$ octahedra require twisting of the tetrahedral chain to be able to achieve a satisfactory linkage, displaying a chain repeat of 3 tetrahedra corresponding in length to two octahedral edges. After [89].

As explained above, the pyroxene structure showed the linkage between a fully extended single silicate chain and an octahedral column, as shown in Figure 3.8(a). However, if the cation octahedra were any larger, the pyroxene chain could change its disposition. In the case of wollastonite CaSiO$_3$ belonging to the pyroxenoid group of minerals, which is also a single chain silicate, a different solution has been found. Figure 3.8(b) shows such a wollastonite chain and its linkage to an octahedral chain. This figure shows two edges of [CaO$_6$] octahedra which have about the same length as 3 [SiO$_4$] tetrahedra, thus forming a chain with a periodicity of 3, running parallel to the octahedral column [89].
Chapter 4

Crystal structure of CaSiO$_3$

4.1 The mineral of wollastonite CaSiO$_3$

Wollastonite is a natural calcium metasilicate, CaSiO$_3$, named after the English chemist and mineralogist W. H. Wollaston [90]. It is an interesting material for study in mineralogy either in natural or synthetic form because of their different polytypes and polymorphs described in many studies [88, 90–102]. Natural wollastonite generally occurs in small amounts in alkaline igneous rocks (e.g. in granular limestone near granite contacts) and is highly contaminated with other minerals like diopside, calcite, dolomite, quartz, hedenbergite, and granites. Wollastonite, CaSiO$_3$, has the theoretical composition 48.3 % CaO and 51.7 % SiO$_2$ but in nature may appear with some substitution of, iron, manganese or magnesium for calcium. The pure mineral of wollastonite is white and acicular and in suspension shows a low oil absorption rate and high alkalinity [90]. Figure 4.1 shows wollastonite from Pargas, Turku ja Pori, Finland.

This mineral can be found naturally in places where there has been a reaction between limestone and intrusive igneous rock. Some localities are Csiklova (Rumania), Chiapas (Mexico), California (USA), Pargas (Finland), Fuka (Japan)[88]. Wollastonite aroused the interest of many producing companies since the 1950s. This is due to the many potential uses for the mineral in the industry, chiefly in the ceramic, paint, plastic,
metallurgy, rubber, and glass industry. In the ceramic industry, for example, it is used to improve the tenacity and to optimize the color stability, in paint industry it is widely used in the types of paint employed for exterior house coatings, and in metallurgy industry, it is used for steel refinement [90, 103].

4.1.1 Synthetic wollastonite

Synthetic wollastonite production has its beginnings in the 1960s when it received more interest from the materials companies. This interest was because of problems arising from the variation in the quality of traditional, natural raw material, and the need to improve the energy-saving technological processes [92]. Previous investigations of The British Ceramic Research Association in the 1960s for synthetic wollastonite production were performed through the reaction between fairly pure SiO$_2$ a CaO with and without a catalyst used ground flint and calcium carbonate (whiting). After that, limestone from Buxton, Derbyshire, and silica sand from Oakamoor, Staffordshire, England were used without a catalyst.

The solid-state reaction yield of calcium metasilicate, either in the high- or the low-temperature form could be produced by adjusting the condition suitable for pressure and temperature. Unsuitable conditions led to the formation of calcium orthosilicate or cristobalite. The synthetic wollastonite was very similar to the natural mineral but
lacked its acicular crystal form, being granular and friable [90]. For research purposes, R. Rashid and collaborators in 2014 [104] have produced wollastonite through the solid-state reaction from Malaysian limestone and silica sand. They fully obtained \( \beta \)-wollastonite (high-temperature polymorph) at the limestone/silica sand molar ratio of 1:1, sintered at 1450 °C for 4 h, with a dense microstructure and olivine as a minor phase [104].

There are two polymorphs of wollastonite, these are, the low- and high-temperature form. According to the mineralogical practice these are known as \( \alpha \)-wollastonite and \( \beta \)-wollastonite, respectively. However, in the cement industry, the low-temperature form is called \( \beta \)-wollastonite and the high-temperature form as \( \alpha \)-wollastonite as described by R. Andrews [90]. Magallanes-Perdomo et al. [94] have studied the devitrification and crystallization process of wollastonite-tricalcium phosphate (W-TCP).
This work has shown that in the low-temperature phase, the crystalline structure of wollastonite-2M starts its formation at about 1006 °C and totally disappears at 1303 °C. Additionally, at about 1185 °C the crystalline pseudowollastonite is detected and continuously grows up to 1375 °C. I. Kotsis and A. Balogh [92] have classified the most common problems during the industrial synthesis of wollastonite based on previous theoretical investigation dated back to J. Hedwall [106] and W. Jander [107]. These situations are referred:

- chemical composition of the starting materials,
- optimum particle size of the starting materials,
- optimum molar ratio of CaO and SiO$_2$,
- effect of mineralizes on the temperature of wollastonite formation,
- kinetics of wollastonite formation,
- possibilities of the synthesis of a given modification of wollastonite.

Many authors have proposed that the most suitable composition as far as its CaO/SiO$_2$ molar ratio is concerned is 0.7-1.2 mol CaO to 1 mol SiO$_2$ [108, 109]. An important tool used in the synthesis of materials is the study of the phase diagram or matter phase diagram. This is a representation between different states of matter, depending on the variables chosen to facilitate the study of it. Particularly, a binary phase diagram is a temperature - composition map which indicates the equilibrium phases present at a given temperature and composition.

B. Phillips and A. Muan [105] have described the phase diagram of the CaO-SiO$_2$ system as shown in Figure 4.2. In this diagram can be seen that wollastonite is converted into pseudowollastonite at 1125 °C (in the notation used in the cement industry). However, this conversion is shifted to other temperatures with increasing pressure [110]. I. Kushiro (1963) [110] has performed the pressure-temperature plane for wollastonite composition as shown in Figure 4.3. Point A is the melting point of
Figure 4.3: Pressure-temperature plane for CaSiO$_3$ composition. Pwo, pseudowollastonite; Wo, wollastonite. After [110].

pseudowollastonite (1544 °C) and B is the temperature of inversion (1125 °C), both point at 1 atm [111]. As observed in Figure 4.3 for high pressure the inversion takes place quickly since the inversion temperature is high in comparison with that at 1 atm. For instance, at 15 kbar, the inversion of wollastonite to pseudowollastonite is completed within 17 minutes at 1470 °C and within 8 minutes at 1580 °C [110].

4.1.2 Polymorphism and Polytypism in wollastonite

Calcium metasilicate (CaSiO$_3$) is represented by different numbers of polymorphs and polytypes [88, 93, 102]. W. A. Deer et al. [88], reported three different structural modification of wollastonite. On the one hand, the low-temperature polymorph is divided into two types, the triclinic wollastonite (1T) and monoclinic wollastonite (2M), the last one also known as parawollastonite (or α-CaSiO$_3$). On the other hand, the high-temperature polymorph is a cyclosilicate called pseudowollastonite (or β-CaSiO$_3$). The low-temperature polymorph (triclinic and monoclinic lattice) exist below
Table 4.1: Cell parameters of CaSiO$_3$ [88].

| Structure               | a (Å) | b (Å) | c (Å) | α     | β     | γ     | Space group | Z  |
|-------------------------|-------|-------|-------|-------|-------|-------|-------------|----|
| Wollastonite-Tc         | 7.94  | 7.32  | 7.07  | 90°   | 95.37°| 103.43°| P1          | 6  |
| Wollastonite-2M         | 15.43 | 7.32  | 7.07  | 90°   | 95.40°| 90°   | P2$_1$/a    | 12 |
| Pseudowollastonite      | 6.90  | 11.78 | 19.65 | 90°   | 90.30°| 90°   | P1 or P$ar{1}$ | 24 |

about 1150 °C and contains single-chains with a chain repeat unit of three tetrahedra [SiO$_4$]$^{4-}$ as shown in Figure 4.4. In addition, the pseudowollastonite polymorph is stable above 1125 °C and melts at about 1550 °C [102] with a structure containing rings of three silicates (Si$_3$O$_9$)$^{6-}$.

We have seen, so far, three polytypes of wollastonite the 1T, 2M, and pseudowollastonite, as mentioned earlier. Deer et al. [88] has classified wollastonites types according to the cell parameters of the crystal structure [88]. Table 4.1 shows the lattice constants $a$, $b$, $c$, $α$, $β$, $γ$; space group and $Z$ for the three polytypes of CaSiO$_3$, these are wollastonite-Tc (1T) with space group P$ar{1}$, wollastonite-2M (2M) with space group P2$_1$/a, and pseudowollastonite ($β$-CaSiO$_3$). In addition, K. Hesse [95] had reported the structure of wollastonite-2M (parawollastonite) from the Death Valley, California, as monoclinic with space group P2$_1$/a, $a = 15.409(3)$, $b = 7.322(1)$, $c = 7.063(1)$ Å, $β = 95.30(2)$° and $Z = 4$.

In addition to the aforementioned polytypes, there are other types of wollastonite classified according to the arrangement of their crystalline structure. In this way, in order to describe the structure of wollastonite and its polytypism (1T, 2M, 3T, etc.), we can follow the notation used by Henmi et al. [100, 101], which was broadly used by many authors [92–95, 102].

As mentioned earlier, the low-temperature polymorph of wollastonite is formed by a single-chain silicate along the b-axis with a chain repeat unit of three [SiO$_4$] tetrahedra. Two edges of [CaO$_6$] octahedra belonging to the octahedra chain have the same length as 3 [SiO$_4$] tetrahedra forming a chain with a periodicity of 3, running parallel to the octahedral column. Mazzucato et al. [93], explained that these single-chain silicates are organized in pairs, that is, an inversion-related chain that represents one basic
(100) slab of the structure. These (100) slabs of structure, one triclinic unit cell thick are the modules that are used to build up the other wollastonite structures. Thus, the polytypism in wollastonite is produced by different stacking sequences of these slabs (100) along the a-axis. Moreover, these slabs either can be stacked in a continuous position with respect to the previous (T) or displaced by b/2 (G) as shown in Figure 4.4.

![Crystal structure of wollastonite (a) and parawollastonite (b) along the c-axis.](image)

**Figure 4.4:** Crystal structure of wollastonite (a) and parawollastonite (b) along the c-axis. The stacking sequences of (100) slabs for wollastonite and parawollastonite are shown; the thick lines indicate the unit cells. First, the continuous position of the slab with respect to the preceding one along the a axis (T) as shown in the three-unit cells outlined on the top (a), or displaced by b/2 (G) as shown in the new disposition of the slabs on the bottom. [102].
In this way, in triclinic wollastonite, slabs disposition is repeated continuously with respect to the previous cell. On the other hand, when oxygen atoms are separated by a distance b/2 along the edge of the slab, a displacement of b/2 of one slab relative to its neighbor is produced. It is possible to express wollastonite structures as a series of different stacking sequences. For instance, the basic triclinic structure is then TTTTTT named 1T wollastonite (a 1-slab repeat, and a triclinic cell). The most common wollastonite structure has a stacking sequence TGTGTG... a 2-slab repeat and a monoclinic cell (hence 2M wollastonite). Other stacking sequences that have been described are TTGGTT (3T wollastonite), TTTGTTTG (4T wollastonite) and GGTGGTT... (4M wollastonite). Other forming wollastonites polytypes including 3T, 4T, 5T, and 7T were discovered by Henmi et al.\[100, 101\]. Figure 4.5 shows the wollastonite polytypes and stacking sequences of 1T, 2M, 3T, 4T, and 4M, according to Henmi et al. [101].

Figure 4.5: The stacking sequences of (100) slabs for wollastonite polytypes including 1T, 2M, 3T, 4T, and 4M. Thick lines indicate the unit cell. After [102].
4.1.3 Pseudowollastonite ($\beta$-CaSiO$_3$)

As explained earlier, pseudowollastonite is the high-temperature polymorph of CaSiO$_3$. This polymorph is stable above 1125 °C and melts at about 1550 °C [102] with a structure containing rings of three silicates (Si$_3$O$_9$)$^{6-}$ (cyclosilicate). Pseudowollastonite is a rare mineral in the natural environment, unlike wollastonite 1T and 2M. Y. Seryotkin et al. [102] have mentioned the presence of natural pseudowollastonite from three localities of specific ultrahigh-temperature and very low pressure. One of them is located in the rich Chillingar oil-field in Iran [112] and two other occur in the so-called Mottled Zone complexes in Israel [113, 114]. Currently, wollastonite has been represented in the Mineral Database by its synthetic species as CaSiO$_3$, space group C2/c according to Yang and Prewitt (1999) [98]. This is due to the lack of data on the natural mineral of the pseudowollastonite.

Yamanaka and Mori [97] have produced a single crystal of pseudowollastonite by using a flux of CaCl$_2$. The presence of at least three polytypes structures of $\beta$-CaSiO$_3$ were found from X-ray precession photographs. The four-layer, six-layer, and disordered stacking polytypes have been found. The structure of the four-layer polytype is the dominant phase with a triclinic unit cell and solved in space group $\bar{C}1$. This structure of the four-layer polytype is formed for four Ca-octahedra layers and ternary rings of three tetrahedra of Si$_3$O$_9$ interposed between the layers. These Ca-octahedra in a layer are compressed in the c-direction, while tetrahedra of the rings are elongated in the same direction (stacking direction). The six-layer polytype has been indicated as having a pseudosymmetry C2/c and is probably isostructural with SrGeO$_3$. Finally, the disordered structure was confirmed by diffuse streaks along c* axis with the presence of many polytypes along c axis [97].

J. Ingrin (1993) [115] has investigated the polytypism in synthetic polycrystalline pseudowollastonite using conventional and high-resolution transmission electron microscopy (TEM and HRTEM). He has found three polytypes of 2, 4, and 6-layers that coexist in the one sample in the form of lamellae parallel to (001). Furthermore, J. Ingrin has proved that these polytype lamellae are stable even after prolonged annealing at high
temperatures greater than 1700 K (1427 °C) which could be indicating that the most frequently reported 4-layer polytype is not the only high-temperature stable polytype.

In 1999, Yang and Prewitt [98] have produced a new high-quality single crystal of pseudowollastonite. A single-crystal X-ray diffraction study revealed a crystal characterized by four-layer polytype with a monoclinic C2/c symmetry rather than triclinic C1 symmetry found by Yamanaka and Mori [97], with cell parameters: $a = 6.8394(5)$, $b = 11.8704 (9)$, $c = 19.6313(7)$ Å, $\beta = 90.667(6)°$ and $V = 1593.7(2)$ Å$^3$. The basic features of pseudowollastonite structure found by Yang and Prewitt were characterized by four layers, each of which is composed of a layer of ternary (Si$_3$O$_9$) tetrahedral rings and a layer of distorted-bicapped Ca octahedra as shown in Figure 4.6(b). This distorted-bicapped octahedron is formed by eight O atoms, with six of them in an octahedral arrangement and two from bridging O atoms of the Si$_3$O$_9$ rings one above and one below the octahedron. The CaO$_8$ polyhedral layers are compressed in the (001) direction, while the ternary rings are elongated in the same direction [98].

Additionally, in 1999 Yang and Prewitt [99] produced the crystal structure of a synthetic two-layer polytype of CaSiO$_3$ pseudowollastonite determined by single-crystal X-ray diffraction data. They have found a monoclinic structure with space group C2/c and unit cell parameters $a = 11.8322(6)$, $b = 6.8624(8)$, $c = 10.5297(5)$ Å, $\beta = 111.245(8)°$, and $V = 796.9(1)$ Å$^3$. This polytype of CaSiO$_3$ contains two unit layers parallel to (001) in a unit cell, the second layer of ternary rings is displaced one-sixth of the $a$ dimension with respect to the first layer of ternary rings as shown in Figure 4.6(a). In the case of the four-layer structure, the first and second layers of ternary rings are stacked directly on top of one another. Similar behavior is shown with the third and fourth layers where the fourth layer lies directly on top of the third layer. Furthermore, the third layer of ternary rings is displaced one-sixth of the $b$ dimension with respect to the second layer. In Figure 4.6, it is observed that the $a$ and $b$ axes in the two-layer structure are inverted with respect to those in the four-layer structure, whereas the CaO$_6$ octahedra are compressed in the $c$ direction in both structures, as well as, the SiO$_4$ tetrahedra is elongated in the same direction [99].
As was described above, the polytypism of pseudowollastonite can be described taking into account the variation of the stacking sequences of the displaced layers of ternary rings with the undisplaced layer. Seryotkin et al. [102] have shown the comparison of stacking sequence of layers of (Si$_3$O$_9$) rings in two- and four-layer pseudowollastonite.
polytypes as shown in Figure 4.6 based on the studies carried out by Yang and Prewitt.

### 4.1.4 Literature review of CaSiO$_3$

As mentioned earlier, the calcium metasilicate or also known as wollastonite (CaSiO$_3$) is an interesting material for study in mineralogy, either in its natural or synthetic form, by the different polytypes described in many studies [88, 91–102]. In the last years, CaSiO$_3$, doped or not, has received great attention because of its luminescence properties and the sensitivity shown for gamma radiation [103, 116–120]. Bailiff and collaborators [121] have studied the use of calcium silicate bricks from the populated settlement of Narodychi in Ukraine for retrospective dosimetry.

Souza et. al. [103] have studied the thermoluminescent properties of pellets containing powdered Wollastonite (from Minas Gerais, Brazil) embedded in Teflon irradiated with gamma radiation from a Co-60 source. The TL glow curves, using a linear heating program with a rate of 10 °C/s, exhibit three main peaks, the first peak is located in the range from 100 to 150 °C; the second peak presents a wide broad emission between 150 and 225 °C with the higher intensity at 200 °C and a third TL peak can be observed at 245 °C, overlapped at the end of the second peak [122]. The dosimetric TL peak at 200 °C was found to be dependent on dose and the dosimetric characterization of this peak has shown linearity at the calibration curve between 0.5 Gy and 10 Gy and supralinear between 5x10$^2$ and 7x10$^3$ Gy. Taking into account these results, it is suggested that this material will be a good material for high dose measurements. Reproducibility of these Wollastonite-Teflon pellets was also studied and the study showed that the repeated TL measurements after annealing and irradiation (cycles of irradiation-reading-annealing) have not shown any appreciable change in their sensitivity. In addition, Souza et al. [40] have investigated the dosimetric characteristics of mixed Wollastonite-Teflon pellets after X-rays irradiation. The TL glow curve, using a linear heating rate of 10 °C/s, presented peaks at 85 °C and 200 °C, the second one being the prominent one.
The second peak at 200 °C was considered as the dosimetric peak displaying linearity at the calibration curve between 1.5 Gy and 6.0 Gy for the radiation energy of 37.05 keV.

S. Kulkarni et al. [120] have synthesized nanocrystalline wollastonite CaSiO$_3$ phosphor by low-temperature combustion method. The TL glow curve of β-irradiated CaSiO$_3$, using a heating rate of 6 °C/s, has shown a prominent peak at 236 °C along with a broad shoulder peak at 172 °C. Furthermore, the deconvolution of the TL glow curve has shown that this prominent high-temperature peak at 236 °C is a superposition of four peaks at 145, 174, 208, and 242 °C which was used to estimate the trap parameters. No studies have been reported about neutron or ion dosimetry using dosimeters based on CaSiO$_3$.

H. Nagabhushana et al. [117, 123] have studied the synthesis, characterization, and photoluminescence properties of CaSiO$_3$:Eu$^{3+}$ (1-5 mol.%.) and CaSiO$_3$:Dy$^{3+}$ (1-5 mol.%.) nanophosphors. These materials were synthesized by a simple low-temperature solution combustion method. Powder X-ray diffraction patterns revealed that these phosphors are crystalline and can be indexed to a monoclinic phase. Photoluminescence (PL) properties of the CaSiO$_3$:Eu$^{3+}$ and CaSiO$_3$:Dy$^{3+}$ phosphors were observed and analyzed. The PL emission spectra of CaSiO$_3$:Eu$^{3+}$ phosphor excited at 254 nm shows strong and sharp peaks which are attributed to $^5D_0 \rightarrow ^7F_2$ emission transitions. This emission spectra consist of well-resolved features at 581, 593, 614, 654, and 724 nm [117]. The PL emission intensity of Dy$^{3+}$ with respect to annealing temperature was studied. The PL emission spectra of CaSiO$_3$:Dy$^{3+}$ phosphor excited at 351 nm consist of well-resolved features peaks at 483, 573, and 610 nm which correspond to emissions of Dy$^{3+}$ [123].

In addition, S. Kulkarni et al. [116] reported EPR studies on CaSiO$_3$:Pb, Mn- nanophosphors which exhibits a broad resonance signal centered at $g = 1.994$. Chakradhar et al. [124] have carried out EPR studies on Fe$^{3+}$ - and Ni$^{2+}$ - doped CaSiO$_3$. The EPR spectrum of Fe$^{3+}$ ions in CaSiO$_3$ exhibits a weak signal at $g = 4.20 \pm 0.1$ and an
intense signal at $g = 2.0 \pm 0.1$ while the spectrum of the Ni$^{2+}$ ion exhibits symmetric absorption at $g = 2.23 \pm 0.1$.

In the present study, both pseudowollastonite and wollastonite-2M have been synthesized in the laboratory and an investigation of the thermoluminescence and its relation with the paramagnetic centers in synthetic wollastonite has been carried out. The measurement of the gamma irradiation effects and thermal treatment employing the EPR technique, in this material, is an attempt to understand those physical properties dependent on EPR point defects. Furthermore, the high sensitivity that is shown by wollastonite, both natural and synthetic form, to gamma radiation [41, 120, 122] make it an interesting material of study not only for electromagnetic radiation but also charged accelerated particles as well as neutrons when doped with elements of high neutron capture cross section.
Chapter 5

Revision of pertinent theoretical background

5.1 The vitreous transition

The most common way to produce glasses is by quickly cooling a certain compound at its fusion point. This procedure allows the glass structure to be reached before the crystallization has time to occur. For more precision of this study, it will be considered a thermodynamic variable, such as the specific volume $V$ as a function of the temperature.

J. Zarzycki [125] has introduced the definition of the glass transition temperature $T_g$. He showed that in a liquid (L) at an elevated temperature, the decrease in temperature first causes a contraction. In this cooling, when the point of solidification (or freezing) $T_f$ is reached two phenomena may occur. First, the crystallization with a discontinuity $\Delta V_f$ (contraction) as shown in curve C at $T_f$ point in Figure 5.1. Secondly, the liquid goes into a supercooled state (SL) following the same continuous curve and ignoring the $T_f$ temperature as shown in curve (SL) in Figure 5.1. In the first stage, as the temperature decreases the crystalline solid contracted again, and the slope of this new curve, below $T_f$, is less than that of the initial curve L (about 1/3). In the second case,
Table 5.1: Average values of the glass transition temperature $T_g$(K)  

| Materials                              | $T_g$(K)  |
|---------------------------------------|-----------|
| SiO$_2$                               | 1500 - 2000 |
| Na$_2$O-CaO-SiO$_2$ (window glass)    | 800 - 820  |
| B$_2$O$_3$                            | 470 - 530  |
| Se                                    | 302 - 308  |
| Glycerol                              | 180 - 190  |

the decrease in temperature produces a contraction of the supercooled liquid (SL) but with the same slope to that of the initial curve (L) towards a certain temperature $T_g$. After that, the slope of the curve decreases to a value close to that of the crystalline solid. This break in the cooling curve at the temperature $T_g$ is the transition from a supercooled liquid to a glass. $T_g$ is known as the transition temperature. Table 5.1 lists experimental values of mean glass transition temperature $T_g$ of some compounds [125].

5.1.1 Devitrification process

As mentioned above when a material, at the melting point is followed by a sufficiently rapid cooling reaches the temperature $T_g < T_f$, a glass is obtained. One material

![Figure 5.1: Variation of the specific volume with temperature. L: liquid, SL: supercooled liquid, C: crystal, V: glass. After [125].](image-url)
with these characteristics, previously mentioned, is the silicate crystal. On the other hand, if the compound is slowly cooled, the crystallization takes place with the formation of crystals throughout the volume. To go into more detail, we will describe the mechanisms and conditions of crystallization.

**Crystallization mechanisms**

In the crystallization of a homogeneous compound phase, the first experimental observation is the fact that crystallization is not a transformation that occurs throughout the whole volume at one time. There are initial and discrete centers where the crystallization is gradually extended. This process goes through the following stages:

**Nucleation**

Nucleation state refers to the formation of agglomerations (clusters or molecules) as starting points for the development of ordered regions. These agglomerations are called *embryos*, which form and disappear due to the structural fluctuation produced by thermal agitation.

The gradual cooling eventually favors the formation and growth of embryos, giving rise to crystallization. It can be shown that an embryo must have a critical dimension to be considered as a starting point to enter the crystallization phase. At this stage, the embryo becomes the nucleus of crystallization. In addition, nucleation is considered homogeneous when it occurs in a completely random manner and the condition for this process is that all volume elements of the initial phase must be structurally, chemically and energetically identical. This condition implies that the whole volume to be chemically homogeneous without structural imperfections. Although in practice this is not possible because the surface of the liquid and the crucible walls that support this compound are, for obvious reasons, imperfections. Moreover, even starting from chemically quite pure compounds, it is inevitable that in fact there are impurities. All of these imperfections serve as nucleation sites since the formation activation energy is lower than in a completely homogeneous medium. Nucleation from impurities is called
**heterogeneous nucleation.** However, since homogeneous nucleation is an ideal case, it may be initially studied in a theoretical way.

**Theoretical focus of homogeneous nucleation.**

Zarzycki [125] has introduced two important parameters on which crystallization depends. Among them: \( I \), it is the number of nuclei produced in a unit volume per unit time that is called the *nucleation rate*. Besides, the velocity \( u \) at which nuclei grow is called *growth rate*. Both \( I \) and \( u \) depend on the temperature as shown in Figure 5.2.

