Optical characterization of ion-doped crystalline and glassy matrices operating under hostile environmental conditions

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Abstract. The aim of this work is to give an overall picture of the activity on gamma radiation effects in the field of scintillators (crystals, glasses) with specific mention to the role of ions doped in different crystalline and glassy matrices. Interesting results were obtained in terms of radiation hardness improvement and of physical-chemical properties modification as a function of the nature of dopant (i.e. rare earth as well as metallic ions) and of the scintillating host glassy and glass-ceramic matrix (silicate, phosphate, borate, oxyfluoride and mixed oxides glasses). The research activities were carried out at the \( ^{60} \)Co gamma Calliope plant, a pool-type irradiation facility located at the Research Centre ENEA-Casaccia (Rome). Since the eighties, the Calliope facility is deeply involved in radiation processing research on materials and on devices to be used in hostile radiation environment such as nuclear plants, aerospace and High Energy Physics experiments, in the framework of international projects and collaboration with industries and research institutions.

1. Scintillating crystals and glasses

Several experimental studies worldwide, are currently in progress to try and determine the effect of doping ions in both crystalline and glassy matrices. The choice of dopants needs to be selected carefully, as each dopant retains its intrinsic optical, luminescent and radiation resistant properties, when incorporated into the host matrices. This makes the doped-material suitable for a wide range of interesting and different applications.

A good scintillator is a material able to convert as large a fraction as possible of the incident radiation energy in the visible range to prompt fluorescence (occurring in times of the order of about \( 10^{-7} \) s), minimising the generally undesirable contribution for phosphorescence (occurring in times of the order of \( >> 10^{-7} \) s) [1][2][3].

Scintillation detector consists of a scintillator (phosphor) material followed by an optional relay element and a photodetector. Wide band-gap materials are employed to convert X-rays to UV/visible photons. It is challenging to find dense, fast and radiation hard scintillator useful in high energy physics, astrophysics, medicine and other applications [4][5][6]. Currently, various scintillators such as NaI:Tl, CsI:Tl, BGO, BaF\(_2\), PbWO\(_4\), YAG, LuAG are used for many applications in the field of research, medicine and industry [3] [7] [8] [9].

The entire scintillation conversion can be divided into three processes: conversion, transport and luminescence. Conversion process involves an interaction of high-energy photon with the material lattice: if the radiation energy is around 1 MeV, the photoelectric and Compton scattering effects
mainly occur [10]. As a result, many electron-hole pairs are created and thermalized in the conduction and valence bands. During the transport stage, these charge carriers migrate through the lattice. Their capture at trapping levels within the material forbidden gap delays migration and energy losses due to non-radiative recombination, which may occur. Finally, the luminescence stage involves radiative recombination of the electrons and holes trapped at the luminescence centre. The overall scintillation process efficiency $\eta$ (number of light photons emitted/MeV), is the product of three factors, $\beta$, $S$ and $Q$, related to the above described processes, respectively. The first ($\beta$) indicates the fraction of electrons-holes pairs actually produced, during the energy absorption, relative to the total that could be formed if there were no other losses. The factor $S$ indicates the fraction of the total electron-hole pairs that is transferred to the luminescence centres. The quantum efficiency $Q$ represents the fraction of excited centres that actually re-emit scintillation photons (figure 1) [11] [12].

Variations in the lattice (like defects and impurities) create local electronic energy levels in the energy gap of the scintillating matrix. If these levels are unoccupied, holes and electrons moving in the conduction band may be trapped by metastable centres, like luminescence and quenching centres and traps (figure 1). In the luminescence centres the transition to the ground state is accompanied by photon emission, while in the quenching centres radiationless thermal dissipation of excitation energy may occur. Finally, traps have metastable levels from which the electrons may subsequently return to the conduction band by acquiring thermal energy from the lattice vibrations, or fall to the valence band by a radiationless transition.

Figure 1. Schematic representation of scintillation process.