As already seen, above the melting temperature \( T_f \) is the stable liquid phase, but when the liquid is supercooled below \( T_f \), theoretically crystal growth between \( T_f \) and \( T_3 \) is possible. But crystallization itself requires that the growth stage is between \( T_2 \) and \( T_4 \). It is then seen that between \( T_2 \) and \( T_3 \), is the overlap region between nucleation and growth, i.e., in the temperature range \((T_2, T_3)\) the nuclei grow to give rise to crystals. If in the common interval \((T_2 - T_3)\), \( I \) or \( u \), or both, are very small, there will be no observable crystallization and the material will pass to the vitreous phase. On the other hand, if \( I \) and \( u \) are high with a greater overlap of the curves, the total crystallization is produced. For the case when \( I \) is high and \( u \) is low, the material obtained will be partially crystalline.
5.2 The crystal structure of minerals

5.2.1 Bonding in crystal structures

Bonding in crystal structures are determined by chemical bonds, that is, the mechanisms or forces that hold atoms together in minerals and rocks. The nature of these bonds is characterized by the electron configuration of the elements that join together to form the material. As a consequence, these bonds influence the properties and behavior of Earth materials such as minerals and rocks.

At the simple level of discussion, it is possible to mention three types of bonding that occur in minerals, defined in terms of the valence electron distribution. Other bond types include van der Waals and hydrogen bonds. It is worth to explain some important definitions which will be mentioned later. For instance, the first ionization energy is the amount of energy required to remove one electron from the electron cloud; in the same way, the second ionization energy is the amount required to remove a second electron and so forth. Furthermore, another useful concept is the electronegativity (En). This is an empirical measure that expresses the tendency of an element to attract electrons when atoms bond. Highly electronegative elements (En > 3.0) have a strong tendency to become anions during bonding (many elements belonging to group VI-A and VII-A of the periodic table).

1. Ionic bonds. Also called the electrostatic bond. This type of bond occurs when a metallic atom (e.g., columns 1 and 2 of the periodic table) links together with a non-metallic atom. The metallic atoms give up their valence electrons to the non-metallic atoms that capture them. In this electron exchange process, the metallic atom which loses the electrons attains the positive charge and is known as the positive ion, while the non-metallic atom that gains the electrons attains the negative charge and called as the negative ion. Both atoms develop stable noble element electron configuration. Because particles of opposite charge attract each other, the cations and anions are held together by the electrostatic
attraction between them. The most common example cited of ionic bonding is that between sodium (Na\(^{+1}\)) and chloride (Cl\(^{-1}\)) ions in the mineral halite (NaCl).

2. **Covalent (electron-sharing) bonds.** Covalent bond occurs when non-metallic atoms link together with other non-metallic atoms. The elements involved in a covalent bond are electronegative (right of the periodic table which are non-metals). They each tend to attract electrons; neither give them up easily because of their high first ionization potentials and electron affinities [83]. In covalent bonding, the atoms involved share valence (thus covalent) electrons. In this sharing process, each atom gains the necessary electrons to achieve a stable electron configuration in its highest principal quantum level.

3. **Metallic bonds.** This type of bond is formed when metallic atoms bond with another metallic atom. Metallic atoms have low first ionization energies and low electronegativities. For these reasons, they do not tend to hold their valence electrons strongly. Consequently, each atom releases valence electrons to achieve a stable electron configuration. These valence electrons released can move freely as part of a ‘sea’ of electrons which provides a cohesive ‘glue’ holding the positive ions together. As a result, metal structures display high electrical conductivity [89].

### 5.2.2 Crystal lattice

In the description of any crystalline structure, a fundamental concept to be considered is the *Bravais lattice*. Firstly, a lattice is in general defined as a discrete but infinite regular arrangement of points (lattice sites) in a vector space. In this way, the Bravais lattice is the distinct lattice-type which when repeated can fill the whole space. W. Ashcroft and N. Mermin [126] give two equivalent definitions of Bravais lattice:
A Bravais lattice is an infinite array of discrete points with an arrangement and orientation that appears exactly the same, from whichever of the points the array is viewed.

A three-dimensional Bravais lattice consists of all points with position vectors \( \mathbf{R} \) of the form:
\[
\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3.
\]
where \( \mathbf{a}_1, \mathbf{a}_2, \) and \( \mathbf{a}_3 \) are any three vectors not all in the same plane, and \( n_1, n_2, \) and \( n_3 \) range through all integral values.

These vectors \( \mathbf{a}_i \) are called *primitive vectors*. In this section, it is possible to explain some basic definitions. Among them, the coordination number. Because of the periodic nature of the Bravais lattice, each point has the same number of nearest neighbors. This number is characteristic of the lattice, and is referred to as the coordination number of the lattice. Furthermore, it is possible to define the reciprocal lattice as the set of wave vectors \( \mathbf{K} \) for which the corresponding plane waves \( e^{i\mathbf{K} \cdot \mathbf{r}} \) have the periodicity of the Bravais lattice \( \mathbf{R} \). Another important definition is that of the Miller indices. The Miller indices of a lattice plane are the coordinates of the shortest reciprocal lattice vector normal to that plane, with respect to a specified set of primitive reciprocal lattice vectors. In this way, a plane with miller indices \( h, k, l \), is normal to the reciprocal lattice vector \( \mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \). In addition, the Miller indices of a plane have a geometrical interpretation in the direct lattice. that is, this plane intersects the axes determined by the direct lattice primitive vectors \( \mathbf{a}_i \) at the points \( x_1\mathbf{a}_1, x_2\mathbf{a}_2, x_3\mathbf{a}_3 \) as shown in Figure 5.3. Where \( x_i \) satisfy the equation of the plane: \( \mathbf{K} \cdot (x_i \mathbf{a}_i) = A \), for suitable choice of constant \( A \) [126]. Furthermore, since \( \mathbf{K} \cdot (\mathbf{a}_1) = 2\pi h \), \( \mathbf{K} \cdot (\mathbf{a}_2) = 2\pi k \), \( \mathbf{K} \cdot (\mathbf{a}_3) = 2\pi l \), we can conclude that the intercepts with the crystal axes of a lattice plane are inversely proportional to the Miller indices of the plane, that is, \( h: k: l \) = \( 1/x_1: 1/x_2: 1/x_3 \).

### 5.2.3 The classification of Bravais lattices

The classification of Bravais lattice from the point of view of symmetry is characterized by the specification of all rigid operations that include all translation through lattice
vector, rotations, reflections, and inversions\cite{126}. The set of operations is known as the *symmetry group* or *space group* of the Bravais lattice. Considering the full symmetry group of Bravais lattice there are fourteen distinct space groups that a Bravais lattice can be. These fourteen Bravais lattices, each with a characteristic unit cell, are grouped into seven symmetry groups. These correspond to the seven crystallographic systems, that is, seven distinct point groups that Bravais lattice can have. We list below these seven crystal systems correspond to seven types of conventional unit cells and the number of Bravais lattice belonging to each system (in parentheses after the name of the system): cubic(3), tetragonal(2), orthorhombic(4), monoclinic(2), triclinic(1), trigonal(1), and hexagonal(1).

### 5.2.4 Ionic crystal

In ionic crystals, the crystal lattice is formed by alternating positive and negative ions, resulting from the transfer of an electron (or more) from one type of atom to another through an ionic bond as explained earlier. The stability of the crystalline lattice is maintained by the electrostatic attraction between the involved ions, such as Na\(^+\) and Cl\(^-\) ions in the NaCl molecule (sodium chloride) or in the Li\(^+\) and F\(^-\) ions in the LiF (lithium fluoride) molecule. Figure 5.4 shows the crystal structure of sodium chloride. It is worth to be mention that the ions, which form the crystalline lattice, may have a structure formed of ionic and covalent bonds as shown in the SiO\(_4\) ion, the basic
crystal structure of silicates. K. Hefferan and J. O’Brien [83] have mentioned the main characteristics of crystals with ionic bonds, which are shown below:

1. Variable hardness.

2. Brittle at room temperatures.

3. Quite soluble in polar substances (such as water).

4. Intermediate melting temperatures.

5. Do not absorb much light, producing translucent to transparent minerals with light colors and vitreous to sub-vitreous luster in macroscopic crystals.

![Figure 5.4: Crystal structure of the sodium chloride. The Na\(^+\) ion is represented by red balls, and the Cl\(^-\) by black balls.](image)

5.2.5 Energy bands

An ion crystal is an insulating solid formed by positive and negative ions, which are attracted by Coulomb forces. These positive and negative ions are periodically distributed in space as shown in Figure 5.6. A consequence of this fact is the all-electron distribution in the crystal. In principle, if we solve the Schrödinger equation of this ideal crystal, we should show that possible energies of the electrons are distributed in bands, but this is a complicated task. For this reason, we consider simple situations, in which in this approximation one can observe the formation of bands.
On the free electron model the allowed energy values are distributed essentially continuously from zero to infinity. Assuming that the electron being confined in a cube of side L, the allowed energies are (energies allowed according to the solution of the Schrödinger equation):

$$\epsilon_k = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m}k^2$$  \hspace{1cm} (5.1)

where \(m\) is the mass of an electron, \(\hbar = \frac{\hbar}{2\pi}\), \(\hbar\) is the Planck constant and \(k\) is the wavevector. For the periodic contour conditions on a cube of side L and volume V, the possible values of \(k_x, k_y, k_z\) are:

\[
k_x, k_y, k_z = 0; \pm \frac{2\pi}{L}; \pm \frac{4\pi}{L}; .... \hspace{1cm} (5.2)
\]

The free electron wavefunctions are of the form

$$\psi_k(r) = \frac{1}{\sqrt{V}}\exp(i\mathbf{k} \cdot \mathbf{r})$$  \hspace{1cm} (5.3)

where \(r\) is the position vector. These wavefunctions represent running waves and carry momentum \(p = \hbar k\).

This wave, similar to the X-ray wave that propagates through a periodic distribution of atoms, undergoes the so-called Bragg reflection, which leads to a discontinuity in energy: energy gap. This gap occurs each time the wavevector \(k\) undergoes the Bragg condition:

\[
(k + G)^2 = k^2 \hspace{1cm} (5.4)
\]

in one dimension it becomes as:

\[
k = \pm \frac{1}{2}G = \pm \frac{n\pi}{a} \hspace{1cm} (5.5)
\]

where \(G = 2\pi n/a\) is the corresponding vector of the reciprocal lattice and \(n\) is an integer. The first reflections and the first energy gap occur at \(k = \pm \pi/a\) and the wave reflected in the linear lattice interferes constructively with the wave reflected by the
neighboring atom. The region in \( k \) space between \(-\pi/a\) and \( \pi/a \) is the so-called first Brillouin zone of this lattice [127]. In \( k = \pm \pi/a \) the wave functions are not running waves, but, standing waves. Let’s see how this happens. From two traveling waves it is possible to form two different standing waves:

\[
\exp(\pm i\pi x/a) = \sin(\pi x/a) \pm i \cos(\pi x/a) \tag{5.6}
\]

being the standing waves:

\[
\psi(+) = \exp(i\pi x/a) + \exp(-i\pi x/a) = 2 \cos(\pi x/a) \tag{5.7}
\]

\[
\psi(-) = \exp(i\pi x/a) - \exp(-i\pi x/a) = 2i \sin(\pi x/a) \tag{5.8}
\]

Figure 5.5: In the upper part is shown components \( \cos^2(\pi x/a) \) and \( \sin^2(\pi x/a) \), for the wave function at \( k = \pm \pi/a \), which are proportional to the probability density \( \psi(+) \) and \( \psi(-) \) respectively. In the lower part the potential exerted by a one-dimensional arrangement of atoms with lattice parameter \( a \) is shown. After [127] where waves labeled as (+) and (-) indicate whether waves are symmetric (+) or antisymmetric (-), and the square of the real part is shown in Figure 5.5. The probability density \( \rho \) of a particle is \( \psi * \psi = |\psi|^2 \). In this case, for the traveling wave \( \exp(ikx) \), we have a constant probability density, that is, \( \rho = \exp(-ikx) \exp(ikx) = 1 \). The probability density is not constant in standing waves, which are linear combinations of plane waves. In fact, in the case, of \( \psi(+) = 2\cos(\pi x/a) \), we have \( \rho(+) = |\psi(+)|^2 \propto \cos(\pi x/a)^2 \). In the same way for the other standing wave \( \psi(-) = 2\sin(\pi x/a) \) the
probability density is \( \rho(-) = |\psi(-)|^2 \propto \sin(\pi x/a)^2 \). In the lower part of Figure 5.5, the electrostatic potential energy of an electron in the field of the positive ions of a linear monoatomic lattice is represented. The potential energy of an electron in this case is negative so that the force between them is attractive.

The traveling wave \( \exp(ikx) \) distributes the electrons along the horizontal line as shown in Figure 5.5. The wave \( \psi(-) \) distributes the electrons in the intermediate space between two ions, thereby raising the potential energy in comparison with that seen by a traveling wave. Whereas the wave \( \psi(+ \) has maximum in the position of the ion, thereby lowering the potential energy in comparison with the average potential energy seen by a traveling wave. The difference between the energies of \( \psi(-) \) and \( \psi(+) \), \( E_g \), is the energy width of the energy gap. Just below the energy gap at points A in Figure 5.6 the wavefunction is \( \psi(+) \), and just above the gap at points B the wavefunction is \( \psi(-) \). The solution of the Schrödinger equation of the free electron in a periodic potential shows the appearance of \( E_g \). For this purpose, Bloch functions are used, but this procedure will not be presented in this work. More information about this demonstration can be seen in the book of C. Kittel [127], chapter 7.
5.2.6 Energy bands in solid due to Pauli principle

A different way of explaining the formation of energy bands is by considering the Pauli Exclusion Principle. It is known that the exclusion principle allows accommodating with two electrons each energy level in an atom (levels with the lowest energies), but with different electron spin (the up and down states of the electron spin).

A solid can be considered to consist of a large number (for instance, $N$) of atoms, initially separated from each other, which are subsequently grouped together and bound to form the ordered atomic arrangement such as in a crystalline material. For relatively large separation distances, each atom is independent of all others and will have the atomic energy levels and the electron configuration that it would have if it were isolated. However, as the atoms get close to each other, the electrons feel the action of the electrons and nuclei of the adjacent atoms. This influence is such that each distinct atomic state can be split into a series of electron states closely spaced in the solid to form the so-called electron energy band [128]. In other words, if $N$ atoms are brought together to form a solid, the Pauli Exclusion Principle still requires that only two electrons in the entire solid have the same energy. In this way, we will have $N$ distinct, but only slightly different energy levels, forming an energy band.

The extent of energy levels splitting depends on the interatomic separation and begins with the outermost electron shells, since they are the first to be perturbed as the atoms coalesce. Z. D. Jastrzebski [129] has shown the dependence of the electron energy as a function of interatomic separation as shown in Figure 5.7(b). In this figure it is interesting to note that in an equilibrium spacing, the band formation may not occur for the electron levels closest to the nucleus, as shown in Figure 5.7(b). The conventional way of representing the structures of the electronic bands in the solids is shown in Figure 5.7(a).

Particularly, in the case of ionic crystals where a large number of positive and negative ions are placed together to form the structure, for example Na$^+$ ions and Cl$^-$ in NaCl crystal, electrons in the crystal will be distributed in bands of energy starting with 1s electrons in Na and Cl occupying lowest energy band and valence electrons in valence
Figure 5.7: (a) The accepted representation of the electron energy band structure for a solid material at the equilibrium interatomic separation. (b) Electron energy as a function of the interatomic separation for an aggregate of atoms, illustrating how the energy band structure at the equilibrium separation in (a) is generated. After [129].

band. To simplify we consider a very large number of atoms of Na. The electronic configuration of each atom is 1s\(^2\)2s\(^2\)2p\(^6\)3s\(^1\) wherein the shell 1s there are 2 electrons, 2 in 2s, 6 in 2p e 1 in 3s. While the atoms are far apart from each other electrons for example in 1s\(^2\) have the same energy \(\xi\) and the total energy is the sum of all this energy. When these \(N_a\) atoms are brought together to form a solid, electrons are now subject to Pauli Principle and except for two electrons that have opposite spins, electrons in the shell 1s\(^2\) must have different energies however small the difference.

Figure 5.8 shows the last band with electrons is that of filled valence electrons, therefore called Valence Band. The next possible band is, normally, empty and is called Conduction Band, between these two bands there is an empty band, so-called band gap. For very pure materials, the electrons cannot have energies located within that band gap. For insulating materials, the spacing between the VB and CB is relatively broad while in the case of semiconductor materials these spaces are narrow. The Fermi energy for these two materials types is located within the spacing between the bands.
near their central region.

5.2.7 Real crystals

Almost all real crystals contain impurities or imperfections, in their structure, also known as crystal defects. These crystal defects are responsible for the variation in the composition and mineral structure from the ideal crystal, as well as, of causing profound effects on the properties of the crystalline material. Usually, crystal defects are classified according to their dimensions as point and line defects. In this work, we are interested just in point defects. Point defects do not have a long-range extent because they involve individual atoms. When these point defects come from the crystalline lattice itself, they are called intrinsic; and when they are caused by atoms foreign to the crystal, these defects are considered extrinsic and called impurities.

On the other hand, in complex minerals structures, the nature of the point defects is not well understood. In this way, Putnis [89] has explained the nature of two main point defects present in simple compounds such as halides, e.g. NaCl, AgCl. The first case is that in which a vacant cation site in a structure is balanced by a vacant anion site to maintain electrical neutrality. That is, the vacancies may appear in pairs in

![Diagram of electron band structures in solid at 0 K for (a) insulators, the filled valence band is separated from the empty conduction band by relatively large band gap (> 2eV); and for (b) semiconductors, which is the same as for insulators except that the band gap is relatively narrow (< 2eV). After [128]](image)
the crystal structure, thereby maintaining the electrical neutrality of the crystal. Such a pair of vacancies is called a Schottky defect and a schematic diagram, for the case of NaCl, is shown in Figure 5.9(a). The other possible type of point defect occurs when an atom moves from its original site, leaving a vacancy, occupying an alternative interstitial site (the spaces between structural sites) which is usually unfilled. This is known as a Frenkel defect leaving the overall charge balance and stoichiometry unaffected, in the same way that the Schottky defect. Figure 5.9(b) shows a schematic representation of a Frenkel defect in AgCl (similar structure to the NaCl). These types of point defects, Schottky and Frenkel, are referred to as intrinsic defects since their numbers are controlled by intrinsic properties of the structure, related to the size of the interatomic forces [89].

5.2.8 Energy levels in the band gap

At this point, it becomes important to describe the hole definition, keeping in mind the electron band structures in a solid as shown in Figure 5.8 and considering an electron from the valence band which is excited towards the conduction band leaving an electron deficiency in the valence band. This electron deficiency is called a hole. The electron in the conduction band is free to move under the action of an applied field towards the direction to the anode because of its negative charge. In the same way, the hole in the valence band is free to move under the action of a field but moves
toward the cathode because of the positive charge behavior of the hole. This positive charge is equal in magnitude to the negative charge of the electron. Actually, the hole itself does not make the moving, it is electrons that move towards the anode in the valence band which produces this effect of moving the holes towards the cathode [130].

An important characteristic of the point defects is that in which they can create levels of energy in the band gap that do not exist in the ideal crystal. We will try to explain this with an example. If we have an MX compound formed by divalent atoms $M^{+2}$ and $X^{2-}$, the replacement of $M^{+2}$ with a monovalent $N^{+1}$ atom results in local deficiency of positive charge and consequently a decrease in the energy required to release an electron from a bound atom $X^{2-}$, in comparison to the ideal crystal. This is equivalent to introducing an energy level just above the valence band. In addition, the release of an electron gives rise to the formation of a hole. In this manner, we can say that such a defect acts as a hole energy level. Similarly, replacing $M^{+2}$ with an $R^{+3}$ atom produces a local negative charge deficiency, introducing a level just below the conduction band that can capture electrons. Such a defect acts as an electron energy level. The electronegativity differences cause a substitution impurity to produce an energy level of electrons or holes, even when there is no difference in the valence between the impurity and the crystal atom it is replacing [130].

Energy levels, in the band gap, created by the defects are called electron and hole traps as they can capture electrons or holes. Usually, the charged traps (electron or hole) are called centers. At absolute zero temperature, the band gap is divided in half by the energy Fermi level (EF). Energy Fermi level is the term used to describe the top of the set of electron energy levels at absolute zero temperature. The electron traps are located between EF and the conduction band, and holes between EF and the valence band. Here the term “trap” is adopted as the energy level in the band gap capable of capturing a positive or negative charge. Electrons and holes in this energy band representation can perform transitions between valence band, conduction band, electron and hole traps. Mckeever [14] has described the common electronic transitions in crystalline insulators. Figure 5.10 shows these transitions.
(a) Ionization process: when a valence band electron receives enough energy from an external source so that it may be released into the conduction band (1). This ionization creates free electron-hole pairs, that is, for every free electron in the conduction band a free hole is left behind in the valence band.

(b) The electron in the conduction band and/or hole in the valence band move freely until caught by an electron trap and/or hole trap. (2) and (5).

(c) These trapped electrons and/or holes may be released from their traps towards the conduction band and/or valence band by heating or optical excitation. (3) and (6). After that, they are once again free to move through the crystal.

(d) Furthermore, free electrons in the conduction band and holes in the valence band may make a recombination transition. That is, they may recombine with a charge carries of opposite sign, either directly (8) or indirectly (4 and 7), when a photon is emitted. The hole trap, in this case, is called the recombination center.

(e) A type of transition (9) without passing through the conduction band (or valence band) is a type of center-to-center transition. This type of transition is normally radiative, that is to say, there is the emission of photons. Materials doped with rare earth exhibit this kind of recombination.
The scheme, shown in Figure 5.11 displays the recombination centers, which are the traps closer to EF. Whilst the traps themselves are those closer to the edges of the conduction and valence bands [14].

### 5.2.9 Luminescence

Luminescence is a phenomenon shown in some materials that have the capability of emitting light after previous irradiation. That is, some of this energy, from irradiation, can be absorbed by the material and re-emitted as light. The wavelength of the emitted light is characteristic of the luminescent material and not of the incident radiation. Studies of the luminescent phenomenon are related to light emission in the visible region, but other wavelengths may be present in the emission spectrum of the material, such as ultra-violet and infra-red. Different kinds of luminescence phenomena have been named according to the type of radiation used. For instance, photoluminescence (excitation by optical or ultra-violet light), cathodoluminescence (electron beam), and radioluminescence (γ radiation, β particles, X-rays, etc.).

The luminescence phenomenon can be characterized by the time interval between excitation (energy absorption) and light emission: $\tau$. For $\tau < 10^{-8} \text{ s}$ the phenomenon is classified as fluorescence and for $\tau > 10^{-8} \text{ s}$ classified as phosphorescence. Thermoluminescence is characterized between minutes $< \tau < 4.6 \times 10^9 \text{ years}$ [14]. However, there
is a better way to distinguish fluorescence and phosphorescence phenomena, which is by the study of the temperature effect upon the decay of the luminescence [14]. For this reason, we consider an energy level that refers to the ground state of an electron (g) and an energy level that refers to the excited state (e), as shown in Figure 5.12a. In fluorescence, the light emission occurs when the electron is excited from the ground state (g) to the excited state (e) (transition i), and subsequently, this electron returns to the fundamental energy level g (transition ii). Fluorescence is a process independent of temperature. On the other hand, the transition from excited (e) to the ground state (g) (transition ii) may not occur directly, that is, the electron becomes trapped to a metastable intermediate state (m) (in the forbidden energy gap between e and g) as shown in Figure 5.12b. The electron will remain in this state (m) until receiving enough energy E to return to the excited state (e) and then to the ground state (g) emitting light (Figure 5.12b). This process is called phosphorescence and the delay observed is represented by the time the electron spends in the electron trap m. The mean time spent in the trap at temperature T is given by (Arrhenius equation) [14]:

\[
\tau = s^{-1} \exp \left( \frac{E}{kT} \right)
\]  

(5.9)

where \( s \) is a constant (s\(^{-1}\)), \( k \) is Boltzmann’s constant, and \( E \) is the energy separation between levels m and (e).
In addition, if we consider a Boltzmann distribution of energies, the probability $p$ per unit of time that an electron escapes from the metastable level $m$ (trap) at a given temperature $T$ is given by:

$$p = s \exp \left( -E/kT \right)$$

(5.10)

In this way, if the transition at level $m$ occurs at an absolute temperature $T$, such that $E >> kT$, the electron will remain in state $m$ for a long period of time [15].
5.3 Thermoluminescence (TL)

The phenomenon of thermoluminescence (TL) or, more technically accurate, thermally stimulated luminescence, is the emission of light by thermal stimulation. As explained earlier, TL is characterized by the emission of light by heating of insulating or semiconductor. This material has previously been subjected to ionizing radiation storing energy. To explain this phenomenon we will use the electron transition representation shown in Figure 5.10.

As explained in section 5.2.8 when ionizing radiation hits the material, it transfers enough energy to the electrons to move from the valence band to the conduction band by photoelectric effect or Compton effect, where they move freely. Eventually, the electrons are trapped in the band gap (in traps). These traps are characterized by the energy $E$, measured from the bottom of the conduction band to the trap. The stability of the trapped charge depends on the depth $E$ of the trap.

After the jump of the electron into the conduction band, a hole in the valence band is produced. This hole moves freely in the valence band but if it is not recombined almost immediately with an electron, it can be captured by a hole trap whose depth from the top of the valence band to the trap is measured. If the depths of the electron

![Figure 5.13: Simple model of TL process. Irradiation (a), electron and holes trapping (b and c), electron release (d), recombination (e). After [131]]
or hole traps are small, it is likely that the trapped electron or hole escapes at room temperature. But if the depth is relatively large, the time at which the charge will remain in the trap becomes large.

Through external thermal excitation, the electron receives enough energy to return to the conduction band, where it moves freely, after that, may recombine with a trapped hole, emitting TL light. A similar phenomenon may occur for the hole but in this case, the valence band is the one that receives the hole from the trap. The hole moves freely in the valence band until finding a trapped electron and then recombine emitting light. Figure 5.13 shows a simple model of energy absorption in a TL material. After that, when the material is heated, the saved energy is released as a light photon after the recombination of an electron from the conduction band into a trapped hole.

Currently, there are several instruments for TL measurements, in which one must ensure the following functions: (a) a well-defined and reproducible system of heating the sample; (b) collecting quantitatively the emitted light; (c) converting the light into an electrical signal and measuring it. During the heating of the TL material, the monitored quantity is the emitted light, which is transformed into electric current, and thus a relationship of the luminous intensity with the radiation dose can be established. This quantity is usually monitored as a function of temperature or wavelength. In the first case, the curve obtained from the TL intensity versus temperature is called the TL emission curve or Glow Curve. In the second case, the TL intensity versus wavelength (λ) is the TL emission spectrum.

### 5.3.1 TL glow curve

A TL emission curve defined above is generally characterized by several peaks, each of which is associated with a certain trap, which can be either electron or hole. This trap, in turn, is characterized by a depth E and a temperature T, in which the maximum of TL emission occurs. An example of TL glow curve composed by 7 peaks is shown in Figure 5.14.
Figure 5.14: TL Glow curve composed by 7 peaks. After [132].

Each thermoluminescent material has a characteristic glow curve. The formation of a TL emission peak is related to the probability of escape of the trapped electron, which in turn is temperature dependent, as shown in Equation 5.10. The shape of a TL peak is defined by the so-called kinetic order, as will be seen in section 5.3.3.

A noteworthy fact is the emission curve dependency on the types of traps and recombination centers present in the crystal, as already mentioned. The presence of more than one peak reveals that the crystal has more than one type of trap, consequently several activation energies.

5.3.2 TL emission spectrum

The most conventional measurement made in the TL emission is that which records the light intensity as a function of temperature, which in turn is related to the depth of the traps. However, the luminescent intensity can also be measured as a function of the wavelength of the emitted light, which in turn, is related to specific transitions to recombination centers. This measurement allows us the study of recombination centers present in the material, as well as, the number of wavelengths in which the bands
Figure 5.15: Representation of the energy band structure, showing trap centers and recombination centers. With several depths of the recombination centers, the TL emission will be composed of several wavelengths ($\lambda_1$ and $\lambda_2$).

Figure 5.16: TL emission spectrum for $\beta$-irradiated CaSiO$_3$: TL intensity-versus-wavelength-versus-temperature. After [132].
the TL intensity measurement as a function of wavelength displays spectral bands that make up the TL emission spectrum. Figure 5.16 shows an example of the TL emission spectrum.

### 5.3.3 Theoretical model for thermoluminescence

In this work we will show the simplest model formulated to describe TL [14, 15]. For this purpose, we consider two types of levels located in the forbidden band: an electron trap \( n(t) \) and a recombination center \( m(t) \) as shown in Figure 5.17. The observed TL intensity can be written as a function of the hole concentration variation rate \( \frac{dm}{dt} \) in the recombination centers and the luminescence efficiency \( \eta(T) \).

\[
I(t) = \eta(T)\left(-\frac{dm}{dt}\right)
\]  

(5.11)

We consider \( \eta(T) \simeq 1 \), which means when all recombination events produce photons and all photons are detected. \( n \) is the concentration of electrons in traps and \( n_c(t) \) is the concentration of free electrons in the conduction band. \( m(t) \) is the concentration of available hole states, for recombination, in the recombination centers at time \( t \), and \( N \) is the total concentration of available electron traps (of depth \( E \) below the conduction band). Furthermore, by the charge conservation we have:

\[
n_c + n = m  
\]  

(5.12)

Besides, the expression \((N - n)\sigma_n\nu_e \) is the probability of electron recapture by the trap, and \( m\sigma_m\nu_e \) is the probability of electron recapture by the recombination center, where \( \sigma_n \) and \( \sigma_m \) are the electron capture cross sections by the trap and the recombination center, respectively. \( \nu_e \) is the thermal velocity of the electrons in the conduction band.

Taking into account the considerations mentioned above, it is possible to formulate the following equations: the variation rate in \( n \) has the contribution of disjoined electrons
Figure 5.17: Model of two level located in the band gap: a trap and a recombination center.

\[ (-np) \text{ and recaptured electrons } n_c(N - n)\sigma_n\nu_e: \]

\[ \frac{dn}{dt} = -np + n_c(N - n)\sigma_n\nu_e \]  \hspace{1cm} (5.13)

where \( p \) is given by equation 5.10. On the other hand, the number of holes \( m \) decreases with the electron transitions from the conduction band to the recombination centers.

\[ \frac{dm}{dt} = -n_c m\sigma_m\nu_e \]  \hspace{1cm} (5.14)

From the derivation of the equation 5.12 of charge conservation, we can obtain:

\[ \frac{dn_c}{dt} = -\frac{dn}{dt} + \frac{dm}{dt} \]  \hspace{1cm} (5.15)

Equations 5.13, 5.14, 5.15 establish the system of coupled differential equations for a simple model of two level located in the band gap for thermoluminescence.

Another important assumption introduced into the rate equations is the quasiequilibrium (QE) condition. The electron concentration in the conduction band, initially zero, does not vary significantly in the TL reading process, that is, the electrons that are disjoined from the trap and pass through the conduction band are quickly captured by the recombination centers or recaptured by the traps. In this way, there is
no accumulation of electrons in the conduction band. This condition is called the QE condition, and can mathematically be represented by the following inequality:

\[
\left| \frac{dn_c}{dt} \right| \ll \left| \frac{dn}{dt} \right|, \left| \frac{dm}{dt} \right|
\]  

(5.16)

Equation 5.15 under condition of QE leads to:

\[
\frac{dm}{dt} \approx \frac{dn}{dt}
\]  

(5.17)

Also, using the QE condition in the equation 5.11:

\[
- \frac{dm}{dt} \approx - \frac{dn}{dt} = I(t)
\]  

(5.18)

we can change variation rates shown in the equation 5.18 for the expressions given in equations 5.13 and 5.14. We obtain:

\[
n_c = \frac{np}{(N-n)\sigma_n\nu_e + m\sigma_m\nu_e}
\]  

(5.19)

Furthermore, replacing the previous result in the equation 5.13.

\[
\frac{dn}{dt} = -np \frac{m\sigma_m}{(N-n)\sigma_n + m\sigma_m}
\]  

(5.20)

Applying the QE approximation for charge conservation in the equation 5.20: m(t) \(\simeq n(t)\), and considering the value of R as \(\sigma_n/\sigma_m\) we can obtain:

\[
\frac{dn}{dt} = -\frac{n^2 p}{n(1 - R) + NR}
\]  

(5.21)
Equations 5.18 and 5.21 represent the general solution for the model of two levels located in the QE condition. In addition, from the equation 5.18 we obtain:

\[ I(t) = \frac{npm\sigma_m}{(N-n)\sigma_n + m\sigma_m} \quad (5.22) \]

or (using the equation 5.10 for p)

\[ I(t) = ns \exp\left(-\frac{E_t}{kT}\right) \left[ 1 - \frac{(N-n)\sigma_n}{(N-n)\sigma_n + m\sigma_m} \right] \quad (5.23) \]

### 5.3.4 First-order kinetics model

Also known as Randall-Wilkins model. In this case, the probability of electron recapture by the trap is considered negligible, i.e. \( m\sigma_m >> (N-n)\sigma_n \). Then, considering this slow recapture condition in equation 5.20 gives:

\[ \frac{dn}{dt} = -np \quad (5.24) \]

Considering a linear heating: \( T(t) = T_0 + \beta t \), we have \( \beta = \frac{dT}{dt} \) and, replacing the expression for p from the equation 5.10 in equation 5.24, we get an expression for the concentration of electrons in traps as a function of temperature, \( n(T) \):

\[ n(T) = n_0 \exp\left[-\frac{s}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right)dT'\right] \quad (5.25) \]

Finally, replacing the before equation in the equation 5.23 we obtain the well-known Randall-Wilkins first-order expression for \( I_{TL}(T) \) [133, 134]

\[ I_{TL}(T) = n_0s \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{s}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right)dT'\right] \quad (5.26) \]


5.3.5 Second-order kinetics model

Also known as the Garlick-Gibson Model. In this case, the recombination probability is considered much lower than the recapture probability, which is expressed by \( m\sigma_m \ll (N-n)\sigma_n \). Additionally assuming that the recapture and recombination cross sections are equal (\( \sigma_m = \sigma_n \)). Moreover, that the trap occupation is considered far from saturation (\( N \gg n \)), and with the charge conservation under the QE condition, equation 5.20 is reduced to:

\[
\frac{dn}{dt} = -\frac{n^2 p}{N} \tag{5.27}
\]

Finally, replacing the before equation in the equation 5.23 and considering a linear heating rate \( \beta \), we obtain the well-known Garlick-Gibson second-order expression for \( I_{TL}(T) \) [135]:

\[
I_{TL}(T) = \frac{n^2_0 s}{N} \exp \left( -\frac{E}{kT} \right) \left[ 1 + \frac{n_0 s}{\beta N} \int_{T_0}^{T} \exp \left( -\frac{E}{kT'} \right) dT' \right]^{-2} \tag{5.28}
\]

5.3.6 General order kinetics model

Experimentally, it has been found that TL peaks fit neither first nor second order kinetics. Therefore, May and Partridge [136] proposed an empirical expression for a general-order TL kinetics, which is given by the following relation:

\[
\frac{dn}{dt} = -n^b s' \exp \left( -\frac{E}{kT} \right) \tag{5.29}
\]

where \( s' \) has the dimensions of \( m^{3(b-1)} s^{-1} \), \( b \) is defined as a general order parameter and is not necessarily 1 or 2. The solution of this equation for \( b \neq 1 \) gives:

\[
I_{TL}(T) = s'' n_0 \exp \left( -\frac{E}{kT} \right) \left[ 1 + \left( b - 1 \right) \frac{s''}{\beta} \int_{T_0}^{T} \exp \left( -\frac{E}{kT'} \right) dT' \right]^{-\frac{b}{b-1}} \tag{5.30}
\]

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where $s'' = s'n_0^{(b-1)}$. The difficulty with the empirical development of the general equation lies in the meaning to the parameter $s'$, whose dimensions changes according to the order of kinetics involved. To overcome this problem Rasheedy [137] proposed a new form for the model, starting from equation 5.29:

$$I_{TL}(T) = -\frac{dn}{dt} = \left(\frac{n^b}{N^{b-1}}\right) s \exp\left(-\frac{E}{kT}\right)$$  \hspace{1cm} (5.31)

which it solves the problem with dimensions. Integration of equation 5.31 gives:

$$I_{TL}(T) = n_0^b s \exp\left(-\frac{E}{kT}N^{1-b}\right) \left[1 + \frac{s(b-1)(n_0/N)^{(b-1)}}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{kT'}dT'\right)\right]^{-\frac{1}{b-1}}$$  \hspace{1cm} (5.32)

This expression removes the difficulty of interpreting the meaning of $s'$. From the above equation, it can be reduced to Randall-Wilkins expression for $b \to 1$ and Garlick and Gibson’s expression to $b = 2$.

### 5.3.7 Methods to estimate the TL parameters

In the mathematical models based on the energy band theory, which predicts the TL intensity as a function of temperature (glow curves), each TL peak may be associated with an energy trap $E$ and a frequency factor $s$. This means that these parameters $E$ and $s$ can be determined from the experimental glow curve through a suitable method. There are several analytical methods for determining the parameters of TL models, which are described by some authors [14, 15]. In this work, we will show some of them.

(a) Initial rise method

In equations 5.26, 5.28 and 5.32 corresponding to the first, second and general kinetics order respectively, it is observed that at low temperature for $T \to T_0$ (the beginning of the peak of TL),

$$I(T) \propto \exp\left(-\frac{E}{kT}\right)$$  \hspace{1cm} (5.33)
In this limit, the relevant occupancies of the state, that is the trap and the recombination center can be considered as being approximately constant, so that equation 5.33 does not depend on the order of kinetics. Thus, from the equation 5.33 we can write [135]:

\[ \ln(I) = C - E/kT \]  \hspace{1cm} (5.34)

where C is a constant. Linear regression from points \( \ln(I) \times 1/T \) for the initial region of the glow curve provides the angular coefficient of the curve \(-E/k\), from which the activation energy is easily determined. In the Randall & Wilkins and Garlick & Gibson equations, it can be seen that the initial rise method is suitable in the temperature range \((T_0, T_c)\), where \( T_c \) must not exceed a temperature corresponding to a 10-15\% of the maximum TL intensity [138].

(b) \( E - T_{stop} \) method

Nahum and Halperin [139] developed a method in which several thermal cleaning cycles are performed, each time using a higher temperature. Applying the initial rise method to the residual TL curves, the E value is calculated for each heating. This heating temperature in each cycle is called \( T_{stop} \). The resulting curve of activation energy E as a function of \( T_{stop} \) is generally ladder-shaped, although the steps do not appear very clearly. Figure 5.18 shows an example of this curve E vs. \( T_{stop} \) for thermoluminescence in diamond [139]. However, E-\( T_{stop} \) method faces difficulties when the activation energies are very close or almost continuous, in this case, the E-\( T_{stop} \) curve does not look like a ladder. Furthermore, the gradual increase in E with temperature occurs when the characteristic TL glow curve has increasing activation energies for the peaks which is not always true [14].

(c) \( T_m-T_{stop} \) method

Another interesting method was introduced by McKeever [140] in which unlike of E in the E-\( T_{stop} \) method, the temperature \( T_m \) of the TL peak is given as a function of \( T_{stop} \). The \( T_m-T_{stop} \) method gives an initial estimate of the number of peaks and their positions. Similar to the previous case, the sample is linearly preheated to a \( T_{stop} \)
temperature. Once the $T_{\text{stop}}$ temperature is reached the sample is allowed to cool and the complete TL curve is read at the same heating rate and the first emission maximum $T_m$ that occurs during heating is noted. The sequence is repeated several times with samples under the same initial conditions as those of the previous sample, increasing the $T_{\text{stop}}$ temperature with each repetition. At last, the values of $T_m$ and $T_{\text{stop}}$ obtained are plotted in a curve of $T_m \times T_{\text{stop}}$.

In this method, the preheating is employed to partially decrease the trapped charge concentration. A first-order peak remains in the same position regardless of the corresponding trap population, the $T_m$-$T_{\text{stop}}$ curve with several overlapping first-order peaks, but not to become a continuous distribution of peaks, should have the shape of a ladder where each threshold corresponds to a TL peak as shown in Figure 5.19. For non-first-order kinetics, the peaks move to higher temperatures as the trap population decreases due to preheating. In this case, $T_m$ increases with $T_{\text{stop}}$ and the $T_m$-$T_{\text{stop}}$ profile will not have the shape of a ladder but that of a smoothed increasing curve. The displacement of the peaks to higher temperatures may also occur due to the existence of peaks associated with energy distributions.
5.3.8 Linearity, sub, and supralinearity.

As explained in section 2.3.1, it is desirable that the dependence of the TL response with the radiation dose be linear in a thermoluminescent dosimeter. In alkaline and alkaline-earth halides, sulfides, carbonates, and oxides, in most cases a low dose linear dependence has been observed and, from a certain dose, the response becomes more than linear, that is, with a supralinear behavior. Furthermore, due to the finite number of traps available, eventually, the TL response versus radiation dose ratio becomes sublinear and saturates (as shown in curve P in Figure 2.1). On the other hand, there are crystals in which supralinearity does not occur (as shown in curve Q in Figure 2.1). Li$_2$B$_4$O$_7$: Cu is an example, where the TL response is linear with dose up to about 103 Gy and then goes into saturation [141]. An example of a material that exhibits supralinearity is LiF (TLD-100). This crystal presents linearity for low doses, but from about 10 Gy its TL response exhibits supralinear behavior [142].

There are currently two important models that attempt to explain the occurrence of
supralinearity. One is described by Mische and McKeever [143], in which, a track interaction model is introduced, and that described by Sunta et al. [144, 145] where an analytical method for the thermoluminescence growth curve is studied. In addition, Mitchell et al. [146] found a TL growth behavior of F-centers in KCl that is composed of two parts: (1) for low doses it is linear, (2) for higher doses a superlinear growth followed by saturation is observed. They admitted that the initial TL growth is due to existing defects that capture electrons to form F-center and the second part is due to the creation of new defects by radiation and then the radiation creates F-centers. Studying some varieties of natural quartz, Farias and Watanabe [147] found varieties of TL versus dose behavior of the main peak at 350 °C. They adopted Mitchell’s model to the case and found a good theoretical fit to the experimental results. At the first stage, the TL signal as a function of dose D is given by:

\[ y_1(D) = y_0 \{1 - \exp(-bD)\} \quad (5.35) \]

where \( b \) is the rate of creation of TL traps per unit dose of radiation, \( y_0 \) is the maximum of oxygen vacancies (OV) centers existing at room temperature. In the second stage: \( C \) being the rate of generation of oxygen vacancies by radiation, \( a \) the probability per unit dose to form TL traps centers by capturing electrons and \( N \) the total number of available oxygen ions for generation of oxygen vacancies, the TL intensity in this second stage can be written:

\[ y_2(D) = \frac{N}{C - a} \left\{a \exp(-CD) + (C - a) - C \exp(-aD)\right\} \quad (5.36)\]

The whole TL versus dose is given by \( y_1(D) + y_2(D) \), which is expected to give linearity, supralinearity followed by saturation.
5.4 Electronic Paramagnetic Resonance (EPR)

The Electronic Paramagnetic Resonance (EPR) technique is a physical process involving electronic spin within a magnetic field. An electron is classically considered to be a very small negatively charged sphere rotating about its own axis. In electrodynamics, a negative charge in rotation produces a circulating current in the direction opposite to the rotation of the sphere. Biot-Savart’s law states that a circular current produces a magnetic field in its vicinity, similar to that of a small magnet, to which the electron is equivalent. In an atom or molecule with more than two electrons, there is a tendency for two neighboring electrons to form magnetically neutral pairs, in which case the magnetic moment is equal to zero. As it was previously mentioned, in section 5.2.8, when electromagnetic radiation hits a material, the ionization of this material creates electron-holes pairs. When an ionized electron gets trapped due to point defects, it forms an atom (or molecule) with an excess of electrons, as well as, an atom with a deficiency of electrons, both with an unpaired electron. These are called “trapped electron” and “trapped hole” centers, respectively. They now have a net magnetic moment, $\mu_e$ due to the unpaired electron spins. In addition, an unpaired electron may be considered as a tiny magnet where the unpaired spin tends to align parallel to the direction of a magnetic field and magnetize. The unpaired electron are detectable with microwave absorption spectroscopy under a external magnetic field called “Electron Paramagnetic Resonance” (EPR) [28].

5.4.1 Fundamental principle of EPR

When the rotating electrons are placed in an external-static magnetic field, the direction of the spin rotation which is initially random becomes parallel or antiparallel to the external magnetic field. Figure 5.20 shows three unpaired electronic spins situations within a material [28]. In situation (a), there is no external magnetic field and electronic spins have random orientations. In (b), a magnetic field $\mathbf{H}$ is applied and spins become parallel or antiparallel to $\mathbf{H}$. These two situations are energetically
Figure 5.20: (a) Without magnetic field, spins are randomly oriented. (b) In a magnetic field $H$, the spins are oriented by the Zeeman Effect. (c) The incidence of an appropriate frequency microwave causes a change in spins orientation. The electron spins excited go into the lower level in the time $T_1$. After [28].

different and are known as “up spin” and “down spin” states. In (c), a microwave impinges on the material.

If the frequency of the microwave were appropriate, i.e. $\nu$, some electrons absorb this energy and change its orientation (opposite orientation). In this way, we can say that there was a resonance, in which the change of orientation of some spins occurs. The electron spins excited by the absorption of the microwave quanta go into the lower level by the lattice vibration in a time called the \textit{spin-lattice relaxation time} ($T_1$) as shown in Figure 5.20(c). The absorption of this energy from the microwave $h\nu_0$ by the unpaired electron is called “electron spin resonance”. The magnetic properties of unpaired electrons are expressed by the following parameters [28]:

- Spin angular momentum, $S(\hbar/2\pi)$ (h: Planck constant).
- Spin quantum number, $S$: $S = 1/2$ for an electron.
- Magnetic quantum number, $M$: $M = +1/2$ and $M = -1/2$ are allowed.
- Bohr magneton, $\beta$: the basic unit of a small magnet for an electron spin.
- Magnetic moment, $\mu_e$: $\mu_e = -g\beta S$. 

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Figure 5.21: Energy levels of an electron spin as a function of $H$. Resonance occurs at $H = H_0 = h\nu/g\beta$. After [28].

- Spectroscopic splitting factor, $g$: $g = 2.0023$ for a free electron.

The separation energy responsible for the different spin states under the external magnetic field $H$ is known as the \textit{Zeeman Effect} and depends on $H$ and $\mu_e$. Then,

$$E_H = g\beta HM = -\mu_e \cdot H$$  \hspace{1cm} (5.37)

where $H$ is expressed in Tesla ($1 \text{ mT} = 10$ gauss). The energy level of an electron with $S = 1/2$ splits for $M = 1/2$ and $M = -1/2$. Figure 5.21 shows this energy level as a function of a magnetic field $H$. As explained before, the direction of spins is modified by the absorption of microwave when the energy difference ($\Delta E = \beta gH$) is equal to the quantum energy of an electromagnetic wave $h\nu$. The resonance condition is given by:

$$g\beta H_0 = h\nu$$  \hspace{1cm} (5.38)

where $H_0$ is the resonance magnetic field. It is possible to obtain the resonance absorption by sweeping the magnetic field but maintaining the frequency $\nu$ constant. Figure 5.21 shows the energy levels of the Zeeman separation in an external magnetic field.
The resonance occurs at $H = H_0 = h\nu/g\beta$. Figure 5.22 shows the microwave power ($P$) as a function of $H$. In $H = H_0$, an absorption band is observed.

### 5.4.2 EPR spectrum

Figure 5.22 shows an absorption spectrum of EPR. In practice, the spectrum is recorded as the first $dP/dH$ derivative as a function of $H$. This is due, firstly, to the greater distinction of individual lines in a complex spectrum and, secondly, to the technical advantage of recording the first derivative. The Gaussian or Lorentzian shape can be seen in the shape of the absorption curve. Figure 5.23 shows the Gaussian and Lorentzian shapes of absorption curves, as well as their first derivatives. The intersection of the derivative with the zero line corresponds to the value of the magnetic resonance field. In a complex spectrum, the number of lines is counted from the maximum (or minimum) values of the first derived curves as shown in Figure 5.24.
5.4.3 The g factor

The spectroscopic splitting factor, or also known as the g factor of an EPR signal is an important parameter in analyzing the EPR spectrum. Unpaired electrons in different environments have slightly different g values and this small difference can be used to identify different paramagnetic centers. The change of g factor occurs indirectly through the magnetic interaction between the magnetic spin moment and the orbital magnetic moment, that is, the spin-orbit interaction. The g factor of a free-electron without orbital motion is 2.0000; the relativistic correction gives $g_e = 2.0023$.

The g-factor of a free paramagnetic ion, which is the Landé factor, not only depends on the spin, but also on the orbital movement. This g value is determined by the Landé formula:

$$g_L = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$$

(5.39)

where L, S, and J are quantum numbers of orbitals, spin and total angular moments: $J = L + S$. For a free electron where $L = 0$, then $J = S$, and by the previous equation 5.39, we obtain $g = 2$. 

![Figure 5.24: Enumeration of the lines number in a complex EPR spectrum.](image)
5.5 Fundamental concepts of neutron physics

The discovery of the neutron was an important contribution to understanding the nature of the particles in the nucleus as well as furnished the solution to many questions about nuclear structure. In 1930, Bothe and Becker discovered artificial gamma radiation when bombarded Li, Be, B, and other light elements with α-particles. The gamma radiation from the bombardment of Li was ascribed to nuclear excitation through inelastic scattering of the α particles. Secondly, for boron, the gamma radiation was attributed to the residual $^{13}\text{C}$ nucleus from the $^{10}\text{B}(\alpha, p)^{13}\text{C}$ reaction. Finally, for beryllium it was observed that the most penetrating gamma radiation was attributed to the nuclear excitation by the α-particle capture. The same reaction Be + α was later studied by Joliot and Curie. They found in addition to the gamma radiation observed by Bothe and Becker, a higher energy gamma radiation [71, 148]. In 1932, James Chadwick based on the previously mentioned observations and additional conclusions proposed the existence of a neutral particle with a mass approximately equal to the proton which is produced together with the gamma radiation.

Chadwick called this new particle neutron and represented by “$n$”, a term widely used until today. The nuclear reaction used by Chadwick to explain the production of neutrons is similar to that used by Bothe for beryllium when bombarded by α-particles as shown in equation 5.40.

$$^{9}\text{Be} + \alpha \rightarrow ^{12}\text{C} + n \quad (5.40)$$

which is commonly written as:

$$^{9}\text{Be}(\alpha, n)^{12}\text{C} \quad (5.41)$$

5.5.1 Neutron sources

Although $^{9}\text{Be}(\alpha, n)$ reaction is still utilized as a neutron source, currently there exists other techniques used as sources of neutrons [148]. For example,
Table 5.2: Classification of neutrons according to kinetic energy [70].

| Class Nomenclature     | Neutron kinetic energy range                      |
|------------------------|--------------------------------------------------|
| Cold Neutrons          | $E \ll 0.025$ eV                                  |
| Thermal neutrons       | $E < 0.5$ eV, $E \approx 0.025$ eV (most probable) |
| Epithermal neutrons    | $1$ eV $\leq E < 1$ keV                         |
| Intermediate neutrons  | $1$ keV $\leq E < 50$ keV                        |
| Fast Neutrons          | $50$ keV $\leq E < 20$ MeV                       |
| Relativistic neutrons  | $E \geq 20$ MeV                                  |

(a) $(\alpha, n)$ reactions.