In order to enhance the probability of visible photon emission during the de-excitation process, small amounts of impurities called “activators” (usually rare-earth ions) are commonly added to scintillators, dispersed into the melting during the crystal growth. Activators, with an energy gap lower than that of the hosting crystal, create special sites in the lattice, not only modifying the normal energy band structure of the pure crystal, but also improving the performance of the scintillating matrix due to the interaction with the radiation induced charged defects (e, h). The transition between the activator excited and ground states (around $10^{-7}$s) can occurs and the emission of a visible photon contributes to the scintillation process (figure 1). Increasing the ion dopant concentration results in a decrease of radioinduced absorption and of the light yield. For this reason, to improve the efficiency of a scintillator, a suitable dopant content must be chosen, being a compromise between the value of light yield and the resistance of the material to radiation.

Among the characteristics of scintillating materials, their radiation resistance is particularly important because high energy physics applications create rather severe environments, with high level of radiation as a result of particle collision. The radiation damage in solid inorganic matrices (ionic crystals, glasses, and various insulators and dielectric materials) generally results in a disruption of their crystalline structure. Any deviation from a perfect crystal lattice such as vacancies, interstitials, impurity atoms, thermal spikes and ionization effects (originated by the passage of charged particles or gamma rays through the material) can be considered as defects [13].

In case of gamma radiation, the initial stage of radiation induced damage is essentially a three-step process consisting of: i) creation of hot electrons and holes by the interaction with high energy photons; ii) their separation during subsequent cooling down and diffusion processes; iii) separate localization of both types of free carrier at suitable lattice sites (traps). Such sites might arise as a
result of lattice distortions (dislocations, domain interfaces, etc.) or point defects (vacancies, impurity ions) or combinations of both of them. Colour centres might be created during phase iii). The lack of a negative ion in the lattice determines a local excess of positive charge which can act as a trap for electrons (F-centre). Electrons in colour centres have energetic levels different from those in the crystal and they can re-absorb the light emitted by scintillator in the visible region, reducing the scintillator performance. Radiation induced charge compensation could occur by oxidation and/or reduction reactions.

Scintillating materials can be investigated by steady state and time dependent characterizations. The former techniques include luminescence and transmission measurements, while the latter decay kinetics and scintillator light yield [11].

To investigate the damage caused by irradiation, the reduction of scintillator light output and optical transmission of the material are usually measured. The former is defined as the loss of the amount of light collected, after irradiation, by the photomultiplier when the scintillating material is exposed to incident radiation. For each type of scintillator it is necessary to measure, at different absorbed doses, the total radiation damage to the light output. The study of the radiation induced defects that involves modification of the optical transmission are usually evaluated by the radiation induced absorption coefficient $\mu$, proportional to the ratio of the transmission before and after irradiation and normalized to the sample thickness.

2. Research and qualification activities at Calliope facility

Nowadays, ionizing radiation is being employed in a wide number of applications of great importance within both the scientific and industrial communities.

The Calliope gamma irradiation facility, located at the Research Centre ENEA-Casaccia (Rome), is deeply involved in qualification and research activities, in the framework of international projects and collaborations with industries and research institutions [14].

Many research activities are focused on the investigation of gamma irradiation effects on chemical and physical properties of different materials, such as radiation detectors, scintillating crystals and glasses, polymers, for several applications (nuclear plants, aerospace, High Energy Physics experiments) [3] [8] [9] [15] [16] [17] [18] [19] [20]. Material characterization and biological research has been carried out on cultural heritage archives and artifacts [21] [22].

Qualifications tests are mainly performed on electronic components and devices for application in hostile environments such as nuclear plant and aerospace and on concrete matrices for nuclear waste disposal and storage. As it will be shown, very special care is devoted to the qualification of electronic devices, which have to be tested according to MIL-STD-883 and/or ESA/SCC BASIC Specifications No.22900 procedures [23] [24] [25] [26] [27].