(b) $(\gamma, n)$ reactions.

(c) $(p, n)$ and $(d, n)$, reactions induced by accelerated charged particles.

(d) Nuclear reactions.

Usually, these sources of neutrons provide fast neutrons with energy of several mega electron volts as shown in Table 5.2.

The binding energy $Q$ attributed to the reaction shown in equation 5.41 is 5.7 MeV, when $\alpha$-particles are produced from the decay of $^{226}$Ra ($E_{\alpha} = 4.78$ MeV). Other types of reactions induced by accelerated charged particles as $(p,n)$ or $(d,n)$, are widely used to produce reaction neutrons with well-defined energies as shown in the following equations:

\[ ^3\text{He} + d \rightarrow ^3\text{He} + n + 3.269 \text{MeV} \] \hspace{1cm} (5.42)

\[ ^3\text{He} + p \rightarrow ^3\text{He} + n - 0.764 \text{MeV} \] \hspace{1cm} (5.43)

\[ ^7\text{Li} + p \rightarrow ^7\text{Be} + n - 1.644 \text{MeV} \] \hspace{1cm} (5.44)

\[ ^9\text{Be} + d \rightarrow ^{10}\text{B} + n + 4.362 \text{MeV} \] \hspace{1cm} (5.45)

For example, to obtain intermediate-energy neutrons ($E_n \gtrsim \text{keV}$) endothermic reactions such as $^7\text{Li}(p,n)$ on thin targets can be used.
5.5.2 Neutron interaction

Neutrons are characterized to be electrically neutral particles and when they interact with matter they are not affected by an electron in the electronic cloud or by the positive charge of the nucleus. Thus, neutrons interact directly with the atomic nucleus and can interact in the following ways [72, 149].

**Elastic scattering.** This process occurs when both the kinetic energy and momentum of the neutron are conserved, i.e., the total kinetic energy of the neutron and the scatterer is unchanged in the collision. There are two types of elastic collisions of neutrons with nuclei. In the first place, the process is called *potential scattering* and it occurs in nuclei of low mass number with neutrons having energies up to a few MeV. There is not a formation of compound nucleus, in this type of process, and scattering is produced by the forces of short-range acting on the neutron when approaching the nucleus. The second type of elastic scattering is called *resonance or compound nucleus scattering*, in this case, the compound nucleus is formed when it absorbs the neutron and then expelled leaving the target nucleus in its ground state and usually with larger kinetic energy. [72].

**Inelastic scattering.** This process occurs when the nucleus reaches an excited state and emits a γ-ray in addition to a neutron. Commonly fast neutrons (50 keV ≤ E < 20 MeV) are involved in this type of interaction because for elements of moderate and high mass number, the minimum excitation energy is generally from 0.1 to 1 MeV. On the other hand, for elements of low atomic number, the excitation energy of the lowest excitation state is large, e.g., around several MeV. Therefore, neutrons with a larger amount of these energies can undergo inelastic scattering. Then, when a fast neutron suffers inelastic scattering the neutron is captured by the nucleus and goes into an excited (virtual) state, later, a neutron of lower kinetic energy is emitted from the nucleus leaving it in an excited (bound) state. The excess of energy, left by the neutron in the nucleus in excitation energy form, is emitted as photons of gamma radiation known as *inelastic-scattering γ-rays*. 
Nuclear reaction: absorption. In a nuclear interaction of the neutrons with a nuclear target, there are two main types of reactions: scattering and absorption. Scattering refers to an exchange of energy between the two particles involved, being the neutron released after the nuclear interaction. In the second place, absorption occurs when the neutron is retained by the nucleus and new particles are formed.

The most important absorption reaction is the radiative capture and fission process and can be of three types.

(1) Radiative Capture \((n,\gamma)\). In this process, the nucleus absorbs a neutron and the isotope formed drops to the ground state by gamma emission. For example, this type of reactions is produced for light hydrogen, which has a relatively high absorption cross section.

\[
{\text{\textsuperscript{1}H}} + {\text{\textsuperscript{0}n}} \rightarrow {\text{\textsuperscript{2}H}}^* \rightarrow {\text{\textsuperscript{2}H}} + \gamma \tag{5.46}
\]

A short expression of this reaction is commonly used showing the incident and emergent particles as well as the target and recoil nucleus.

\[
{\text{\textsuperscript{1}H}}(n,\gamma){\text{\textsuperscript{2}H}} \tag{5.47}
\]

(2) Capture with particle emission. In this process, the capture of a neutron may result in the decaying of the compound nucleus by the emission of a charged particle as a proton \((n, p)\) or \(\alpha\) particle \((n, \alpha)\) as shown in the following reactions.

\[
{\text{\textsuperscript{7}Be}}(n, p){\text{\textsuperscript{7}Li}} \tag{5.48}
\]

\[
{\text{\textsuperscript{10}B}}(n, \alpha){\text{\textsuperscript{7}Li}} \tag{5.49}
\]

(3) Fission. The capture of a neutron, e.g., by \(\text{\textsuperscript{233}U}\), \(\text{\textsuperscript{235}U}\), \(\text{\textsuperscript{239}Pu}\), or \(\text{\textsuperscript{241}Pu}\) may cause the nucleus to split apart in two or more fragments.

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There are four main types of reactions with slow-neutrons (0 < E < 1 keV) involved in the nuclear reactions which were mentioned above as the emission of gamma radiation (n, γ), ejection of proton (n, p) and α particle (n, α) and fission (n, f). The radiative capture (n, γ) is the most common process produced by slow-neutrons and it occurs with a wide variety of elements. The (n, p) and (n, α) reaction by slow-neutron interaction are limited to a few nuclides of the low mass number. In addition, the fission by slow neutrons is limited to some high mass number elements. The interaction of slow neutrons with lithium-6 and boron-10 are characterized by the emission of an α particle. The nuclear reaction with boron-10 can be expressed as:

\[
^{10}\text{B} + ^1\text{n} \rightarrow ^{11}\text{B}^* \rightarrow ^7\text{Li} + ^4\text{He}
\]

where He\(^4\) represents an alpha particle. Boron-10 and Cadmium-113 are used for reactor control because these isotopes have a high probability (n, α) of reaction with slow-neutrons.

On the other hand, the interaction of fast neutrons with an atomic nucleus is important for the study of the nuclear reactor, despite their probabilities are commonly small and also have little effect on reaction operation [72].

### 5.5.3 Cross sections as nuclear area

The concept of a nuclear cross section can be understood as the cross-sectional area, or “target area” presented by a nucleus to an incident neutron. If the nucleus is considered as spheres of radius R and the neutrons as point projectiles, then the cross section \(\sigma\) (cm\(^2\)) of each nucleus can be expressed as,

\[
\sigma = \pi R^2
\]

For an incident beam with \(n\) neutrons per cm\(^3\) moving with velocity \(v\), then the number of neutrons passing through a thin sheet of material of area A will be \(nv\) per cm\(^2\) per
second as show in Figure 5.25. The collision rate will be given by [150],

\[
\text{collision per cm}^2 \text{ second} = (nv) \cdot \frac{N_0 \sigma}{A} = nv\sigma N \cdot t \tag{5.52}
\]

where \(N_0\) is the number of nuclei contained in the thin sheet and \(N_0 \sigma / A\) the probability of collision. \(N/A\) is the number of nuclei per cm\(^2\) equal to \(N \cdot t\), being \(N\) the number of nuclei per cm\(^3\) and \(t\) the thickness of the sheet.

The equation 5.52 can be rewrite as:

\[
\sigma = \frac{\text{collision per cm}^3 \text{ second}}{nvN} \tag{5.53}
\]

where \(nv\) is the flux density of neutrons per cm\(^2\) per second, being an important quantity in many neutron experiments.

The cross-section expression shown in 5.53 is used for different types of nuclear interactions as neutron scattering, capture or fission. Thus, the collision cross-section corresponding to the sum of all processes is commonly called total cross-section. The partial cross-section as scattering, capture or fission can be considered as partial areas of the total cross-section area \(\sigma_T\).

\[\begin{align*}
\text{Area: } A & \quad \text{n}\text{v} \\
\pi R^2 & \quad N_0/A = Nt \\
\text{t} & \\
\end{align*}\]

Figure 5.25: Neutron cross section as geometrical area of nuclei. After [150].
5.5.4 Attenuation of a neutron beam

Considering a collimated beam of neutrons impinging perpendicularly on a thin sheet of area A (see Fig. 5.26),

![Figure 5.26: Collimated beam of neutrons impinging on material of area A.](image)

where $I_0$ is the initial flux density of neutrons in n/cm$^2$·s, $I$ is the flux of neutrons at distance $x$ from the front face of the material.

As shown in Figure 5.26, neutron through the differential range $dx$, thus the decrease in intensity of the flux density denoted by $dI$ will be,

$$dI = -I\sigma N dx$$

(5.54)

where $N\sigma dx$ is the probability of collision as mentioned in the last section (see equation 5.52). It is important to mention that since neutrons are being removed in $dI$, a variation of $I$ will be negative [151]. Through simple calculation, it is possible to obtain,

$$I = I_0 e^{-\sigma N x}, \quad 0 < x < t$$

(5.55)

where $t$ is the thickness of the sheet.
5.5.5 Charge-particle interaction in matter

Whilst uncharged radiations (x-rays, γ radiation, and neutrons) could easily pass-through of a slab of matter and lose its energy in a few random events, charged particles lose their energy in a different way when it impinges on a material. We will not go into detail, but we will only mention the most important types of charged-particles Coulomb-force interaction. The charged-particles Coulomb-force interaction can be characterized by the classical impact parameter \( b \) and the classical atomic radius \( a \).

(a) **Soft collision** \( (b \gg a) \): it occurs when a charged particle passes an atom at a considerable distance. Thus, the Coulomb force of the particle affects the atom as a whole exiting it to a higher energy level.

(b) **Hard collision** \( (b \sim a) \): it occurs when the classical parameter \( b \) is of the order of the atom size. In this case, it is more probable that the incident particle interacts initially with a single atomic electron, which is then ejected with considerable kinetic energy. Whenever an inner shell electron is ejected from an atom by a hard collision, characteristics X-rays or/and auger electrons will be emitted just as if the same electron had been removed by a photon interaction [152].

(c) **Coulomb-force interaction with the external nuclear field** \( (b \ll a) \): it occurs when the impact parameter of a charged particle is much smaller than the atomic radius. This interaction is most important for electrons on the atom. In all but 2-3% of cases, electron is scattered through almost elastic scattering, losing almost no energy. In the other 2-3% of cases, electron loses almost all of its energy through inelastic radiative (bremsstrahlung) interaction.

(d) **Nuclear interaction by heavy charged particles**: it occurs when a heavy charged particle with high kinetic energy \( (\sim 100 \text{ MeV}) \) and with the impact parameter less than the nucleus radius. In this case, the charged particles may interact inelastically with the nucleus. When the charged particles impinge on one or more individuals nucleons of the nucleus, this interaction might starts an intranuclear cascade process. In this way, after the interaction a highly excited nucleus is produced, which decays...
from its excited state by emission of the so-called evaporation particles and gamma radiation [152].

On the other hand, one important quantity used in ion beam dosimetry is the **Linear Energy Transfer (LET)** [59]. This concept has been defined by ICRU (1962) as, “The linear energy transfer (L) of the charged particles in a medium is the quotient of $dE_L$ by $dl$ where $dE_L$ is the average energy locally imparted to the medium by a charged particle of specified energy in traversing a distance of $dl$, that is, $L = dE_L/dl$.”
Chapter 6

Objectives

One of the purposes of this work is the low cost and easy production of CaSiO$_3$ polycrystals, expecting to be the new sensitive TL materials for electromagnetic, neutron, and charged radiation, having in mind their use in nuclear medicine and radiotherapy mainly in Brazil.

For that reason, both pseudowollastonite and wollastonite-2M have been synthesized in the laboratory by the devitrification method. In addition, CaSiO$_3$ doped with B, Dy, Cd, and Eu were produced to investigate the effect of such doping for the detection of gamma and neutron radiation. After gamma radiation dose (from Co-60, Cs-137, X-rays), the TL response of CaSiO$_3$, doped or not, was investigated from very low dose of the order of mGy to very high radiation doses of the order of kGy-MGy.

Besides, synthetic undoped and doped CaSiO$_3$ polycrystals were exposed in a mixed radiation field (neutron and non-neutron radiation) from the research reactor IEA-R1 (IPEN-SP) and their TL analysed.

A comparison between TL intensities of the main peak after reactor exposure and gamma irradiation. Additionally an estimation of the gamma dose absorbed on the polycrystals of CaSiO$_3$ after reactor operation was calculated.
An analytical study of the \((n, \gamma)\) reaction was carried out after thermal neutron irradiation on the sample of CaSiO\(_3\) in order to understand the interaction of these neutrons with elements of the synthetic CaSiO\(_3\) (Ca, Si, and O).

An investigation of the thermoluminescence and paramagnetic centers in synthetic wollastonite, measuring the effects of gamma irradiation and thermal treatment employing the EPR technique were carried out.

Pellets of synthetic calcium silicate were produced in order to improve the handling and the mass standardization of CaSiO\(_3\) samples.

Pellets of CaSiO\(_3\) were irradiated with gamma-dose from Co-60 and Cs-137 source and their TL and dose-response analyzed.

Additionally, irradiation of synthetic CaSiO\(_3\) pellets with proton and carbon ion beam from a synchrotron were programmed. Their TL response were studied and compared with the results of the gamma irradiation.

Finally, an application of these synthetic CaSiO\(_3\) pellets in nuclear medicine was performed. For that reason, a matrix of pellets was placed on the surface of a rectangular phantom with two sources of Tc-99m. The objective of this experiment is found the position of these sources through gamma irradiation from the solution of Tc-99m on the pellets of CaSiO\(_3\). This experiment simulates the tumor localization using radiotracers for tumor imaging.
Chapter 7

Materials and Methods

In this chapter, we describe the method of obtaining artificial polycrystals of undoped and doped CaSiO$_3$. The chapter also discusses the irradiation process with gamma, neutron, and accelerated ion on the polycrystals produced. The measuring types of equipment and techniques used in this work and the procedures for the production of CaSiO$_3$ pellets have also been discussed.

7.1 Experimental details

7.1.1 Production of $\alpha$-CaSiO$_3$ and $\beta$-CaSiO$_3$ polycrystals

For the production of calcium silicate polycrystalline, CaSiO$_3$, the devitrification method was used [94]. In this way, 12.0 g (44.4 wt. %) CaO and 15.0 g (55.6 wt. %) of SiO$_2$ was used, according to the suggestion given by Kotsis and Kurczyk [92, 108].

by the reaction,

$$\text{CaO} + \text{SiO}_2 \rightarrow \text{CaSiO}_3$$  \hspace{1cm} (7.1)

The starting materials, CaO (Anidrol-PA ACS, 99.9%) and SiO$_2$ were mixed and brought into a high-temperature furnace. In this way, the mixture was heated at
about 1500 °C for one hour. This temperature is above the melting temperature of the mixture. The melt in the oven is then cooled slowly such that after 24 hours it reaches room temperature (devitrification method). The maximum temperature to be reached (1500 °C), in this work, was found through the CaO-SiO$_2$ binary phase diagram [153, 154].

Two different phases of CaSiO$_3$ were obtained according to the diffractogram of the polycrystals obtained using computer software and compared with a standard spectrum. These phases are known as $\alpha$-CaSiO$_3$ (Wollastonite-2M) and $\beta$-CaSiO$_3$ (Pseu-
dowollastonite).

### 7.1.2 Production of B, Dy, Cd, and Eu-doped CaSiO$_3$

P. Bilski [19] has mentioned that the highest sensitive of LiF:Mg,Ti as far as their dopants are concerned was obtained using 180 ppm Mg$^{2+}$ and 10 ppm Ti$^{4+}$ as mentioned in Chapter 2. In this way, in this work, it was used boron (B), cadmium (Cd), Dysprosium (Dy) and Europium as dopants of CaSiO$_3$ keeping in mind their use as gamma and thermal neutron detection. Elements, such as, B, Cd, Dy, and Eu show high cross section for thermal neutron capture ($\sigma$). For example; B-10, $\sigma = 0.5 \pm 0.1$ barn; Cd-113, $\sigma = 20600 \pm 400$ barn; Dy-162, $\sigma = 194 \pm 10$ barn; Eu-153, $\sigma = 312$ [155].

Initially, it was used 135 ppm B, after that, its TL analyzed after gamma irradiation. The amounts in ppm of those dopants were gradually increased and their TL responses studied.

| Element | Amount (ppm) |
|---------|--------------|
| B       | 135          |
| Cd      | 392          |
| Dy      | 500          |
| Eu      | 1000         |
To produce doped CaSiO$_3$, before melting, 135 ppm B, 392 ppm Cd, 500 ppm Dy, and 1000 ppm Eu was added in each batch. The chemical components used for the doping process is given by the following processes,

1. Boron-doped calcium silicate: in this case boric acid H$_3$BO$_3$ (Anidrol/PA ACS, 99.9%) was used to obtain 135 ppm boron on the polycrystalline sample.

2. Cd-doped calcium silicate: in this case cadmium nitrate (Cd(NO$_3$)$_2$) (Anidrol/PA ACS, 99.9%) was used to obtain 392 ppm of Cd on the sample.

3. Dy-doped calcium silicate: in this case dysprosium oxide Dy$_2$O$_3$ (Meick/PA ACS, 99.9%) was used to obtain 500 ppm of Dy on the sample.

4. Eu-doped calcium silicate: in this case, Europium oxide (Eu$_2$O$_3$) (sigma Aldrich/PA ACS, 99.9999%) was used to obtain an amount of 1000 ppm of Eu on the sample.

Table 7.1 shows the amounts in ppm of each element used as a dopant in the production of doped CaSiO$_3$. The sample of CaSiO$_3$ obtained (doped or not) is a white polycrystal as shown in Figure 7.1. The undoped calcium silicate and the Cd-doped CaSiO$_3$ obtained in this work are shown in Figure 7.1(a) and 7.1(b) respectively.

7.1.3 X-ray powder diffraction

XRD data of all powder samples (≤ 80 µm) at room temperature were obtained on Rigaku Miniflex 300 diffractometer with Cu k$_{α1}$ (1.5405980 Å) radiation between 10 and 70 at a 0.02° (in 2θ) scanning step and a 1 s step time.

7.1.4 TL measurements

TL measurements were carried out using Harshaw TL reader model 4500 in a nitrogen atmosphere; the heating rate was kept at 4 °C/s. Five TL reading measurements were carried out to obtain an average TL glow curve. Except for the study of the fading of
Figure 7.1: (a) Synthetic polycrystal of CaSiO$_3$, (b) synthetic polycrystal of Cd-doped CaSiO$_3$.

TL peaks at room temperature, all TL readings were done 24 h after the irradiation took place, time enough to reach the stability of the TL peaks of CaSiO$_3$ polycrystals.

In addition, the TL spectra measurements were recorded using a Risø TL/OSL reader, model TL/OSL-DA-20 and the samples irradiated using $^{90}$Sr/$^{90}$Y beta calibrated source mounted on the Risø equipment. This source emits beta particles with a maximum energy of 2.27 MeV having a dose rate of 0.082 Gy/s. The spectra were recorded from 200 to 700 nm using a monochromator in front of the PMT, at a 10 nm for $\alpha$-CaSiO$_3$ and $\beta$-CaSiO$_3$ scanning step. For TL measurements, the heating rate used was 4 $^\circ$C/s, and with an aliquot mass of 10 mg (80 - 180 $\mu$m grain size).
7.1.5 EPR measurements

EPR measurements were performed at room temperature utilizing a MiniScope MS5000 spectrometer from Freiberg Instruments. The EPR spectra were recorded at 9.45 GHz (X-band) microwave frequency, 20 mW microwave power, field modulation of 0.2 mT at 100 kHz, and sweep time of 200 s. Three-accumulation scans were performed for each spectrum. In this way, step annealing in normal atmosphere was performed for EPR measurements of samples previously irradiated with gamma dose of 6 kGy (from Co-60). This means that the sample of about 170 mg is carried to a specific temperature, from 40 to 500 °C with 10 °C step, and maintaining at this temperature for a period of 5 min, after that, cooling to room temperature was performed and then the EPR spectrum is recorded.

7.1.6 Gamma irradiation

The polycrystalline samples of CaSiO$_3$ (doped or not) were crushed and sieved to retain grains 80-180 µm in size for TL measurements, while grains smaller than 80 µm in diameter were used in the X-rays diffraction analysis.

The irradiations for low dose of the order of mGy was done at the Radiations Metrology Department (GMR) of the Institute for Energy and Nuclear Researches (IPEN) using a Cs-137 source of 662 keV gamma rays and with a dose rate of 9.44 $\mu$Gy/s at 30 cm from the source. For high doses in the region of hundreds of Gy and kGy were done at the Radiations Technology Center (CTR) of IPEN using a Co-60 source type gamma-cell with a dose rate of 0.64 kGy/h, and a panoramic type source with a dose rate of 7.88 Gy/h at 40 cm from the source. The gamma irradiation was performed at room temperature. Figure 7.2(a) and 7.2(b) show the Co-60 source type gamma-cell and Cs-137 source type panoramic, respectively, used for gamma irradiation at IPEN.

For ultra-high doses in the region of kGy and MGy (from 70 kGy to 1.2 MGy), samples were irradiated with a Co-60 gamma beam from the gamma-cell irradiator at the
Figure 7.2: (a) Gamacell equipment with source of $^{60}$Co from CTR-IPEN, (b) Cs-137 source at 662 keV gamma-radiation from GMR-IPEN.

Nuclear Energy Department of the Federal University of Pernambuco, Brazil, operating at 1.79 kGy/h.
7.1.7 Irradiation with neutron beams from IPEN’s IEA-R1 reactor.

The research reactor IEA-R1 belonging to IPEN São Paulo is a swimming pool-type reactor operating at 5 MW power and has 144 irradiation positions in the core, distributed in 15 irradiation elements for long irradiations and a pneumatic system for short irradiations (up to 5 minutes). Nine horizontal beam tubes (Beam Holes) that provide neutron beams are also available, used in nuclear physics experiments.

![Diagram of reactor core with labeled positions](image)

**Figure 7.3:** Position of irradiation (13B) and shelf positions in the reactor core of the IEA-R1 nuclear reactor.

It was programmed with the controller of the IEA-R1 reactor, the irradiation of the following samples: $\alpha$-CaSiO$_3$ and CaSiO$_3$ doped with B, Cd, Dy, and Eu. The irradiation was performed in two different stages. In the first place, CaSiO$_3$:Dy and CaSiO$_3$:Eu, later, $\alpha$-CaSiO$_3$, CaSiO$_3$:B, and CaSiO$_3$:Cd were irradiated. Furthermore, irradiation was made at different fluences of neutrons (thermal, epithermal and a small fraction
with fast neutrons). In this way, CaSiO$_3$ polycrystals (doped or not) in grains selected between 80 and 180 $\mu$m grain sizes were used, similarly as used in the section 7.1.6.

Seven samples of each type of polycrystal (CaSiO$_3$ doped or not) with about 80 mg were prepared. Each of the samples was sealed in silica tubes each of about 4 mm diameter and 20 mm long. Then, each such tube was placed inside a somewhat larger aluminum tube to be irradiated in a 13B position (irradiation element) in the reactor core as shown in Figure 7.3. In addition, in the irradiation position 13B there are eight subdivisions called shelves, in which the samples are placed. For technical reasons, irradiation was carried out in two different shelf positions (1 and 5) inside the 13B position as can be observed in Figure 7.3. The time of irradiation in the shelf position 1 and 5 was programmed in different periods. As soon as the Radiation Protection team released the polycrystals, the detectors were read for TL.

![Silica and aluminum tubes used in the neutron irradiations of the CaSiO$_3$ samples.](image)

**Figure 7.4:** Silica and aluminum tubes used in the neutron irradiations of the CaSiO$_3$ samples.

Figure 7.4 shows the silica tubes with the samples of CaSiO$_3$ inside as well as the aluminum tube used for irradiation in the reactor.
7.1.7.1 Neutron fluences at 13B position in the IEA-R1

IEA-R1 reactor from IPEN, in operation, produces neutron and non-neutron radiation. The neutron radiation is classified according to the neutron energy, that is, as thermal, epithermal and fast (the latter in a small fraction). Thermal neutrons are considered those with energy < 0.625 eV, for epithermal neutron between 0.625 eV - 0.5 MeV, and for fast neutron between 0.5MeV - 10 MeV, [156]. Figure 7.5 shows approximate normalized differential flux density $\phi'(E)$ of neutrons in cm$^{-2}$s$^{-1}$eV$^{-1}$ of a water-moderated research reactor, adapted from Attix et al. [59].

Figure 7.5: Neutrons flux in a water-moderated research reactor. After [59].

Although no research has been able to measure neutron and non-neutron effects separately from the TL glow curves of these detectors subjected to a mixed radiation field, it is possible to obtain a clear correspondence between some TL glow curve peaks and thermal neutron fluence, which is a kind of curve calibration.
Table 7.2: Neutron fluxes during irradiation at 13B position in the reactor core.

| Shelf Position | Thermal flux (n/s·cm²) | Epithermal flux (n/s·cm²) | Fast flux (n/s·cm²) |
|----------------|------------------------|--------------------------|---------------------|
| 1              | (9.70 ± 0.26)×10¹¹     | (1.13 ± 0.03)×10¹¹       | (9.39 ± 0.25)×10¹⁰  |
| 5              | (5.50 ± 0.15)×10¹²     | (7.33 ± 0.20)×10¹¹       | (3.99 ± 0.11)×10¹¹  |

Table 7.3: Thermal neutron fluences at 13B position in the reactor core acting on Eu and Dy-doped CaSiO₃.

| Shelf Position | Irradiation time (s) | Thermal neutron fluences (n/cm²) |
|----------------|----------------------|---------------------------------|
| 1              | 61 ± 30              | (5.90 ± 3.0)×10¹³              |
| 1              | 154 ± 30             | (1.49 ± 0.30)×10¹⁴             |
| 1              | 307 ± 30             | (2.98 ± 0.30)×10¹⁴             |
| 1              | 614 ± 30             | (5.96 ± 0.33)×10¹⁴             |
| 5              | 272 ± 30             | (1.50 ± 0.17)×10¹⁵             |
| 5              | 380 ± 30             | (2.09 ± 0.17)×10¹⁵             |
| 5              | 5425 ± 109           | (2.98 ± 0.10)×10¹⁶             |

Any object placed inside a reactor in operation is subject to γ radiation, thermal neutron, epithermal neutrons, and fast neutrons, with fluxes given in Table 7.2. The flux numbers that are shown in Table 7.2 are measured at the position inside the reactor known as 13B in the nuclear core. Neutron fluxes were measured using gold foil activation method introduced by M. Koskinas [157].

Table 7.3 shows the shelf position, time of irradiation, and thermal neutron fluences for the CaSiO₃:Eu and CaSiO₃:Dy samples. Likewise, Table 7.4 shows the shelf position, time of irradiation, and thermal neutron fluences for the α-CaSiO₃, CaSiO₃:B, and CaSiO₃:Cd samples.
Table 7.4: Thermal neutron fluences at 13B position in the reactor core acting on $\alpha$-CaSiO$_3$, CaSiO$_3$:B, and CaSiO$_3$:Cd samples.

| Shelf Position | Irradiation time (s) | Thermal neutron fluences (n/cm$^2$) |
|----------------|----------------------|-----------------------------------|
| 1              | 60 ± 30              | $(5.8 \pm 3.0) \times 10^{13}$    |
| 1              | 180 ± 30             | $(1.75 \pm 0.30) \times 10^{14}$  |
| 1              | 300 ± 30             | $(2.91 \pm 0.30) \times 10^{14}$  |
| 1              | 600 ± 30             | $(5.82 \pm 0.30) \times 10^{14}$  |
| 5              | 240 ± 30             | $(1.32 \pm 0.17) \times 10^{15}$  |
| 5              | 360 ± 30             | $(1.98 \pm 0.17) \times 10^{15}$  |
| 5              | 5400 ± 109           | $(2.97 \pm 0.10) \times 10^{16}$  |

7.1.8 Production of calcium silicate pellets

In order to improve the handling and the mass standardization of CaSiO$_3$ samples, powder of this polycrystal will be used to pellets production. The procedure for pellets production from the CaSiO$_3$ in powder is given by:

(a) **Milling process**: these polycrystalline samples of undoped CaSiO$_3$ were crushed and sieved to retain grains smaller than 80 $\mu$m in diameter. This powder is placed in a sealed container together with two milling alumina spheres. Then, the container is left in a mill for 24 hours in order to homogenize and reduce the particle size of the sample (smaller than 80 $\mu$m).

(b) **Powder compaction**: at this stage, a steel device with three 6 mm diameter channels was used as shown in Figure 7.6(a). Later, 50 mg of the powder, obtained in the previous stage, is placed in the hole. After that, steel pins are also placed inside the hole and on top of the powder to keep it fixed inside the steel device (see Figure 7.6(b)). The device with the sample inside is carried to the press and subjected to a pressure of 11 ton/cm$^2$ using a hydraulic press as shown in Figure 7.6(c). Later, pellets of 6 mm in diameter and 1 mm thick but not resistant enough to handling are obtained.
Figure 7.6: (a) Steel device and steel pins for pellets production, (b) steel pins placed on top of the powder inside the device, (c) hydraulic press at GMR-IPEN, (d) pellets of CaSiO$_3$ of 6 mm in diameter and 1 mm thick.

(c) **Thermal sintering**: using the thermal sintering technique the pellets obtained previously is carried at about 1200 °C for 30 minutes (best condition of time and temperature to obtain suitable hardness pellets) and then cooled slowly until it reaches room temperature. After that, a handling-resistant pellet is obtained as shown in Figure 7.6(d).

Preparation and sintering of the powder were done in LACIFID laboratory, whilst the pellets compression were carried out at the GMR-IPEN. The calibration of these
pellets was carried out irradiating them with gamma radiation from Cs-137 source at IPEN.

### 7.1.9 Irradiation with proton and carbon ion beam

In this section, the pellets of CaSiO$_3$ (TLDs) produced previously (section 7.1.8) were irradiated with proton beam and carbon ion beam from an upper synchrotron of HIMAC (Heavy Ion Medical Accelerator in Chiba, Japan) at NIRS (National Institute of Radiological Sciences).

![Irradiation design of calcium silicate pellets with proton and carbon ion beam.](image)

**Figure 7.7:** Irradiation design of calcium silicate pellets with proton and carbon ion beam.

The procedure of this experiment is given by:

(a) First, 3 pellets, in a plastic bag, were attached in the irradiation position, that is, on the center of PMMA plate as shown in Figure 7.7.

(b) Pellets were irradiated at 160 MeV proton beam and 290 MeV/n carbon ion beam (nominal values). The beam has spread over a uniform area of 10 cm (with an uncertainty of about 5%) in diameter at the irradiation position as shown in Figure 7.7.

(c) The given dose was monitored with ionization chamber installed in the beam line. Doses at which pellets were exposed varies from 1 mGy to 10 Gy.
7.1.10 Application: detection of Tc-99m source using CaSiO$_3$ pellets.

In this section, pellets of $\beta$-CaSiO$_3$ have been produced for application in nuclear medicine, that is, the detection of a solution of Technetium-99m (Tc-99m) using CaSiO$_3$ pellets. The experiment was performed at the Heart Institute University of São Paulo - USP (INCOR). The description of this experiment is given by:

(1) Matrices of 6x7 and 5x10 of these TLDs were prepared and placed inside and placed in an acrylic holder for TLDs as shown in Figure 7.8(a).

(2) A glass bowl phantom and a syringe with a solution of Tc-99m were used in this experiment as shown in Figure 7.8(b) and 7.8(c), respectively.

(3) Then, a syringe with a solution of Tc-99m is placed inside of the glass bowl phantom as shown in Figure 7.8(c).

(4) A matrix of 5x10 TLDs was placed on the surface of the phantom containing a solution of 32.0 mCi in one point and in another point 15.5 mCi solution of Tc (99m) for about 12-15 minutes as shown in Figure 7.8(d).

(5) A matrix with 6x7 dosimeters was placed on the surface of a phantom containing a solution of 29.9 mCi Tc-99m for about 20 minutes.
Figure 7.8: (a) Acrylic holder with pellets of CaSiO$_3$, (b) glass bowl phantom, (c) syringe with a solution of Tc-99m, (d) syringe with the solution of Tc-99m placed inside of a glass bowl phantom with water, (e) pellets placed on the surface of the glass bowl phantom.
7.2 Measuring Equipments

7.2.1 Thermoluminescence TL

To perform the thermoluminescence measurements the Harshaw TLD Model 4500 from the LACIFID Laboratory was used. Figure 7.9 shows the Harshaw-4500 equipment used at the LACIFID Laboratory. Heating of the samples and recording of the glow curves of CaSiO$_3$ polycrystal were carried out in Harshaw 4500 TL reader keeping 4 °C/s heating rate up to a maximum of 400 °C. The emitted light is converted into signals through a photomultiplier tube and by a computational interface that is controlled by software called WINREMS (Windows Based Radiation Evaluation and Management System). The TLD reader has a built-in infrared (IR) filter. This equipment has a KG-1 type heat-absorbing glass filter and a Hamamatsu type R647-34 photomultiplier tube.

![Figure 7.9: Thermo Scientific, Harshaw-4500 equipment used at the LACIFID Laboratory.](image)

This photomultiplier tube is a photoemissive cathode or also known photocathode followed by focusing electrodes, the dynodes (electron multiplier) and an electron collector (anode) in a vacuum tube. The light coming from the TL emission of the sample falls on the photocathode and the photocathode emits a photoelectron into the vacuum. Through voltages of the focusing electrodes, these photoelectrons are directed towards the electron multiplier. At this point, electrons are multiplied by a secondary emission
process. The multiplied electrons are then collected by the anode as an output signal as shown in Figure 7.10.

![Schematic diagram of Harshaw-4500 to measure thermoluminescence.](image)

**FIGURE 7.10**: Schematic diagram of Harshaw-4500 to measure thermoluminescence.

### 7.2.2 X-ray diffraction (XRD)

To perform the XRD measurements, the MiniFlex-300 from the Federal University of São Paulo, UNIFESP (for its acronym in Portuguese) was used as shown in Figure 7.11. MiniFlex-300 is the fifth generation MiniFlex with a general-purpose X-ray diffractometer that can perform qualitative and quantitative analysis of polycrystalline materials, running at 300 watts. In qualitative analysis, the instrument is able to identify unknown substances by comparing experimental diffraction data against a database of known phases. Whilst in quantitative analysis, the equipment is used to
characterize solid mixtures to determine relative abundance of crystalline compounds [158].

The basic principle of X-ray diffraction can be explained through the irradiation with X-rays having a specific wavelength (e.g. CuKα rays) of a polycrystalline body which is an aggregate of tiny crystals. When X-ray incidence angle is changing with respect to the sample, the diffracted X-ray will be detected sequentially and those angles where each lattice plane of the crystal satisfies the Bragg condition: \(2d \cdot \sin \theta = \lambda_0\). Where 
- \(d\): Lattice interplanar spacing of crystal (sample).
- \(\theta\): X-ray incidence angle (Bragg angle);
- \(\lambda_0\): wavelength of characteristic X-rays due to the X-ray tube. This lattice interplanar spacing \(d\) may be calculated by measuring the Bragg angle \(\theta\) and through the standard data ICDD (International Center for Diffraction Data), it is possible to identify these small crystals.

![Figure 7.11: Miniflex-300 for X-ray diffraction (XRD) instrument [159].](image)

7.2.3 The IEA-R1 nuclear research reactor

The IEA-R1 nuclear research reactor of the Institute for Energy and Nuclear Researchers of São Paulo (IPEN-SP) used in this work for neutron irradiation is located
on the campus of the University of São Paulo, Brazil. The reactor is a swimming pool type, designed by the Babcock & Wilcox Company, having reached its first critical condition on September 16, 1957. A top floor view of the IEA-R1 reactor is shown in Figure 7.12.

The IEA-R1 reactor is moderated and cooled with light-water utilizing beryllium and graphite elements as reflectors. The reactor is designed to operate at a maximum power of 5 MW and has 144 irradiation positions in the core, distributed in 15 irradiation elements for long irradiations and a pneumatic system for short irradiations (up to 5 minutes). Nine horizontal beam tubes (“Beam Holes”) that provide neutron beams are also available, used in nuclear physics experiments, solid state physics, on boron neutron capture cancer therapy (BNCT) and neutronography research [160].

![Figure 7.12: A top floor view of the IEA-R1 nuclear research reactor at IPEN. Image obtained of Proceedings of the International Conference on Research Reactors: Safe Management and Effective Utilization, Australia - 2007.](image)

### 7.2.4 Furnaces at the LACIFID laboratory

For the polycrystals production two furnaces from the LACIFID laboratory were used.
Firstly, an EDG-F-1700 furnace was used which reaches a maximum temperature of 1700 °C with a type B thermocouple (Platinum - 30 % Rhodium x Platinum - 6 % Rhodium). Secondly, a furnace that was assembled in the laboratory was used and this furnace reaches a maximum temperature of 1500 °C with a type S thermocouple.
(Platinum - 10 % Rhodium x Platinum). Figure 7.13 shows the two types of furnaces mentioned above.

For the heat treatment (annealing) of the samples of CaSiO$_3$ polycrystals, other types of furnaces were used which reach a maximum temperature of 1200 °C. These furnaces have a type K thermocouple (Chrome x Alumel). Additionally, it is important to mention that the $\alpha$-CaSiO$_3$ was produced using the EDG-F-1700 furnace whereas $\beta$-CaSiO$_3$ and CaSiO$_3$ doped with B, Dy, Cd, and Eu were produced in the furnace shown in Figure 7.13(b).

### 7.2.5 EPR Spectrometer

The MiniScope MS5000 spectrometer from Freiberg Instruments at the Lacifid laboratory was used for EPR measurements.

MiniScope MS5000 spectrometer is a rectangular device of easy handling with dimension of 397 x 262 x 192 mm and weight of 45 kg as shown in Figure 7.14. This equipment consists of a magnetic field controller, microwave source, resonant cavity, microwave detection system and a signal detector. The microwave source emits electromagnetic radiation, which is conducted by a waveguide to a resonant cavity.

The detector is a diode, which captures the signal absorbed by the sample when it is struck by the microwave. Thus, the detector converts the microwave power to an electrical current. The magnetic field controller has two parts, one part that sets the field values and the timing of the field sweep time, and the other regulates the current in the windings of the magnet to reach the desired magnetic field value.

The resonance cavity amplifies the weak signals of the paramagnetic samples, storing microwave energy, such that, for a given resonant frequency, the signal resulting from the modulation is a sine wave with amplitude proportional to the absorption derivative in the region. Then the signal is compared with another reference signal, where the ones having equal frequency and same field modulation phase are detected. The operating microwave frequency of this device is in the X-band (9.2 - 9.6 GHz) with a power of
1 \mu W - 100 mW. The magnetic field has a field modulation range from 1 \mu T to 1 mT, modulation frequency range: 10 kHz - 100 kHz, magnetic field range: 30 - 650 mT, and sweep time range: 1 s - 2 h.
Chapter 8

Experimental Results and Discussion

8.1 Diffraction patterns

8.1.1 $\alpha$-CaSiO$_3$ and $\beta$-CaSiO$_3$ polycrystals

The diffractograms of the $\alpha$-CaSiO$_3$ and $\beta$-CaSiO$_3$ polycrystals are shown in Figure 8.1 and Figure 8.2, respectively.

As mentioned in Chapter 4, the low-temperature phase of CaSiO$_3$ is the wollastonite-2M which appears at 1006 °C and totally disappears at 1303 °C [94]. On the other hand, the crystalline pseudowollastonite structure appears at 1185 °C and continues growing up to 1375 °C. M. Perdomo [94] has mentioned that Wollastonite-2M and pseudowollastonite coexist in a non-equilibrium condition from 1185 to 1303 °C during the devitrification process.

In this work, the two phases of wollastonite obtained ($\alpha$-CaSiO$_3$ and $\beta$-CaSiO$_3$) could be because of the different cooling processes used in each case. In the first mixture ($\alpha$-CaSiO$_3$), the cooling system of the oven itself was used, which consists of a series of fans placed in the oven. In the second mixture ($\beta$-CaSiO$_3$), the temperature was
decreasing linearly using a temperature controller. In both cases, a temperature controller was used to program previous temperature stages of 5 hours (at about 1300, 1100, 900, and 700 °C) before reaching room temperature. Finally, after these processes, polycrystalline materials were obtained.

Comparing the powder XRD pattern of $\alpha$-CaSiO$_3$ to the 00-043-1460 and 01-076-0937 files of the X’Pert HighScore program [161], all the peaks of the polycrystals were identified as belonging to wollastonite-2M (00-043-1460 - Semiquant. 94 %) and Cristobalite low (01-076-0937 - Semiquant. 6 %), respectively.

Comparing the powder XRD pattern of $\beta$-CaSiO$_3$ to the 01-074-0874 and 01-071-0785 files of the X’Pert HighScore program [161], all the peaks of the polycrystals were
8.1.2 Dy, B, Cd, and Eu-doped CaSiO$_3$

The diffractograms of the Dy, B, Cd, and Eu-doped CaSiO$_3$ polycrystals are shown in Figure 8.3. Comparing the powder XRD pattern of the Dy, B, Cd, and Eu-doped CaSiO$_3$ to the 01-074-0874 and 01-071-0785 files of the X’Pert HighScore program [161] all the peaks of the polycrystals were identified as belonging to Pseudowollastonite (01-074-0874 - Semiquant. 96 %) and Cristobalite low (01-071-0785 - Semiquant. 4 %), respectively.
Figure 8.3: XRD pattern of CaSiO$_3$ doped with Dy, B, Cd, and Eu polycrystals produced in this work, to be compared with XRD patterns from Archive 01-074-0874 (pseudowollastonite) and 01-071-0785 (Cristobalite low - ICSD collection code: 009327) - X’Pert HighScore program [161].
Small differences were found between diffraction patterns of Dy, Cd, B, and Eu-doped CaSiO$_3$.

Dy-doped CaSiO$_3$ was identified as belonging to Pseudowollastonite (01-074-0874 - Semiquant. 90 %) and Cristobalite low (01-071-0785 - Semiquant. 10 %), respectively.

B-doped CaSiO$_3$ was identified as belonging to Pseudowollastonite (01-074-0874 - Semiquant. 96 %) and Cristobalite low (01-071-0785 - Semiquant. 4 %), respectively.

Cd-doped CaSiO$_3$ was identified as belonging to Pseudowollastonite (01-074-0874 - Semiquant. 94 %) and Cristobalite low (01-071-0785 - Semiquant. 6 %), respectively.

Finally, Cd-doped CaSiO$_3$ was identified as belonging to Pseudowollastonite (01-074-0874 - Semiquant. 97 %) and Cristobalite low (01-071-0785 - Semiquant. 3 %), respectively.
8.2 Gamma radiation dosimetry

8.2.1 $\alpha$-CaSiO$_3$ polycrystal

(1) TL measurements

The dose-response of synthetic materials for dosimetry applications is a very important property. An ideal dosimeter should have linear behavior for all dose range. In order to determine the dose-response of the $\alpha$-CaSiO$_3$ polycrystal from low-dose of the order of mGy up to high-dose of the order of kGy, samples in grains of $\alpha$-CaSiO$_3$ were irradiated with different gamma-doses (see section 7.1.6).

Samples of $\alpha$-CaSiO$_3$ irradiated with doses higher than about 10 mGy presented a small TL peak at 120 °C and a prominent peak at 270 °C using 4 °C/s heating rate. TL glow curves of $\alpha$-CaSiO$_3$ irradiated with low dose between 10 mGy and 30 mGy is shown in Figure 8.4(a), and between 0.2 Gy and 1 Gy is shown in Figure 8.4(b). Figures 8.4(c) and 8.4(d) shows the glow curves of $\alpha$-CaSiO$_3$ irradiated with gamma doses larger than 5 Gy up to 100 kGy and doses larger than 0.2 kGy up to 50 kGy, respectively. These results show that the synthetic pure CaSiO$_3$ is a very sensitive ionic crystal as far as its thermoluminescence is concerned and to a wide range of gamma radiation dose, from 30 mGy to 50 kGy.

Figure 8.5 shows the maximum TL dose-response of the main peak of $\alpha$-CaSiO$_3$ for doses ranging from mGy to kGy range. Analyzing the dose-response curves with log axes in the same scale, as shown in Figure 8.5, it can be observed that the TL response of peak at 234 - 270 °C peak has a linear behavior as the curve slope equals to 45° in the dose range from few cGy up to about few Gy and after that TL response is supralinear up to about 7 kGy and then it saturates. This means that we have here a detector that responds from few cGy to 7 kGy. As to the models that explain supralinearity, there are in fact, many. Broadly, they are divided into that is assumed to happen in the irradiation stage and the other during heating for reading TL (see subsection 5.3.8). One of the first models was introduced by Cameron and Zimmerman [162]; it assumes
that besides existing TL traps the irradiation creates new traps that are responsible for supralinearity. Mische and McKeever [143] introduced a track interaction model. In this case, it has been shown that the mechanisms that govern the response to the thermoluminescence dose are operative in the heating stage of the TL process and not during the radiation absorption stage.

Note: although it is desirable if the curve in Figure 8.5 were linear for all doses, however, a curve with supralinearity can be used in dosimetry.

(2) Reproducibility

The reproducibility of the dosimeters can be affected after repeated usage [15]; therefore, this is one of the most important factors for dosimeter materials. For analysis of
Figure 8.5: TL intensity behavior of the 250 - 270 °C peak as a function of gamma radiation doses of α-CaSiO₃ polycrystal. The dashed line indicates linearity.

the reproducibly of the undoped synthetic α-CaSiO₃ sample, 1.80 mg of this sample (in grains) was irradiated with 1.0 Gy of test-dose, read, and annealed, and irradiated again; this procedure was repeated four times to the same sample. Figure 8.6 shows the reproducibility and the sensitivity by intensity of the peak at 270 °C, decreasing by 20 % after the first sequence of radiation-reading-annealed during the procedure of TL readout.

(3) Fading

Another important property of any TL material is the fading [14]. We irradiated CaSiO₃ with 1 Gy of gamma dose and kept it in the dark. Its TL was read out after, one, two, etc. hours up to 32 days. The result is shown in Figure 8.7 and 8.8. Figure 8.7 refers to the peak at 270 °C. It shows that there is decay is about 20% in the first 2 to 3 hours, but after that, there is no decay. Therefore, we say CaSiO₃ has small fading. Figure 8.8 refers to the peak at 120 °C. It shows that there is decay is about 90% in 5 days, after that the TL intensity gradually decreases until it disappears.
(4) TL parameters

With the purpose of finding the number and position as well as the activation energy of the TL peaks contained in the complex experimental glow curve of the $\alpha$-CaSiO$_3$ polycrystal, the $E-T_{\text{stop}}$ method was used [15, 140]. Further, by the initial rise method, it is possible to calculate the energy of the trap activation. This method is based on the fact that at the low-temperature end of the peak, that is, the initial part of the TL glow curve can be well described by exponential behavior such as $\exp(-E/kT)$. Later, by the Arrhenius plot: $\ln(TL) \text{ vs } 1/T$ which will be approximated a straight line, the activation energy $E$ can be easily obtained from the slope $-E/k$. For a reliable result, it is only considered below 15% of the maximum TL intensity [138]. In this work, the activation energy was found using different pre-heating temperature ($T_{\text{stop}}$) from 60 to 330 °C at a 5 °C scanning step. Figure 8.9 shows the obtained activation energies ($E$) using the $E-T_{\text{stop}}$ method for the $\alpha$-CaSiO$_3$ sample.

Another broadly used method is the glow-curve deconvolution (GCD) to compute characteristics parameters like $E$, $s$ and the order of the kinetic ($b$) of individual glow
peaks on the experimental TL glow curve [163]. Therefore, using the previous result found by the E-Tstop method and applying the equation proposed by Kitis et al. [163] we obtain the deconvolution of the TL glow curve of $\alpha$-CaSiO$_3$ when irradiated to
Figure 8.9: Activation energy vs. $T_{\text{stop}}$ method for the $\alpha$-CaSiO$_3$ sample.

Table 8.1: TL peak position, activation energy (E) and frequency factor of TL trap of $\alpha$-CaSiO$_3$.

| TL peak ($^\circ$C) | E(eV) | $s(s^{-1})$ | $\tau$ (years at 25 $^\circ$C) |
|---------------------|-------|-------------|--------------------------------|
| 139                 | 0.97  | 1.85x10$^{11}$ | 0.004                          |
| 169                 | 1.19  | 1.22x10$^{13}$ | 0.33                           |
| 210                 | 1.21  | 1.21x10$^{12}$ | 7                              |
| 252                 | 1.28  | 5.26x10$^{11}$ | 258                            |
| 271                 | 1.43  | 5.57x10$^{12}$ | 8.3x10$^3$                     |
| 329                 | 1.48  | 6.78x10$^{11}$ | 4.8x10$^5$                     |

1 kGy from a Co-60 source as shown in Figure 8.10.

Figure 8.10 shows the TL experimental peaks at 125 and 272 $^\circ$C and six computed TL peaks separated using different orders of kinetics at about 139, 169, 210, 252, 271, and 329 $^\circ$C. The position, activation energies E and frequency factor (s) of the TL peaks for the $\alpha$-CaSiO$_3$ sample are presented in Table 8.1.

Figure of merit (FOM) is the usual expression to verify the effectiveness of the TL glow curve fitting. The expression for the FOM calculation is given by:
Figure 8.10: Glow curve deconvolution (GCD) of the TL glow curve for the $\alpha$-CaSiO$_3$ sample irradiated with gamma dose of 1 kGy from a Co-60 source. A good fit between the experimental glow curve (circles) and the simulated glow curve (red line) can be achieved by assuming the presence of six peaks. In all cases, a mass of about 1.80 mg and 4 °C/s heating rate were used.

$$FOM = \frac{\sum_{i=1}^{N} |TL_{exp} - TL_{comp}|}{\sum_{i=1}^{N} TL_{comp}}$$

where $TL_{exp}$ and $TL_{comp}$ represent the experimental and computed TL intensity, respectively. $N$ is the number of points on the TL curve analyzed. FOM values of the order of a few percentages generally indicate an acceptable fit. The FOM obtained for the TL glow curve fitting shown in Figure 8.10 is about 2.5%.
8.2.2 $\beta$-CaSiO$_3$ polycrystal

(1) TL measurements

$\beta$-CaSiO$_3$ sample exhibits TL peaks at approximately 124, 237-250, and 306 °C using a 4 °C/s heating rate. The glow curves of the $\beta$-CaSiO$_3$ sample irradiated with gamma low dose from 30 mGy to 500 mGy are shown in Figure 8.11(a). Figure 8.11(b), 8.11(c), and 8.11(d) show the glow curves of the $\beta$-CaSiO$_3$ sample irradiated with gamma dose from 1 to 10 Gy, 30 to 300 Gy, and 500 Gy to 50 kGy, respectively. This shows that the main glow peak is at 306 °C when irradiated from 30 mGy to 10 Gy and after that, the main glow peak shifts to about 250 °C. The result presented in Figure 8.11 shows that the synthetic polycrystalline of $\beta$-CaSiO$_3$ is a very sensitive ionic crystal as far as their TL is concerned for gamma radiation dose from 30 mGy to 30 - 50 kGy.

Figure 8.12 shows the maximum TL response of the main TL peak of $\beta$-CaSiO$_3$ for dose ranging from 30 mGy to 50 kGy. Analyzing the dose-response curves with log axes on the same scale, as shown in Figure 8.12, it can be observed that the TL response of all peaks at 124, 237-250, and 306 °C have a linear behavior as the curve slope equals to 45° in the dose range from about 30 mGy to 1 Gy. After that, TL responses are supralinear up to about 300 Gy for 124 and 306 °C peaks, and supralinear up to 3 kGy for 237-250 °C peak. Afterward, all peaks are saturated.

(2) Fading

As mentioned earlier, anomalous fading is an important characteristic of natural and synthetic crystalline materials. For this purpose, $\beta$-CaSiO$_3$ sample was irradiated with 5 Gy gamma dose and kept in the dark at room temperature for different storage time. Its TL was read after 1, 3, 6, etc. hours up to about 32 days (775 hours). Figure 8.13 shows the results of fading for TL peaks at 117-131, 252, and 306 °C. The TL peak at 117 °C is a low-temperature peak and is commonly unstable at room temperature and decays by about 84% after 32 days of storage time. TL peak at 252 and 306 °C
Figure 8.11: TL Glow Curves of $\beta$-CaSiO$_3$, irradiated with gamma dose (a) from 30 to 500 mGy, (b) from 1 to 10 Gy, (c) from 30 to 300 Gy, (d) from 500 Gy to 50 kGy. In all cases, a mass of about 1.93 mg and 4 °C/s heating rate were used.

are the high-temperature peaks having a decay of about 7% and 3%, respectively, in the first 48 hours. After that time, there is no decay.

(3) TL parameters

In the same way that $\alpha$-CaSiO$_3$, the E-$T_{stop}$ method was used to find the number and position as well as the activation energy of the TL peaks contained in the complex experimental glow curve of the $\beta$-CaSiO$_3$ polycrystal. Further, by the initial rise method, it is possible to calculate the energy of the trap activation. In this work, the activation energy was found using different pre-heating temperature ($T_{stop}$) from 60 to 330 °C at a 5 °C scanning step. Figure 8.14 shows the obtained activation energies (E) using the E-$T_{stop}$ method for the $\beta$-CaSiO$_3$ sample.
Figure 8.12: TL intensity behavior of the 124, 237-250 and 306 °C peaks as a function of gamma radiation doses of $\beta$-CaSiO$_3$ polycrystal. The dashed line indicates linearity.

Figure 8.13: TL intensity of the $\beta$-CaSiO$_3$ sample irradiated with 5 Gy against the storage time at room temperature.
Another broadly used method is the glow-curve deconvolution (GCD) to compute characteristics parameters like $E$, $s$, and the order of the kinetic ($b$) of individual glow peaks on the experimental TL glow curve. Therefore, using the previous result found by the E-Tstop method and applying the equation proposed by Kitis et al. [163] we obtain the deconvolution of the TL glow curve of the $\beta$-CaSiO$_3$ sample irradiated with gamma dose of 5 Gy from a Co-60 source as shown in Figure 8.15.

The TL glow curve in Figure 8.15 presents three defined peaks and the GCD method shows seven. The TL experimental shows peaks at 122, 259, and 306 °C and seven computed TL peaks separated using different orders of kinetics at about 121, 133, 147, 201, 247, 306, and 337 °C. The FOM obtained for the TL glow curve fitting shown in Figure 8.15 is about 1.3%.

The position, activation energies $E$ and frequency factor ($s$) of the TL peaks for the $\beta$-CaSiO$_3$ sample are presented in Table 8.2.

(4) TL spectra: The TL emission spectrum of the polycrystal $\beta$-CaSiO$_3$ presented two very broad bands centered at 370 and 520 nm as shown in Figure 8.16. This means...
Figure 8.15: Glow curve deconvolution (GCD) for the TL glow curve of the $\beta$-CaSiO$_3$ sample irradiated with gamma dose of 5 Gy from a Co-60 source. A good fit between the experimental glow curve (circles) and the simulated glow curve (red line) can be achieved by assuming the presence of seven peaks. A mass of about 1.80 mg and 4 °C/s heating rate were used.

Table 8.2: TL peak position, activation Energy (E) and frequency factor of TL trap of $\alpha$-CaSiO$_3$.

| TL peak (°C) | E(eV) | $s$(s$^{-1}$) | $\tau$ (years at 25 °C) |
|-------------|-------|---------------|-------------------------|
| 121         | 1.16  | 2.40x10$^{14}$| 0.005                   |
| 133         | 1.20  | 2.69x10$^{14}$| 0.023                   |
| 147         | 1.22  | 1.39x10$^{14}$| 0.095                   |
| 201         | 1.28  | 1.07x10$^{13}$| 12.80                   |
| 247         | 1.33  | 1.77x10$^{12}$| 5.4x10$^2$              |
| 306         | 1.61  | 2.27x10$^{13}$| 2.3x10$^6$              |
| 337         | 1.68  | 1.62x10$^{13}$| 3.9x10$^7$              |

that one should expect two recombination centers in the same way that $\alpha$-CaSiO$_3$. TL glow curves with the emission in the region 370 nm show TL peaks at around 70, 140, and 335 °C, whereas that emission band at 520 nm corresponds to two TL peaks at approximately 70 and 135 °C. It is important to mention that for the case of the band emission of 370 nm, the TL peak at 335 °C overlapped the TL peak at 270 °C. The
peak around 70 °C decay completely in a few minutes. In Figure 8.16, TL peaks are observed at approximately 70 °C due to that measurement of the TL emission curve was done immediately after irradiation.

8.2.3 Dy, B, Cd-doped CaSiO$_3$

(1) TL measurements

To compare with the glow curves from the undoped sample ($\alpha$-CaSiO$_3$ and $\beta$-CaSiO$_3$), in Figure 8.17, the glow curves of doped synthetic samples with Cd, B, and Dy irradiated between 0.5 and 50 kGy are presented. For instance, $\beta$-CaSiO$_3$ sample has shown a low-temperature peak at 120 °C and a prominent peak at around 250 °C. On the other hand B, Cd, Dy-doped CaSiO$_3$ samples presented a low-temperature peak.

![Figure 8.16: TL spectra of the $\beta$-CaSiO$_3$ sample after beta irradiation dose of 12.2 Gy. A mass of about 10 mg and 4 °C/s heating rate were used.](image)
Figure 8.17: TL glow curves of CaSiO₃: X, (a) X = Cd, (b) X = Dy and (c) X = B, irradiated with gamma dose of 0.5 - 50 kGy. (d) TL intensity versus doses of the TL peaks at 270 °C for three doped samples.

at 120 °C and a prominent peak at around 245 °C. This result indicates that these TL peaks in CaSiO₃ are due to intrinsic defects.

Additionally, it is possible to observe in the TL glow curves of the doped samples, in figure 8.17, a small peak around 370 °C, which is more intense for the case of the CaSiO₃:Dy sample. Figure 8.17(d) shows the TL response of the main TL peak for doses ranging from 0.5 and 50 kGy of doped CaSiO₃ samples. These curves have an increasing behavior between 0.5 - 3 kGy and then go into saturation from 7 to 50 kGy.
8.2.4 Eu-doped CaSiO$_3$

(1) TL measurements

Glow curves of CaSiO$_3$:Eu are shown in Figure 8.18 for radiation doses from 0.5 up to 50 kGy (Figure 8.18(a)) and from 70 kGy to 1200 kGy (Figure 8.18(b)). These glow curves show 3 peaks at 125-150, 226, and at around 342 - 370 ºC. We note that there is the following difference in comparison with these doped with B, Cd, and Dy; in Eu-doped CaSiO$_3$ the peak 3 is prominent while in other cases the peak 2 is very intense compared to peak 3. Nothing was found in the literature about this effect of adding 1000 ppm Eu as an impurity.

Figure 8.19 shows the maximum TL response of the main TL peak for doses ranging from 0.5 kGy to 1.2 MGy of CaSiO$_3$:Eu. Analyzing the dose-response curves with log axes, as shown in Figure 8.19 it can be observed that the TL response of the peak at around 342 - 370 ºC has a non-linear and increasing behavior from 500 Gy to 30 kGy. After that, this curve seems to go into saturation; however, it repeats the same increasing behavior until it is saturated at 500 kGy. From which the intensity TL decreases with the increase in dose up to 1.2 MGy.

![Figure 8.18: TL glow curves of CaSiO$_3$:Eu (1000 ppm) irradiated with gamma dose (a) from 0.5 to 50kGy and (b) from 70 kGy to 1200 kGy.](image)
Figure 8.19: TL intensity behavior of the 342 - 370 °C peak as a function of gamma radiation doses for the CaSiO$_3$:Eu sample. The dashed line indicates linearity.

Figure 8.20: TL spectra of the CaSiO$_3$:Eu sample after gamma irradiation dose of 50 kGy from a Co-60 source.
(2) TL spectra

The TL emission spectrum of the polycrystal CaSiO$_3$:Eu presented one prominent very broad band centered at 420 nm and another band centered at 580 nm as shown in Figure 8.20. This means that one should expect two recombination centers. TL glow curves with the emission in the region 420 nm show TL peaks at around 150, 230 and 369 °C, whereas that emission band at 580 nm corresponds to a low-intensity TL peak at approximately 248 °C.

The emission bands for the case of CaSiO$_3$:Eu are higher than the emission bands of the $\beta$-CaSiO$_3$. It could be produced by the Eu dopant on the crystal structure. Supplementary studies to understand this behaviour will be part of future work.
8.3 Neutron irradiation at IPEN’s IEA-R1 reactor.

8.3.1 $\alpha$-CaSiO$_3$ and B, Cd, Dy, and Eu-doped CaSiO$_3$ polycrystals.

Since thermal and epithermal neutrons interact with Ca, Si and O through (n, $\gamma$) reaction and as outgoing $\gamma$ induces TL in the dosimeters, the measured effect comes essentially from thermal and epithermal effects [59, 72]. In a nuclear reactor, few reactions of fast neutrons with atomic nuclei, except scattering and fission, are important. However, the (n, p) reaction may be mentioned which is produced when fast neutrons are captured by $^{16}$O [72].

![Figure 8.21: TL Glow curve of (a) $\alpha$-CaSiO$_3$, (b) CaSiO$_3$:B, (c)CaSiO$_3$:Cd, and (d)CaSiO$_3$:Dy for different fluences of thermal neutron.](image)
Figure 8.22: TL intensity of the 235-245 °C peak vs. thermal neutron fluence for \( \alpha \)-CaSiO\(_3\) and B, Cd, and Dy-doped CaSiO\(_3\).

Figure 8.21(a) shows TL glow curves of undoped \( \alpha \)-CaSiO\(_3\) irradiated with neutrons with fluences indicated in the figure (thermal neutrons fluences). In this case TL glow curves shown a prominent TL peak at 235-245 °C.

In the same way, Figure 8.21(b) shows glow curves of CaSiO\(_3\):B irradiated with different fluences of thermal neutrons. Similar glow curves are exhibited by CaSiO\(_3\) doped with Dy and Cd as shown in Figures 8.21(c) and 8.21(d), respectively displaying TL peaks at 120-125 °C, 235-245 °C and 375-380 235-245 °C, being the second one the prominent. Compared to the glow curve of undoped \( \alpha \)-CaSiO\(_3\), it is to be noted that the doping induces smaller peaks around 120 - 125 °C and another one around 375 - 380 °C.

Figure 8.22 presents a maximum TL intensity (peak at 235-2345 °C) as a function of thermal neutron fluence (fluence-response curves) in linear-log scale of undoped \( \alpha \)-CaSiO\(_3\), and B, Cd, and Dy-doped CaSiO\(_3\). For those samples doped with B-, Cd-, and Dy- fluence-response curves show an oscillatory behaviour. Thus, it is possible to suppose that the dopant element (B, Dy, and Cd) could remain activated after
radiation with neutrons and decay within in few hours. In this way, the polycrystals of CaSiO$_3$ doped with B, Cd and Dy cannot be used for thermal neutron detection due to the oscillatory behaviour in the fluence-response curve. On the other hand, the fluence-response curve for $\alpha$-CaSiO$_3$ unlike the others has a growing behaviour.

Now Figure 8.23 shows TL glow curves of CaSiO$_3$:Eu, which is essentially the same as that of Eu-doped CaSiO$_3$ irradiated with gamma radiation (see Figure 8.18).

**Figure 8.23:** TL Glow curve of CaSiO$_3$:Eu for different fluences of thermal neutron.

Figure 8.24 presents TL intensity as a function of neutron fluence in log-log scale of CaSiO$_3$:Eu. The fluence-response curve for CaSiO$_3$:Eu has a growing behavior up to $1.50 \times 10^{15}$ n/cm$^2$, after that, decays. In addition, it is interesting to note that doped or non-doped except for the Eu-doped sample, all of them presented relatively close responses to both gamma radiation and thermal neutron. Eu-doped calcium silicate detector presented also three peaks but at 150, 240 and 375-380 °C, the last one being the prominent one.

After analyzing the above results, it is possible to conclude that the undoped sample ($\alpha$-CaSiO$_3$) shows a non-oscillating behavior of the fluence-response curve after nuclear
Figure 8.24: TL intensity of the 375-380 °C peak vs. thermal neutron fluence for CaSiO₃:Eu.

reactor exposure. For this reason, in the next section, we will compare the responses curves of the α-CaSiO₃ sample after gamma and reactor irradiation.
8.4 Comparison between gamma and neutron irradiation on the $\alpha$-CaSiO$_3$ polycrystal.

First of all, samples of $\alpha$-CaSiO$_3$ in grains (80-180 $\mu$m diameter) were irradiated with different gamma-doses. Figure 8.25(a) shows TL glow curves of the $\alpha$-CaSiO$_3$ irradiated with gamma doses from 500 Gy to 1.2 MGy. For gamma irradiation dose from 500 Gy to 1 kGy the TL peak at about 272 $^\circ$C is prominent. However, for gamma irradiation dose of 7 kGy to 1.2 MGy the prominent TL peak is that at about 234 $^\circ$C. In the same way as gamma irradiation, for thermal neutron fluence from $1.75 \times 10^{14}$ to $2.91 \times 10^{14}$ the TL peak at about 234 $^\circ$C is prominent. Figure 8.25(b) shows the TL glow curves of the undoped $\alpha$-CaSiO$_3$ for different thermal neutron fluences from $5.82 \times 10^{13}$ to $2.97 \times 10^{16}$ n/cm$^2$.

It is worth noting that TL glow curves of the $\alpha$-CaSiO$_3$ have not shown large changes during gamma or neutron irradiation. That is the main TL peak shifts slightly with the increase in radiation dose until reaching a fixed TL main peak at very high radiation doses as shown in Figure 8.25. Thus, the monitoring of the deposited gamma or neutron dose by TL in this material, after gamma or neutron irradiation, can be performed using the maximum intensity of the TL main peak following its increase or decrease after irradiation.

Figure 8.26 shows the TL response of the main TL peak (around at 234 $^\circ$C) as a function of gamma dose (blue circle). It can be observed that the TL response has a linear behavior up to 7 kGy and then it saturates, after that, TL response decreases slowly with the increase in dose from 50 kGy to 1.2 MGy.

On the other hand, the curve in red (red triangle) shows the response of the main TL peak (around at 234 $^\circ$C) after reactor exposure, as a function of thermal neutron fluences ranging from $5.82 \times 10^{13}$ to $2.97 \times 10^{16}$ n/cm$^2$. This curve has a growing linear behavior from $5.82 \times 10^{13}$ to $1.75 \times 10^{14}$ n/cm$^2$. After that, a growing non-linear behavior is shown, from $2.91 \times 10^{14}$ to $1.98 \times 10^{15}$ n/cm$^2$ thermal neutron fluence. Consequently, it can be proposed that TL response for neutron irradiation can go into saturation.
Figure 8.25: TL glow curves of $\alpha$-CaSiO$_3$ irradiated with high and ultra-high gamma dose from 500 Gy to 1.2 MGy, (b) TL glow curve of $\alpha$-CaSiO$_3$ irradiation with different thermal fluences from 5.82x10$^{13}$ to 2.97x10$^{16}$ n/cm$^2$.

to thermal fluences greater than of 1.98x10$^{15}$ n/cm$^2$ and then slowly decreasing in intensity, in the same way as gamma dose irradiation.

Moreover, it can be observed in Figure 8.26 that the TL response higher than 2.91x10$^{14}$ n/cm$^2$ fluences is lesser than the TL responses for high-gamma radiation (higher than 4 kGy). This may be due to the radiation damage effect on the sample when it is exposed to ultra-high neutron radiation (higher than 2.91x10$^{14}$ n/cm$^2$) but this effect requires
supplementary studies. Piesch et al. [164] and Gambarini et al. [62] have observed that LiF dosimeters when exposed to high fluences of thermal neutrons lose linearity and undergo radiation damage. For this reason, Gambarini et al. [62] proposed a rough correction of the results by means of re-calibrating the dosimeters through gamma radiation after neutron irradiation.

![Figure 8.26](image)

**Figure 8.26:** TL intensity behavior of the main peak at about 234 °C as a function of gamma doses (blue circle) and the TL intensity of the main peak at about 234 °C as a function of thermal neutron fluence (red triangle).

Additionally, it can be observed in Figure 8.26 that the TL responses lower than 2.91x10^{14} n/cm^{2} is similar to those irradiated with gamma radiation lower than 4 kGy.

In this way, taking advantage of this behavior it is possible to calculate the gamma dose absorbed by the CaSiO\textsubscript{3} after reactor irradiation. That is, after reactor exposure, the nuclear reactor enters a state of interruption where no neutron fluxes are emitted but gamma radiation continues to be emitted through the active core of the reactor. For this reason, we make an extrapolation of the TL response lower than 2.91x10^{14}
n/cm² as shown in Figure 8.27. In this way, Figure 8.27 shows that for a thermal neutron fluence value of zero we have a TL intensity of about $1.38 \times 10^4$ (a.u.).

On the other hand, for gamma radiation dose the TL response is supralinear from few Gy to 7 kGy as mentioned in subsection 8.2.1. This supralinear behavior can be expressed by the equation $TL = 26.8 \times \text{Dose} - 5890$. Thus, for a TL intensity of $1.38 \times 10^4$ a.u. (neutron extrapolation), we have, using the supralinear equation for gamma radiation dose, a value of gamma dose of about 730 Gy.

Thus, this result shows us that the amount of gamma absorbed dose by the material after the neutrons flux ceases at the point of irradiation 13 B (shelf 1) is about 730 Gy. This result is of interest for the IEA-R1 reactor, because no residual gamma irradiation dose has been calculated up to now.

![Figure 8.27: Extrapolation of the TL intensity behavior of the main peak at about 234 °C for fluences lower than $2.91 \times 10^{14}$ n/cm².](image)

Figure 8.27: Extrapolation of the TL intensity behavior of the main peak at about 234 °C for fluences lower than $2.91 \times 10^{14}$ n/cm².
8.5  \((n, \gamma)\) reaction in the \(\text{CaSiO}_3\) polycrystal.

The interaction of the thermal neutrons from the research reactor IEA-R1 with polycrystalline calcium silicate has been analyzed analytically in this section. In the irradiation of \(\alpha\)-CaSiO\(_3\) with thermal neutrons, the main effect is the \((n, \gamma)\) reaction that takes place with Ca, Si and O. For this reason, the energy of \(\gamma\) radiation emitted when a thermal neutron is absorbed by each element of the \(\text{CaSiO}_3\) \((n, \gamma)\) reaction has been calculated.

Since each element can exist in different types, called isotopes, we need to consider the natural abundance of the isotopes of each element studied. We shall consider \(^{40}\text{Ca}\), \(^{28}\text{Si}\), and \(^{16}\text{O}\) as the most abundant isotopes according to Meija et al. [165].

8.5.1 \(^{40}\text{Ca}(n, \gamma)^{41}\text{Ca}\) reaction

Table 8.3 shows the isotopes of Calcium with their respective isotopic abundance.

| Isotope | Atomic mass (u) | Isotopic abundance (amount fraction) |
|---------|----------------|-------------------------------------|
| \(^{40}\text{Ca}\) | 39.962 5909(2) | 0.969 41(156) |
| \(^{42}\text{Ca}\) | 39.962 5909(2) | 0.006 47(23) |
| \(^{43}\text{Ca}\) | 42.958 766(2) | 0.001 35(10) |
| \(^{44}\text{Ca}\) | 43.955 482(2) | 0.020 86(110) |
| \(^{46}\text{Ca}\) | 45.953 69(2) | 0.000 04(3) |
| \(^{48}\text{Ca}\) | 47.952 5228(8) | 0.001 87(21) |

Then, the \(^{40}\text{Ca}(n, \gamma)^{41}\text{Ca}\) reaction will be:

\[
^{40}\text{Ca} + _{0}^{1}n = ^{41}\text{Ca} + \gamma \quad (8.2)
\]
The capture of the thermal neutron (slow neutron) by a nucleus results in the release of a large amount of energy. The energy that is released in this reaction is called the binding energy of a neutron in the particular nucleus formed. The Q-value of a nuclear reaction is the measure of the energy “release” or “absorbed” by the reaction. It is calculated by the difference between the sum of the masses of the initial reactants and the sum of the masses of the final products, in energy units (usually in MeV) \[166\]. In this case, for the \(^{40}\text{Ca}(n, \gamma)^{41}\text{Ca}\) reaction, the Q value is:

\[
Q = M_0(^{40}\text{Ca}) \cdot c^2 + M_0(n) \cdot c^2 - M_0(^{41}\text{Ca}) \cdot c^2
\]

(8.3)

where \(M_0(^{40}\text{Ca})\) is the atomic mass of \(^{40}\text{Ca}\) and \(M_0(^{41}\text{Ca})\) is the atomic mass of \(^{41}\text{Ca}\). We shall consider the most abundant isotope of calcium, the \(^{40}\text{Ca}\) with an abundance (in amount fraction) of 0.969 41(156) and an atomic mass of 39.962 5909 u \[165\]. The atomic mass for \(^{41}\text{Ca}, M_0(^{41}\text{Ca})\) is 40.96227806(26) \[167\]. \(M_0(n)\) is the relative atomic mass of the neutron equal to 1.008 664 915 74(56) u \[168\]. Thus, using the equation for Q mentioned earlier, we obtain, \(Q(\text{Ca}) \approx 8362.7 \text{ keV}\) which is in good agreement with Gruppelaar and Spilling \[169\]. Gruppelaar and Spilling with the help of the least-squares program have calculated a more accurate Q-value for the \(^{40}\text{Ca}(n, \gamma)^{41}\text{Ca}\) reaction as \(Q = 8363.4 \pm 1 \text{ keV}\).

### 8.5.2 \(^{28}\text{Si}(n, \gamma)^{29}\text{Si}\) reaction

In the same way, as Ca, Table 8.4 shows the isotopes of Silicon with their respective isotopic abundance.

In this case, for the \(^{28}\text{Si}(n, \gamma)^{29}\text{Si}\) reaction, the Q value is,

\[
Q = M_0(^{28}\text{Si}) \cdot c^2 + M_0(n) \cdot c^2 - M_0(^{29}\text{Si}) \cdot c^2
\]

(8.4)

where \(M_0(^{28}\text{Si})\) is the atomic mass of \(^{28}\text{Si}\) and \(M_0(^{29}\text{Si})\) is the atomic mass of \(^{29}\text{Si}\). \(M_0(n)\) is the relative atomic mass of the neutron equal to 1.008 664 915 74(56) u \[168\].
Thus, using the equation 8.4 and considering the isotopic abundance of Si as well as the atomic mass of $^{28}$Si and $^{29}$Si for the $^{28}$Si(n,γ)$^{29}$Si reaction, the calculated Q-value is, $Q(\text{Si}) \approx 8473.60$ keV which is in good agreement with Spits et al. [170]. Spits et al. [170] have calculated more accurate Q-values for $^{28}$Si(n, γ)$^{29}$Si reaction as $Q(\text{Si}) = 8473.5 \pm 0.5$ keV.

8.5.3 $^{16}$O(n, γ)$^{17}$O reaction

Similarly to the previous cases, Table 8.5 shows the isotopes of Oxygen with their respective isotopic abundance.

| Isotope | Atomic mass (u) | Isotopic abundance (amount fraction) |
|---------|-----------------|-------------------------------------|
| $^{16}$O | 15.994 914 620(2) | [0.997 38, 0.997 76] |
| $^{17}$O | 16.999 131 757(5) | [0.000 367, 0.000 400] |
| $^{18}$O | 17.999 159 613(6) | [0.001 87, 0.002 22] |

In this case, for the $^{16}$O(n, γ)$^{17}$O reaction, the Q value is,

$$Q = M_0(^{16}\text{O}) * c^2 + M_0(n) * c^2 - M_0(^{17}\text{O}) * c^2$$

(8.5)

where $M_0(^{16}\text{O})$ is the atomic mass of $^{16}$O and $M_0(^{17}\text{O})$ is the atomic mass of $^{17}$O. Thus, using the equation 8.5 and considering the isotopic abundance of O and the values
of the atomic mass of $^{16}\text{O}$ and $^{17}\text{O}$ for the $^{16}\text{O}(n, \gamma)^{17}\text{O}$ reaction [165], the calculated Q-value is $Q(\text{O}) \approx 4143.08$ keV which is in good agreement with Firestone et al. [171]. They have calculated more accurate Q-values for $^{16}\text{O}(n, \gamma)^{17}\text{O}$ reaction as $Q(\text{O}) = 4143.06 \pm 0.10$ keV.

### 8.5.4 Neutron absorption

The results of calculation of the total thermal neutrons absorbed on the sample of CaSiO$_3$ is presented in this section. For this purpose, a sample of CaSiO$_3$ in grains (0.080-0.180 mm in size) inside a cylindrical geometry tube (silica tube) has been considered. Total neutron absorption $N$ at a distance $x$ from the sample can be expressed by the equation [172]:

$$N(x) = N(0) \cdot e^{-\mu x} \quad (8.6)$$

where $N(x)$ and $N(0)$ are the neutron fluence at a depth $x$ in the material and before entering the material respectively. $\mu$ is the linear absorption coefficient (cm$^{-1}$): $\mu = N_A \cdot \rho \cdot \sigma_A \cdot \omega / A$. $N_A$ is Avogadro’s number, $\rho \approx 1.47$ g/cm$^3$ is the sample density, $\sigma_A$ is the energy-dependent capture cross-section for each element, $A$ is the atomic mass and $\omega$ is the weight fraction of each element in the material. $\sigma_A$ for thermal neutrons capture is called thermal cross section. For $^{40}\text{Ca}$, the thermal cross section is $0.41 \pm 0.02$ barn, for $^{28}\text{Si}$ is $0.177 \pm 0.004$ barn, and for $^{16}\text{O}$ is $190 \pm 0.019$ mbarn. These values were obtained from the book: *Atlas of Neutron Resonances and Thermal Cross Section* [155].

Figure 8.28 shows the cylindrical disposition of the sample of CaSiO$_3$ during neutron exposition. For calculation purposes, the effect of the silica and aluminum tube, as well as the particle size of the sample in neutron irradiations were not considered. The total thermal neutrons absorbed $n_{\text{abs}}$ by each element on the sample was calculated using the equation 8.7 which was calculated analytically from the $N(x)$ equation mentioned.
above (equation 8.6) and considering a cylindrical disposition of the sample.

\[ n_{abs} = I_0 \cdot t \cdot r \cdot z_0 (\pi - \int_0^\pi e^{-2N\cdot\sigma\cdot r\cdot\sin\theta} d\theta) \]  

(8.7)

Where \( I_0 \) is the initial flux density of neutrons in n/cm\(^2\)-s, \( t \) is the irradiation time of the flux on the sample, \( r \) is the radius of the transverse circumference of the silica tube and \( z_0 \) is the height of the sample inside the silica tube (\( 2r = 4.00 \pm 0.05 \) mm, \( z_0 = 6.00 \pm 0.05 \) mm). \( N = \rho \cdot N_A \cdot \omega / A \). \( I_0 \cdot t \) is the neutron fluence and \( \theta \) is the azimuthal angle in a cylindrical coordinate disposition as shown in Figure 8.28. Therefore, for the thermal fluence \( f = (29.1 \pm 3.0) \times 10^{13} \) n/cm\(^2\), the amount of total thermal neutrons absorbed \( n_{abs} \) by each element on the sample is: \( n_{abs}(\text{Ca}) = (919 \pm 96) \times 10^8 \); \( n_{abs}(\text{Si}) = (603 \pm 63) \times 10^7 \); and \( n_{abs}(\text{O}) = (118 \pm 12) \times 10^9 \) neutrons. Finally, with the above considerations, the total energy released or total Q-value of all nuclear reactions produced on the sample during thermal neutron irradiation was obtained. The total energy released at a given fluence \( f \): \( Q_{(f,\text{CaSiO}_3)} \) is calculated using the equation 8.8.

\[ Q_{(f,\text{CaSiO}_3)} = n_{(f,\text{Ca})} \cdot Q_{(\text{Ca})} + n_{(f,\text{Si})} \cdot Q_{(\text{Si})} + n_{(f,O)} \cdot Q_{(O)} \]  

(8.8)

where \( n_{(f,X)} \) is the number of neutrons absorbed by X for each thermal neutron fluence.
Q(X) is the energy released from the nuclear reaction produced during the absorption of a thermal neutron. X = Ca, Si, and O. Table 8.6 shows the total energy released at different thermal neutron fluences. The Q-values used in this calculation for Ca, Si, and O were taken from [169–171].

### Table 8.6: Total released energy calculated on the sample of CaSiO	extsubscript{3} at each thermal neutron fluence.

| Thermal neutron fluence (n/cm	extsuperscript{2})[x10	extsuperscript{13}] | Total released energy (MeV)[x10	extsuperscript{11}] |
|--------------------------------------------------|----------------------------------|
| 5.8 ± 3.0                                         | 2.62 ± 0.90                      |
| 17.5 ± 3.0                                        | 7.87 ± 0.93                      |
| 29.1 ± 3.0                                        | 13.1 ± 1.0                       |
| 58.2 ± 3.3                                        | 26.2 ± 1.1                       |
| 132 ± 17                                          | 59.3 ± 5.4                       |
| 198 ± 17                                          | 89.0 ± 5.4                       |
| 2970 ± 100                                        | 1330 ± 34                        |

On the other hand, it is important to be mention that not all energies released in the sample of CaSiO	extsubscript{3} during neutron irradiation by the nuclear reactions are absorbed. Only a small portion will contribute to the total deposited dose. In (n, γ) reactions for Ca, Si and O, the excited compound nucleus, after neutron capture, emits its excess energy as gamma radiation leaving the nucleus in the lowest energy state. This energy emitted is about 8.36 MeV for Ca, 8.47 MeV for Si and about 4.14 MeV for O, as shown earlier. Usually, this excess energy is emitted as several photons from keV to MeV [72, 173]. Part or all of the energy emitted can be absorbed, or may even reach other elements on the sample, in its trajectory. In this case, several other kinds of processes may appear where photon interaction is involved [152]. In addition, taking into account that the sample is small of the order of mm	extsuperscript{3}, it allows the gamma radiation of high intensity to escape.

For this purpose, the calculation of the deposited dose on the sample of CaSiO	extsubscript{3} after neutron irradiation was carried out with the help of colleagues from the Nuclear
Table 8.7: Calculated deposited dose in a sample of CaSiO₃ (80 mg) at each thermal neutron fluence.

| Thermal neutron fluence (n/cm²)[x10¹³] | Deposited dose (Gy) |
|----------------------------------------|---------------------|
| 5.8 ± 3.0                              | 41.5 ± 0.2          |
| 17.5 ± 3.0                             | 125 ± 1             |
| 29.1 ± 3.0                             | 208 ± 1             |
| 58.0 ± 3.3                             | 415 ± 2             |
| 132 ± 17                               | 935 ± 5             |
| 198 ± 17                               | 1400 ± 7            |
| 2970 ± 100                             | 21000 ± 100         |

Engineering Center of the Nuclear and Energy Research Institute, São Paulo (CEN-IPEN/SP). The code used for this calculation was the MCNP5 (Monte Carlo N-Particle Transport Code). This code takes into account the neutron energy either, thermal, epithermal or fast neutrons during the neutron interaction with the polycrystal. In addition, the simulation was considered the real geometrical disposition and the sample of CaSiO₃ located inside the silica tube and it, in turn, located inside the aluminum tube as explained before.

Additionally, all neutrons (thermal, epithermal, and fast neutrons) before reaching the sample interacts with aluminum (first) and silica tube (second) through different processes mainly through the (n, γ) reaction producing the emission of photons. Al and Si having a low cross-section for thermal neutrons capture of the order of mbarn [155]. These photons produced in the interaction of neutron with the aluminum and silica tube, which was not initially absorbed, subsequently may be absorbed by the sample of CaSiO₃. These photons absorbed by the sample was also taking into account by the calculation of the total deposited dose. Table 8.7 shows this calculated deposited dose for each thermal neutron fluence through the Monte Carlo simulation. It is important to mention that in the calculation process gamma produced by the reactor was not considered. However, all neutron irradiation on the sample was considered.
8.6 Center responsible for the TL peaks of CaSiO$_3$
estimated by EPR analysis

8.6.1 Comments

Rudras and Fowler (1987) [174] have shown that in crystalline SiO$_2$ oxygen vacancies are produced easily at room temperature (RT). Whenever the crystal is irradiated with ionizing radiation, electrons from a large number of pairs of electron-hole (e-h) produced by the radiation are captured two by each oxygen vacancy. Toyoda and Ikeya (1991) [175] found that heating the crystal, one of the two electrons is released leaving oxygen vacancy with one electron, that was called later as E$_1'$. At around 300 °C, it is observed the maximum number of E$_1'$ - center formed. From 300 °C on the remaining electron is liberated and around 450 °C no E$_1'$ - center is left.

Figure 8.29 show the formation scheme of the E$_1'$ center and peroxy radical [28].

![Figure 8.29: A formation of the E$_1'$ center and peroxy radical.](image)

A crystal of quartz usually contains aluminum and titanium, and an ion of Al$^{3+}$ replaces Si$^{4+}$ in SiO$_4$ to form [AlO$_4$]$^{-}$ center. To keep neutrality, a monovalent cation M$^+$ is
attracted to form [AlO$_4$/M$^+$]$^0$ center. When the crystal is irradiated with $\gamma$-radiation, M$^+$ is removed leaving [AlO$_4$/h]$^0$ where h is a hole. This is called aluminum center, Toyoda and Ikeya (1991) have shown its existence by EPR measured at 77 K. Figure 8.30 shows the behavior with the heating of E$'_1$ - centers and aluminum center.

Electrons liberated from oxygen vacancies that captured two electrons recombine with holes in aluminum center emitting TL light. In the present case, we have CaSiO$_3$ crystal. We assume that as in the case of quartz, oxygen vacancies are formed at RT. When the crystal is irradiated, a large number of e-h pairs are liberated and oxygen vacancies capture electrons two by each vacancy. The ionization by irradiation creates hole center around Ca ion: [CaO$^-$/h] so that with heating crystal electrons liberated by oxygen vacancies that had captured electrons will recombine with holes in [CaO$^-$/h] - center emitting TL light.
8.6.2 Case of B, Cd, Dy, and Eu-doped CaSiO$_3$

The dopants are B, Cd, Dy, and Eu. Cd has valence two, B and Dy, three and Eu can have valence two or three. For B, Cd, and Dy as dopants with less than 500 ppm in amount we expect, without proof as yet, the following centers: [BO$_4$/h], [CdO$_4$/h] and [DyO$_4$/h]. Heating the crystal, these centers decay with temperature liberating 1 hole, 2 holes, and 1 hole, respectively.

As in the case of quartz, oxygen vacancies capture electrons during the irradiation of crystal and under heating electrons are liberated that recombine with holes and emit TL light. In the case of Eu, 1000 ppm of this element was added to CaSiO$_3$. No proof was found yet, but Eu-doped CaSiO$_3$ liberates a large part of holes at a temperature in the region of 300 - 400 °C, therefore, the TL peak around 360 °C is the prominent.

8.6.3 $\beta$-CaSiO$_3$ polycrystal

The room temperature EPR spectrum of gamma-irradiated (dose: 6 kGy) $\beta$-CaSiO$_3$ is shown in Figure 8.31. It is inferred from thermal annealing studies that three different centers contribute to the observed spectrum. The centers are labeled in Figure 8.31.

In a perfect $\beta$-CaSiO$_3$ lattice, Ca and Si atoms are expected to be situated in their respective sites. However, antisite cation exchange may be present resulting in partial replacement of Ca atoms by Si atoms. This exchange called as cation exchange disorder is a point defect in crystal lattices where cations exchange positions. Kuklja [176] has predicted the presence of such defects based on theoretical calculations. This prediction is supported by X-ray diffraction [177] and X-ray absorption fine structure studies [178]. It has also been possible to directly observe these defects using advanced electron microscopy [179].

The line labeled as center I in Figure 8.31 is characterized by a rhombic g-tensor with principal values $g_1 = 2.0135$, $g_2 = 2.0094$ and $g_3 = 2.0038$. The linewidth of the line corresponding to $g = 2.0094$ is about 12 gauss (1.2 mT). The EPR line is
broad and could arise from a possible unresolved hyperfine structure. The unresolved structure can arise from the interaction of the unpaired electron with nearby nuclear spins. Calcium and silicon in CaSiO$_3$ have isotopes with nuclear spins $7/2$ and $1/2$ ($^{49}$Ca and $^{29}$Si, respectively) [180]. It is possible that the electronic spin will interact with Ca ions and also with Si ions. In CaSiO$_3$, a number of lattice defects may form due to non-stoichiometry and cation disorder mentioned earlier. First principle calculations suggest that the possibility of formation of oxygen vacancies is high in a lattice with antisite cation disorder [181]. F$^+$-center will form easily in a lattice with cation disorder by trapping electrons at oxygen vacancies. On the other hand, calcium and silicon vacancies can trap holes and form V-centers or O$^-$ ions [182]. The relatively broad line of center I arising from unresolved hyperfine structure indicates the delocalization of the unpaired electron and an interaction with nearby nuclei. It has been suggested that in oxides [183] charges must be trapped near double or more charged defects allowing the charge to be delocalized and interact with nearby nuclei.
The observed magnitude of g-values and the large orthorhombicity of g-tensor are characteristic of an $O^-\text{ion}$ which results from the capture of a hole at $O^{2-}\text{ions}$.

Examples are $O^-\text{ion}$ observed in systems like KNbO$_3$ [184] and SrTiO$_3$ [185]. The hole resides in $O^-\text{(2p)}$ orbital resulting in one of the principal g-value close to free-spin value. On the basis of these observations, center I in CaSiO$_3$ is tentatively attributed to an $O^-\text{ion}$. The thermal annealing behavior of center I is shown in Figure 8.32. It is observed that the center decays in the broad temperature range starting from about 50 to 290 °C. It is speculated that the decay extends a little beyond 290 °C and the spectrometer may not have the sensitivity to detect this weak signal. As the decay of the center extends over a range of TL peaks, it is suggested that center I ($O^-\text{ion}$) could be the recombination center for TL peaks at 124, 147, and 306 °C. The thermal stabilities of individual dominant TL peaks are shown in Figure 8.33. This behavior of TL peaks indicates that neither center I nor II can be associated exclusively with an individual TL peak. Rather it appears that center I is the recombination center for multiple TL peaks.
The EPR line labeled as center II in Figure 8.31 has an isotropic g-value of 2.00025 and a linewidth of 2 G (0.2 mT). Oxygen vacancies present in the lattice due to reasons mentioned earlier can trap electrons and form F$^+$-centers. Earlier observation of this center is in LiF [186] where the center exhibited a very large linewidth and a g-value close to free-electron value. The inherent linewidth of F$^+$-center is very small (1G) as observed in MgO [187]. The amount of delocalization of the unpaired electron decides the linewidth along the magnetic moment and relative abundance of the isotopes of the ions. In alkali halides, electron is observed to be considerably delocalized and F$^+$-center in these systems exhibit large linewidths. For example, linewidth of 58 G and 20 G are observed in LiCl and KCl, respectively [188]. On the other hand, the center in BaO has a small linewidth of 3.5 G [189]. Apart from alkali halides, F$^+$-center can form in oxide systems. In both alkali halides and oxides, the g-value has been found to be close to free-electron value with g-shifts being either positive or negative.

In $\beta$-CaSiO$_3$, the linewidth is not large and the g-shift is small. On the basis of these observations, center II is tentatively identified as an F$^+$-center. Figure 8.32 shows...
the thermal annealing results of center II. It is seen that the intensity of the EPR line decreases in the temperature range from about 70 to 300 °C. It is observed that the decay temperature range of center II is almost the same as center I. This behavior compels us to speculate that this center is also associated with 124 °C, 147 °C and 306 °C TL peaks and perhaps is also a recombination center for all these peaks. Center II line intensity is quite small and as with center I may completely decay at a temperature which is slightly higher than 300 °C.

EPR line labeled as center III in Figure 8.31 originates from a single defect center displaying an orthorhombic g-tensor with principal values $g_1 = 1.9830$, $g_2 = 1.9741$ and $g_3 = 1.9046$. The center is seen to exhibit relatively large g-anisotropy and the principal values are similar to Ti$^{3+}$ center [190]. It is speculated that titanium ion is present in CaSiO$_3$ as an impurity and incorporated into the lattice during the synthesis of CaSiO$_3$. Large g-shifts are expected for the Ti$^{3+}$ center as the spin-orbit coupling of titanium ion is high ($\lambda = 154$ cm$^{-1}$: free-ion value). The first observation on Ti$^{3+}$ center was in X-irradiated rose quartz by Wright et al. [190]. In rose quartz, centers arise from titanium ion located substitutionally at silicon sites. Two sets of lines were observed and both were assigned to Ti$^{3+}$ centers. Wright et al. [190] attributed the centers to Ti$^{3+}$ centers based on the weak anisotropic hyperfine structure coming from low abundance odd titanium isotopes namely, $^{47}$Ti and $^{49}$Ti. On the basis of the experimentally observed orientation of the principal g-axes and from the fact that titanium forms tetrahedral compounds, it was suggested that titanium has substituted silicon atoms. It was further suggested that the titanium center is formed from the capture of an electron, released due to gamma irradiation, on the titanium central atom located at the center of a distorted tetrahedron in α-quartz.

Several Ti centers have been observed in silicate minerals and CaSiO$_3$ is also a silicate system. Ding et al. [191] have shown in a theoretical study that Ti$^{3+}$ ion located in an orthorhombically elongated tetrahedral [TiO$_4$]$^{5-}$ cluster on W$^{6+}$ site in ZnWO$_4$ is characterized by the principal g-values 1.967, 1.955, and 1.989. The experimentally observed g-values in ZnWO$_4$ are 1.843, 1.895, and 1.933 [192]. In another case of Ti$^{3+}$ ions at a low symmetry tetrahedral Si$^{4+}$ site in Beryl (Be$_3$Al$_2$Si$_6$O$_{18}$), Yang et al. [193]
have calculated the principal g-values to be 1.998, 1.917, and 1.875. In an EPR study on Beryl, the experimentally observed values are 1.998, 1.907, and 1.866 [194].

On the basis of these theoretical and experimental results, center III in CaSiO$_3$ is tentatively attributed to a Ti$^{3+}$ center. Titanium impurity ions are located at Si sites in CaSiO$_3$. They capture an electron during irradiation resulting in the formation of Ti$^{3+}$ center. Figure 8.32 shows the thermal annealing behavior of center III. It is observed that the center becomes unstable around 110 °C and decays in the temperature range 110 °C - 210 °C. This decay relates to the 147 °C TL peak and perhaps also with the 124 °C peak.

### 8.6.4 $\alpha$-CaSiO$_3$ polycrystal

Figure 8.34 shows the room temperature EPR spectrum of irradiated $\alpha$-CaSiO$_3$ (gamma dose: 6 kGy). EPR lines labeled as center I are assigned to O$^-$ ion based on the reasons mentioned earlier in the discussion of $\beta$-CaSiO$_3$. Similarly, center III lines are attributed to Ti$^{3+}$ center. The centers observed in $\beta$-CaSiO$_3$ are also seen in $\alpha$-CaSiO$_3$. The thermal annealing behavior of O$^-$ ion is shown in Figure 8.35. O$^-$ ion becomes unstable around 50 °C and decays in the temperature range 50 - 350 °C. As the decay of the center extends over a range of TL peaks, it is suggested that center I (O$^-$ ion) could be the recombination center for TL peaks at 139, 169, and 329 °C. This behavior of TL peaks indicates that neither center I nor II can be associated exclusively with an individual TL peak. Rather it appears that center I is the recombination center for multiple TL peaks.

F$^+$ center line is not seen in Figure 8.34 as its intensity is low and is overlapped by the EPR line of O$^-$ ion. However, with the diminishing intensity of O$^-$ ion at higher annealing temperatures, F$^+$-center line is seen around 190 °C. F$^+$-center thermal annealing behavior is shown in Figure 8.35 which is represented as center II in the same way as for $\beta$-CaSiO$_3$. It is seen that the intensity of EPR line increases in the temperature range from about 190 to 260 °C, after that, the EPR line decreases from
Figure 8.34: Room temperature EPR spectra of irradiated $\alpha$-CaSiO$_3$ (gamma dose: 6 kGy). The line labeled as I is due to an O$^-$ ion. The Ti$^{3+}$-center is indicated as center III.

Figure 8.35: Thermal annealing behavior of Center I (O$^-$ ion), Center II (F$^+$ center) and Center III (Ti$^{3+}$ center) in $\alpha$-CaSiO$_3$ (wollastonite-2M). The intensity was normalized by the maximum value of the EPR signal for each center.
270 °C to 360 °C. As the center’s annealing behavior could not be properly monitored at low annealing temperatures. But for high temperatures it is observed that the decay temperature range of center II is almost the same as center I. This behavior compels us to speculate that this center is also associated with 139, 169, and 329 °C TL peaks and perhaps is also a recombination center for all these peaks. Figure 8.35 shows the thermal annealing behavior of Ti$^{3+}$ center. Center becomes unstable around 110 °C and decays in the temperature range 120 - 230 °C. This decay relates to the 169 °C TL peak and perhaps also with the 139 °C peak.
8.7 Pellets of $\beta$-CaSiO$_3$ for gamma radiation

8.7.1 Gamma irradiation

In order to determine the dose-response of $\beta$-CaSiO$_3$ pellets (6 mm diameter and 1 mm thickness) were irradiated with different gamma-doses from 1 mGy to 10 Gy using Cs-137 and Co-60 sources. TL glow curves of $\beta$-CaSiO$_3$ pellets irradiated with dose from 100 mGy to 10 Gy are shown in Figure 8.36. The gamma irradiation was performed at room temperature and under conditions of electronic equilibrium using a 3 mm thick acrylic layers placed on each side of the tablet covering it completely.

Glow curves in Figure 8.36 present one prominent well-defined peak at about 169 °C, and two possible peaks at about 272 °C and 322 °C when irradiated with gamma dose from Cs-137 source. Furthermore, using the previous result found by $\beta$-CaSiO$_3$ in section 8.2.2 we can obtain the deconvolution of the TL glow curve of $\beta$-CaSiO$_3$ pellets when irradiated with gamma dose of 5 Gy as shown in Figure 8.37.

![Figure 8.36: TL Glow Curves of pellets of $\beta$-CaSiO$_3$ irradiated with gamma dose from 100 mGy to 10 Gy (Cs-137; Co-60).](image-url)
8.7.2 Glow curve deconvolution

The TL glow curve in Figure 8.37 present three possible peaks and the GCD method shows seven. The TL experimental shows peaks at 169, 265 and 326 °C and seven computed TL peaks separated using different orders of kinetics at about 134, 156, 169, 223, 267, 321 and 350 °C. The FOM obtained for the TL glow curve fitting shown in Figure 8.37 is about 1.17 %.

8.7.3 Thermal annealing

As mentioned earlier, the glow curves shown in Figure 8.36 present one prominent well-defined peak at about 169 °C which is unstable at room temperature, that is, this peak shows high fading as shown in Figure 8.13.

For that reason, previous thermal annealing of 210 °C for 10 s (TT210°Cx10s) is carried out before a TL measurement. The purpose of this procedure is to delete the
Figure 8.38: TL Glow Curves of pellets of $\beta$-CaSiO$_3$ irradiated with gamma dose from 1 mGy to 100 mGy (Cs-137) after previous thermal annealing of about 210 °C for 10 s.

TL peak intensity at 169 °C. Figure 8.38 shows these TL glow curves of $\beta$-CaSiO$_3$ pellets irradiated with gamma dose from 1 mGy to 100 mGy (Cs-137) after the previous thermal annealing mentioned above. Therefore, it is possible to observe in Figure 8.38 the two high-temperature dosimetric peaks at about 270 °C and 320 °C.

8.7.4 Dose-response curve

Figure 8.39 shows the maximum TL response of the peak at about 270 °C of $\beta$-CaSiO$_3$ in pellets as a function of gamma irradiation dose, for doses ranging from 1 mGy to 5 Gy. Each point is the average of five pellets measured. Analyzing the dose-response curves with log axes in the same scale, as shown in Figure 8.39. It can be observed that the TL response of peak at 270 °C has a linear behavior from 1 mGy to 5 Gy, with a calibration equation, equals to $I_{TL} = 0.375 \cdot \text{Dose}$. 

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8.7.5 Minimum detectable dose

As shown above the peak at 270 °C has a linear behavior from 1 mGy to 5 Gy. As a result, the minimum detectable dose (MDD) can be calculated. The MDD value is obtained intercepting the linear fit behavior of TL peak with three times the standard deviation of zero dose TL reading (3σTL) [195], in this way, a MDD of \( \sim 60 \mu \text{Gy} \) was obtained as shown in Figure 8.40.

8.7.6 Dose rate dependence: possible application in radiotherapy

As mentioned in subsection 2.3.1, dosimetric materials must satisfy certain important characteristics to be considered as a suitable TL dosimeter. Among the main requirements imposed on these materials are, to have a linearity response with the irradiation...
dose, high sensitivity for different radiation types, a low energy dependence, low fading, and good stability low Z effective in order to approximate that of human tissue (7.35-7.65) [17].

On the other hand, to the conventional radiotherapy where dose rates of clinically (0.1âĂŠ0.2 Gy/s) are used, recent studies where ultra-high dose rate irradiation, is involving, termed FLASH radiotherapy (FLASH-RT) has appeared as an innovative modality able to improve therapeutic responses and limiting normal tissue injury [196]. In this case, TL dosimeters that are not influenced by the dose rate and with a low energy-beam dependence are required [196].

For this reason, a study of the dose rate dependence was carried out using a Cs-137 source as shown in Figure 8.41. Three different rate dose of about 8.26, 11.9, and 33.0 mGy/h were used in the experiment. As can be observed in Figure 8.41 there is no discernible dose-rate effect for β-CaSiO₃ pellets in the range from 8.26 to 33.0 mGy/h. That is, β-CaSiO₃ could be used as a TL dosimeter in conventional- and
FLASH- radiotherapy but supplementary studies need to be carried out to support this result. A study of the TL dependence for a higher dose rate than 33.0 mGy/h will be proposed as a part of future works.

**Figure 8.41:** Dose rate dependence of the response of $\beta$-CaSiO$_3$ detectors in a Cs-137 source. The response is normalized to the reading at a dose rate of 33.030 mGy/h. Three detectors were used at each dose rate setting.

### 8.7.7 Energy dependence of $\beta$-CaSiO$_3$ pellets

In this subsection, pellets of $\beta$-CaSiO$_3$ were irradiated with different X-ray energies at the dosimetry laboratory of the University of São Paulo in order to know the energy dependence of this material. For this purpose, the irradiation with energies of 22 keV, 40 keV, 80 keV, and 150 keV from an X-ray tube Philips MG 450 were carried out. Furthermore, pellets of $\beta$-CaSiO$_3$ were irradiated with gamma radiation from a Cs-137 (gamma energy of 661.7 keV) and Co-60 sources (gamma energies of 1.17 and 1.33 MeV).
Figure 8.42 shows the results of the energy dependence of the relative TL intensity of peak at 260 °C, with the same dose of 1 mGy, for different photon energies. It can be observed that between 22 keV and 150 keV the TL intensity decrease, after that, the TL intensity remains constant with the increase in energy.

Additionally, the concept of effective atomic number $Z_{eff}$ has been introduced in order to characterize the energy response of different materials. Equation 8.9 shows the calculation of the effective atomic number, where $a_i$ is the fractional electron content of element $i$ with atomic number $Z_i$. The value of $m$ varies from 3 to 4 [34]. The effective atomic number of the $\beta$-CaSiO$_3$ calculated with equation 8.9 and using a value of $m = 3.5$, we obtain, $Z_{eff}(\text{CaSiO}_3) = 15.72$.

$$Z_{eff} = \sqrt{\sum_i a_i Z_i^m} \quad (8.9)$$
8.7.8 Challenge: application for environmental and personnel monitoring

As shown above $\beta$-CaSiO$_3$ has a high the $Z_{\text{eff}}$ (15.72). However for energies higher than 150 keV, $\beta$-CaSiO$_3$ there is no energy dependence. That is, $\beta$-CaSiO$_3$ could be used as a TL dosimeter in nuclear medicine such as personal dosimetry and radiotherapy.

Furthermore, it was found by many researchers that a suitable combination of filters can give an almost energy independent response and still retain the advantage of the higher sensitivity in film dosimeters [197]. Keeping this in mind, S. Morato and collaborators [198] adapted this method to TL dosimeters with high effective Z, such as the CaSO$_4$:Dy detector. This study had in mind the possibility of introducing a new TL dosimeter for environmental and personnel monitoring.

In this way, pellets of $\beta$-CaSiO$_3$ is a good candidate to be used in environmental and personnel dosimetry using the method developed by S. Morato and collaborators [198].
8.8 Pellets of $\beta$-CaSiO$_3$ for proton and carbon ion beam radiation

Pellets of $\beta$-CaSiO$_3$ (TL calcium silicate detectors) were irradiated at 160 MeV proton beam and 290 MeV/n carbon ion beam from an upper synchrotron of HIMAC (Heavy Ion Medical Accelerator in Chiba, Japan) at NIRS (National Institute of Radiological Sciences) as earlier mentioned in section 7.1.9.

(1) Proton beam irradiation

TL glow curves of $\beta$-CaSiO$_3$ pellets irradiated with proton beam with doses from 5 mGy to 1 Gy is shown in Figure 8.43. Glow curves in Figure 8.43 present one well-defined peak at about 165-170 °C, and two possible peaks at about 270 °C and 315 - 320 °C similarly to that of the gamma irradiation shown in Figure 8.36.

![Figure 8.43: TL glow curves of $\beta$-CaSiO$_3$ pellets irradiated at 160 MeV proton beam with dose from 5 mGy to 1 Gy. A heating rate of 4 °C/s was used.](image)

Figure 8.44 shows the maximum TL response of the TL peak at about 270 °C of the TL glow curves shown in Figure 8.43 for doses ranging from 5 mGy to 1 Gy in comparison with the dose-response curve for gamma irradiation shown in Figure 8.39 (gamma dose from 1 mG to 5 Gy). The dose-response curve for the case of proton
irradiation is obtained with previous thermal annealing of 210 °C for 10 s in the same way as was performed for gamma irradiation case.

Analyzing the dose-response curves with log axes in the same scale, as shown in Figure 8.44. It can be observed that the TL response of the TL peak at 270 °C has a linear behavior from 5 mGy to 1 Gy, with a calibration equation, equals to \( I_{\text{TL}} = 0.344 \cdot \text{Dose} \).

As observed in Figure 8.44 the slope of the dose-response curve for proton irradiation is slightly less than the dose-response curve for gamma irradiation. It is because the deposition of dose during proton irradiation depends on the linear transference energy (LET) of proton in the material.

(1) Carbon beam irradiation

TL glow curves of \( \beta \)-CaSiO\(_3\) pellets irradiated with carbon beam with doses from 1 mGy to 1 Gy is shown in Figure 8.45.
Glow curves in Figure 8.45 present one well-defined peak at about 165-170 °C, and two possible peaks at about 270 °C and 322 °C similarly to that of the gamma irradiation shown in Figure 8.36.

Figure 8.46 shows the maximum TL response of the TL peak at about 270 °C of the TL glow curves shown in Figure 8.45 for doses ranging from 1 mGy to 10 Gy in comparison with the dose-response curve for gamma irradiation shown in Figure 8.39. The dose-response curve for the case of carbon irradiation is obtained with previous thermal annealing of 210 °C for 10 s in the same way as was performed for gamma irradiation case.

Analyzing the dose-response curves with log axes in the same scale, as shown in Figure 8.46. It can be observed that the TL response of peak at 270 °C peak has a linear behavior from 1 mGy to 10 Gy, with a calibration equation equals to $I_{TL} = 0.229\cdot$Dose.

As observed in Figure 8.46 the slope of the dose-response curve for carbon irradiation is less than the dose-response curve for gamma irradiation. It is because the deposition of dose during carbon irradiation depends on the linear transference energy (LET) of carbon in the material.
Figure 8.46: TL intensity behavior of the 270 °C peak of pellets of $\beta$-CaSiO$_3$ as a function of (a) carbon beam radiation doses (red) from 1 mGy to 10 Gy; and (b) gamma radiation doses (black) from 1 mGy to 5 Gy. The dashed line indicates linearity.

8.8.1 Challenge: application in radiotherapy

As mentioned in subsection 2.7.2, in the last years, increased demand for dosimetry of charged particle beams has taken the interest of investigators due to its utility in cancer diagnosis and therapy. Heavy charged particles, such as carbon ions and proton, ensure a well-defined penetration at the location of interest, in treatment inside the body, displaying a minimum scattering and stiffer particle trajectories, low straggling effects, and sharper field edges [77, 78].

In this section, we can observe that after proton beam irradiation on the $\beta$-CaSiO$_3$ pellets are sensitive to proton radiation in the range of 5 mGy to 1 Gy. The dose-response curve, in this case, displays a linear behavior using the dosimetric peak at 270 °C. Additionally, we can observe that the $\beta$-CaSiO$_3$ pellets are sensitive to carbon radiation in the range of 1 mGy to 10 Gy. The dose-response curve, in this case, displays a linear behavior using the dosimetric peak at 270 °C.
In this way, $\beta$-CaSiO$_3$ is a good candidate to be used in accelerated proton and carbon beam dosimetry. It will be important to perform an additional study to support this result. For this reason, an analytical study of accelerated ions interaction on $\beta$-CaSiO$_3$ pellets will be proposed as a part of future works.
8.9 Application: detection of Tc-99m source using CaSiO$_3$ pellets.

As mentioned in subsection 7.1.10, pellets of $\beta$-CaSiO$_3$ have been produced for application in nuclear medicine, that is, in the detection of a solution of Technetium-99m (Tc-99m) using $\beta$-CaSiO$_3$ pellets through obtaining images of TL intensities. The tracer used in this work is the technetium-99m, this is the most common medical radioisotope used in nuclear medicine because of its optimal nuclear properties of a short half-life and a gamma photon emission of 140 keV.

Towards a better understanding of this experiment, we will show a design of the top view of the element disposition as shown in Figure 8.47. The rectangular phantom, with a dimension of 10x10x20 cm$^3$ was filled with water simulating the human body. The syringes with the technetium solution are immersed in the phantom with water simulating little sources. Matrix with pellets is placed on one side of the rectangular phantom and in front of the syringes with the Tc-99m solution.

Figure 8.47(a) shows the design of the experiment for the case of two syringes with a solution of Tc-99m whose activities are 32.0 and 15.5 mCi respectively; and a matrix of 5x10 pellets. In this case, the exposure time of the CaSiO$_3$ pellets to the Tc-99m solution was approximately 20 minutes.

Figure 8.47(b) shows the design of the experiment for the case of one syringe with a solution of Tc-99m whose activity is 29.9 mCi; and a matrix of 6x7 pellets. In this case, the exposure time of the CaSiO$_3$ pellets to the Tc-99m solution was approximately 12 minutes.

As shown in Figure 8.47, the solution of Tc-99m emits gamma radiation which passes through the water and hits the $\beta$-CaSiO$_3$ detectors leaving a deposited dose.

The deposited dose on the $\beta$-CaSiO$_3$ pellets will depend on the distance between the source (solution of Tc-99m) and the detector, and the time of irradiation. For the
same time of irradiation, detectors near to the source will be hits for more photons dose than these detectors far to the detector and then accumulate a more absorbed.

After irradiation of the $\beta$-CaSiO$_3$ in pellets, TL measurements were performed in our laboratory. For the case of the matrix with 5x10 TLDs, the TL reading of pellets resulted in an image showing two sources of Tc-99m with TL intensities proportional to the activity of Tc used as shown in Figure 8.49.

In the same way, for the case of the matrix with 6x7 TLDs, the TL reading of pellets resulted in an image showing the one source of Tc-99m with TL intensities proportional to the activity of Tc used as shown in Figure 8.48.
Figure 8.48: Image of the TL reading of pellets of $\beta$-CaSiO$_3$ showing two sources of 32.0 mCi and 15.5 mCi Tc-99m.

Figure 8.49: Image of the TL reading of pellets of $\beta$-CaSiO$_3$ showing the source of 29.9 mCi Tc-99m.
8.9.1 Challenge: application in nuclear medicine

This experiment simulates an in vivo experiment where the tumor localization is carried out using radiotracers for tumor imaging [199].

As can be observed in Figures 8.48 and 8.49 using our laboratory made TL dosimeters in pellets of 6 mm diameter by 1 mm thick, we can produce images, not exactly equal to that produced by scintigraphic equipment, but still usable for diagnosis. We are planning to produce pellets of 4 mm diameter and 1 mm thickness so that a better image can be obtained. Additionally, for future experiments pellets will be placed on a flexible acrylic stand and each pellet closer to each other for future experiments as shown in figure 8.50.

In Brazil, any place far from large cities like São Paulo, Rio de Janeiro, Belo Horizonte, Ribeirão Preto, etc., where a nuclear medicine center exists, population, especially poor ones, has no access to such medical facility. Our idea is to use our detector to substitute any sophisticated system. Tc-99m or old radioactive Na can be provided without difficulty, therefore, pseudo-nuclear medicine can be done at any place far from big city.
Chapter 9

Conclusions

9.1 Diffraction patterns of synthetic materials

- In this work polycrystals of CaSiO$_3$ in two phases ($\alpha$- and $\beta$-) and those doped with B, Dy, Eu, and Cd were produced by the devitrification method.

- The diffractograms of $\alpha$-CaSiO$_3$ was identified as belonging to wollastonite-2M (00-043-1460 - Semiquant. 94 %) and Cristobalite low (01-076-0937 - Semiquant. 6 %), respectively, using the X’Pert HighScore program.

- The diffractogram of $\beta$-CaSiO$_3$ was identified as belonging to Pseudowollastonite 01-074-0874 - Semiquant. 96 %) and Cristobalite low (01-071-0785 - Semiquant. 4 %), respectively, using the X’Pert HighScore program.

- The diffractograms of the Dy, B, Cd, and Eu-doped CaSiO$_3$ polycrystals were identified as belonging to Pseudowollastonite and Cristobalite low, respectively, using the X’Pert HighScore program.

- For Dy-doped CaSiO$_3$ was identified as belonging to Pseudowollastonite (01-074-0874 - Semiquant. 90 %) and Cristobalite low (01-071-0785 - Semiquant. 10 %), respectively. B-doped CaSiO$_3$ was identified as belonging to Pseudowollastonite (01-074-0874 - Semiquant. 96 %) and Cristobalite low (01-071-0785 - Semiquant.
4 %), respectively. Cd-doped CaSiO$_3$ was identified as belonging to Pseudowollastonite (01-074-0874 - Semiquant. 94 %) and Cristobalite low (01-071-0785 - Semiquant. 6 %), respectively. Finally, Cd-doped CaSiO$_3$ was identified as belonging to Pseudowollastonite (01-074-0874 - Semiquant. 97 %) and Cristobalite low (01-071-0785 - Semiquant. 3 %), respectively.

9.2 Gamma radiation dosimetry

- $\alpha$-CaSiO$_3$ polycrystal obtained in this work has shown to be a good sensitive detector for gamma radiation displaying TL glow curves with two principal TL peak at about 120 and a prominent dosimetric peak at 270 °C.

- The dose-response curve for the $\alpha$-CaSiO$_3$ polycrystal using the prominent TL peak at 270 °C has shown a linear behavior for doses from mGy to 5 Gy, then this curve turns supralinear up to about 7 kGy and saturating beyond. In this way, this detector can be used in the range of mGy to 7kGy.

- One advantage of $\alpha$-CaSiO$_3$ detectors is that although it has presented two TL peaks in the glow curve, the peak at about 250 °C is dominating, such that the other peak can be ignored.

- Thermal fading for $\alpha$-CaSiO$_3$ have shown an unstable low-temperature peak at 120 °C but stable high-temperature peak at 270 °C which decay about 20 % in the first 2 to 3 hours, but after that, there is no decay up to 32 days.

- TL glow curves of $\alpha$-CaSiO$_3$ show TL experimental peaks at 125 and 272 °C and six computed TL peaks separated using different orders of kinetics at about 139, 169, 210, 252, 271, and 329 °C. The FOM obtained for the TL glow curve fitting is about 2.5%.

- $\beta$-CaSiO$_3$ polycrystal obtained in this work exhibits TL peaks at 124, 250, and 306 °C. This material shows a broad range of dosimetric capability to low gamma
radiation dose of the order of 30 mGy and to high doses in the region of kGy using the dosimetric TL peaks at 250 and 306 °C.

- Thermal fading for $\beta$-CaSiO$_3$ have shown an unstable low-temperature peak at 117 °C but stable high-temperature peaks at 252 °C and 306 °C which decay about 7% in the first 48 hours, but after that, there is no decay up to 32 days.

- TL glow curves of $\beta$-CaSiO$_3$ present TL experimental peaks at 122, 252 and 306 °C and seven computed TL peaks separated using different orders of kinetics at about 121, 133, 147, 201, 247, 306 and 337 °C. The FOM obtained for the TL glow curve fitting is about 1.3%.

- The high luminescent sensitivity showing by $\alpha$-CaSiO$_3$ and $\beta$-CaSiO$_3$ polycrystals to gamma radiation dose (mGy - kGy) makes it an interesting material for applications in radiation dosimetry.

- Polycrystals of CaSiO$_3$ doped with B, Cd, Dy, and Eu have been irradiated for high gamma radiation doses (from 0.5 to 50 kGy) displaying an increasing behavior between 0.5-3 kGy and then go into saturation from 7 kGy to 50 kGy.

- No improvement was found for doped polycrystals detectors in comparison to that of undoped CaSiO$_3$ regarding the sensitivity to gamma radiation.

- Doped with B-, Cd-, and Dy-CaSiO$_3$ presented a similar behavior as the undoped one. However, doping with Eu, the crystal presented a prominent third peak and weak first and second peak. One possibility, to be confirmed, as to whether Eu$^{3+}$ substitutes for silicon ion in [SiO$_4$] and transforms into [EuO$_4$/h] center, such that the main electron-hole recombination occurs around 342 - 370 °C.

- TL emission spectra of $\beta$-CaSiO$_3$ present a very intense 370 nm band and a weak 520 nm band. This result shows that $\beta$-CaSiO$_3$ polycrystal has in principle two recombination centers that participate in the TL process. The electron transition responsible for these emission lines will be part of a study in the near future.
• TL emission spectrum of the polycrystal CaSiO$_3$:Eu presented one prominent broad band centered at 420 nm and another band centered at 580 nm. This means that one should expect two recombination centers that participate in the TL process.

• The emission bands for the case of CaSiO$_3$:Eu are higher than the emission bands of the $\beta$-CaSiO$_3$. It could be produced by the Eu dopant on the crystal structure. The electron transition responsible for these emission lines will be part of a study in the near future.

9.3 Neutron irradiation at IPEN’s IEA-R1 reactor

• Polycrystals of $\alpha$-CaSiO$_3$; and B-, Cd-, Dy-, and Eu-doped CaSiO$_3$ were exposed to reactor radiation at the position 13B, shelf 1 and 5.

• After reactor exposure for different thermal neutron fluences, TL glow curves for $\alpha$-CaSiO$_3$ display a prominent TL peak at 235-2345 °C.

• After different thermal neutron irradiation, TL glow curves of CaSiO$_3$ doped with B, Cd and Dy display TL peaks at 120-125 °C, 235-2345 °C and 375-380 °C, 235-2345 °C, being the second one the prominent. The doping induces smaller peaks around 120 - 125 °C and another one around 375 - 380 °C.

• The fluence-response curves for the doped samples show an oscillatory behavior using the maximum TL peak at 235-2345 °C. These samples cannot be used for thermal neutron detection due to their oscillatory behavior in the fluence-response curve.

• the fluence-response curve for $\alpha$-CaSiO$_3$, unlike the others, has a growing behavior using the maximum TL intensity at 235-2345 °C.

• After thermal neutron irradiation, the Eu-doped calcium silicate detector presented also three peaks but at 150, 240 and 375-380 °C, the last one being the
prominent one, which is essentially the same as that of Eu-doped CaSiO$_3$ irradiated with gamma radiation.

- A comparison between the responses curves of the $\alpha$-CaSiO$_3$ after gamma and reactor irradiation show that these curves have similar behavior for thermal neutron fluences lower than $2.91 \times 10^{14}$ n/cm$^2$ and for gamma dose irradiation lower than 4 kGy.

- For thermal neutron fluences higher than $2.91 \times 10^{14}$ n/cm$^2$ the TL response is lesser than TL responses for high-gamma radiation (higher than 4 kGy). This may be due to the radiation damage effect on the sample when it is exposed to ultra-high neutron radiation, but this effect requires supplementary studies.

- The gamma dose absorbed by the CaSiO$_3$ after neutron exposure was calculated by extrapolation of the TL response lower than $2.91 \times 10^{14}$ n/cm$^2$ of thermal neutron fluence and extrapolation of TL response lower than 4 kGy of gamma radiation dose.

- It was found that the amount of gamma absorbed dose by the material after the neutrons flux ceases at the point of irradiation 13 B (shelf 1) is about 730 Gy.

- The total released energy during the interaction of the thermal neutron on the $\alpha$-CaSiO$_3$ sample in the position of irradiation was calculated ranging from about $2.62 \times 10^{11}$ to $1.33 \times 10^{14}$ MeV. Additionally, the Monte Carlo calculation of the deposited dose for all neutrons interaction varies from 42 Gy for a thermal fluence of $5.82 \times 10^{13}$ n/cm$^2$ to 21 kGy for a thermal neutron fluence of $2.97 \times 10^{16}$ n/cm$^2$.

### 9.4 Center responsible for the TL peaks of CaSiO$_3$ estimated by EPR analysis

- Three defect centers are observed in $\beta$-CaSiO$_3$ and these are tentatively attributed to an O$^-$ ion, F$^+$-center, and Ti$^{3+}$ center. O$^-$ ion and F$^+$-center seem
to be the recombination centers associated with 124 °C, 147 °C and 306 °C TL peaks. Ti$^{3+}$ center is related to 147 °C and also possibly with the 124 °C TL peak.

- Two defect centers are observed in $\alpha$-CaSiO$_3$ and these are tentatively attributed to an O$^{-}$ ion and Ti$^{3+}$ center. F$^{+}$ center line is not seen at room temperature because its low intensity is overlapped by the EPR line of O$^{-}$ ion. However, with the diminishing intensity of O$^{-}$ ion at higher annealing temperatures, F$^{+}$-center line is seen. O$^{-}$ ion and F$^{+}$-center seem to be the recombination centers associated with 139 °C, 169 °C and 329 °C TL peaks. Ti$^{3+}$ center is related to 169 °C and also possibly with the 139 °C TL peak.

9.5 Pellets of synthetic $\beta$-CaSiO$_3$ for gamma, proton and carbon beam radiation

- Pellets of $\beta$-CaSiO$_3$ were calibrated with gamma-doses from Cs-137 and Co-60. It can be observed that the TL response of peak at 265 °C (after thermal annealing of 210°Cx10s) has a linear behavior from 1 mGy to 5 Gy, with a calibration equation equals to $I_{TL} = 0.375 \cdot \text{Dose}$.

- The minimum detectable dose (MDD) for the $\beta$-CaSiO$_3$ detector is $\sim 60 \mu$Gy.

- The energy dependence of the $\beta$-CaSiO$_3$ pellets shows that between 22 keV and 150 keV the relative TL intensity decrease, after that, it remains constant with the increase in energy of the photon. In all cases, the same irradiation dose was maintained. The effective atomic number of the $\beta$-CaSiO$_3$ found in this work is $Z_{eff}(\text{CaSiO}_3) = 15.72$.

- For energies higher than 150 keV, $\beta$-CaSiO$_3$ there is no energy dependence. That is $\beta$-CaSiO$_3$ could be used as a TL dosimeter in radiation dosimetry for energies higher than 150 keV.
• The study of the dose rate dependence of the $\beta$-CaSiO$_3$ detector using different rates dose from a Cs-137 source has shown no discernible dose-rate effect on this material in the range from 8.26 to 33.0 mGy/h.

• The dose readout in Harshaw TL reader presented a good agreement with doses found using ion chamber in the case of proton beams and slightly less in the case of carbon beam due to the LET dependency.

• Pellets of $\beta$-CaSiO$_3$ have shown a linear dose-response curve for low doses from 1 mGy to 5 Gy after gamma, proton, and carbon beam irradiation.

• For detection of radiation doses involving accelerated proton and carbon beam, a nuclear reaction and coulomb barrier effect are involved. The effect of such nuclear or Coulomb interaction of the accelerated particles on the sample is under study.

9.6 Application: detection of Tc-99m source using $\beta$-CaSiO$_3$ pellets.

• The detection of Tc-99m sources using $\beta$-CaSiO$_3$ pellets was performed.

• The image was obtained using the TL intensities read in Harshaw-4500 after exposure of $\beta$-CaSiO$_3$ detector to Tc-99m for about 15 minutes.

• The TL reading of these pellets resulted in an image showing the source of Tc-99m with TL intensities proportional to the activity of Tc used and the distance between the source and detectors.

• The behavior of the TL glow curves of the synthetic $\beta$-CaSiO$_3$ in pellets at low-dose makes it a strong candidate for use in medical applications especially for detection of radiation sources through images.
• Matrices of $\beta$-CaSiO$_3$ pellets can be used in actual Nuclear Medicine Center, especially, in any place far from a large city where the population has no access to a sophisticated medical facility.

9.7 Challenges for the future:

(a) Pellets of $\beta$-CaSiO$_3$ could be used in environmental and personnel dosimetry using the method developed by S. Morato and collaborators [198] where regardless of its effective Z value a suitable combination of filters can give an almost energy independent response and still retain the advantage of the higher sensitivity.

(b) $\beta$-CaSiO$_3$ could be used as a TL dosimeter in conventional- and FLASH- radiotherapy but supplementary studies of the TL dependence for a higher dose rate than 33.0 mGy/h will be necessary.

(c) $\beta$-CaSiO$_3$ is a good candidate to be used in accelerated proton (160 MeV) and carbon (290 MeV/n) beam dosimetry. It will be important to perform an additional study to support this result. For this reason, an analytical study of accelerated ions interaction on $\beta$-CaSiO$_3$ pellets will be proposed as a part of future works.

(d) In Brazil, any place far from large cities like São Paulo, Rio de Janeiro, Belo Horizonte, Ribeirão Preto, etc., population, especially poor ones, has no access to such medical facility. Our idea is to use our detector to substitute any sophisticated system. Tc-99m or old radioactive Na can be provided without difficulty, therefore, pseudo-nuclear medicine can be done at any place far from a big city.
Chapter 10

Suggestion for future work

• The study of the effect by adding 1000 ppm Eu as an impurity on CaSiO$_3$ polycrystal by means of EPR measurements for different dose irradiation and different annealing temperatures. Under heavy irradiation, it is expected to identify the defects centers responsible for the TL peaks, especially for the prominent peak at about 340 - 370 °C. The annealing procedures can establish a connection of these defects to TL peak temperatures.

• The study of CaSiO$_3$ polycrystalline doped with different quantities in ppm of Eu as a neutron detector keeping in mind its high cross-section for thermal neutron capture.

• Supplementary study in order to know the damage produced in the polycrystal after very-high neutron irradiation.

• Analytical studies of the interaction of accelerated proton and carbon ion beam on the polycrystal of CaSiO$_3$ considering the nuclear reaction and coulomb barrier effect.

• The production of smaller CaSiO$_3$ pellets of 4 mm diameter and 1 mm thickness size and in vivo experiments at INCOR-USP.
Appendix A

Part of the work presented in this thesis was published in two papers in Journal of Luminescence, entitled “Synthetic polycrystals of CaSiO$_3$ un-doped and Cd, B, Dy, Eu-doped for gamma and neutron detection” and “Thermoluminescence and defect centers in β-CaSiO$_3$”. In the same way, another part of the work was submitted in Radiation Physics and Chemistry Journal as “Calculated and experimental response of calcium silicate polycrystalline to high and very-high neutron doses”. This is currently under review.
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