The Calliope facility is a pool-type irradiation facility equipped with a $^{60}\text{Co}$ $\gamma$ source in a high volume (7x6x3.9 m$^3$) shielded cell. The present source has cylindrical geometry with the 48 source rods arranged in two concentric cylinders of about 20 cm outer radius and 26 cm height. The emitted radiation consists of two $\gamma$ photons of 1.173 and 1.332 MeV emitted in coincidence, with a mean photon energy of 1.25 MeV. The maximum licensed activity for this plant is $3.7 \times 10^{15}$ Bq (100 kCi).

Four kinds of dosimeters are used to determine the dose rate at which to irradiate the sample: Fricke solution, Red Perspex, alanine-ESR and TLD dosimeters [28].

An overview of some activities carried on at the Calliope facility related to doping and gamma radiation effects on crystal and glassy scintillators will be given in the following.

3. Scintillating crystals

3.1 Lead tungstate

Recently, PbWO$_4$ (PWO) has been chosen as a scintillating medium [7]. Position and shape of the peaks in scintillation spectra, decay kinetics, light yield and radiation resistance are the important parameters for any scintillation material. In as-grown PWO crystals, the emission spectrum is rather
complicated and both regular lattice (420 nm “blue” emission) and defect-related (500 nm “green” emission) centres can contribute to the emission light [29] [30] [31] [32]. Under irradiation, a band at around 400 nm, responsible for the re-absorption of the scintillating light, is created. Together, two electron centres related to the radiation induced F’ and F-centres, absorb scintillating light at 540 and 720 nm (figure 2). Considerable improvement of radiation resistance was found by doping PWO crystals with large and stable trivalent ions, such as La$^{3+}$, Lu$^{3+}$, Gd$^{3+}$ and Y$^{3+}$ [33] [34] [35] [36], as evident by transmittance and radiation induced absorption coefficient curves reported in figure 2 for La$^{3+}$. These positive effect can be explained considering that the Coulomb charge excess of trivalent ions at divalent lattice sites considerably reduces the possibility of temporary or stable localization of holes created during irradiation.

![Figure 2](image_url)

Figure 2. Transmittance curves of undoped and La$^{3+}$-doped PWO crystals. Inset: radiation induced absorption coefficient $\mu$ trends for the same samples [34].

Gadolinium doping appeared particularly interesting due to an additional effect, that consists in the improvement of the energy transfer efficiency in crystalline and glassy matrices. This sensitization mechanism was developed in some scintillating materials, with the addition of a high concentration (30%) of trivalent gadolinium ions. Gd$^{3+}$ enables an efficient energy transfer to luminescence centres giving a sensible increase of the light emission, as confirmed by luminescence and decay kinetic measurements [3] [37] [38].

3.2 Cerium fluoride
Cerium fluoride (CeF$_3$) crystal was studied in the past to investigate its potential for fast scintillation and radiation hardness but is experiencing a rekindled interest as a scintillator for calorimetry at the LHC at CERN. For this reason, extensive researches were carried out to optimize the growth and post-preparation parameters and to obtain high reproducibility in term of optical and scintillation quality.

Pure CeF$_3$ crystals show emission peaks at 286 nm, 300 nm and 340 nm [7] [39]. Its optical and luminescence properties could be modified as a function of the amount of divalent ions (e.g. Ba$^{2+}$) added to the matrix, leading to a slight increase of the transmission band edge (figure 3(a)) and a shifting of the maximum of the emission peak to around 380 nm.

![Figure 3](image_url)

Figure 3. (a) Transmittance curves of undoped and Ba$^{2+}$-doped CeF$_3$ crystals annealed and not annealed after growth; (b) $\mu$ trends at the emission peak wavelength (340 nm) for the undoped samples annealed and not annealed after growth.

The results obtained after gamma irradiation on the same samples (data here not reported) show that the crystal doped with 0.5% Ba is characterized by the highest radiation hardness and stability.
Thermal treatment performed after the crystals growth limits also the radiation damage, as shown in figure 3(b) for undoped samples at the emission wavelength of 340 nm [40].

4. Glassy matrices

Over the last decade, glassy matrices have been of great interest in different technological applications. Due to their low cost, ease of production, chemical stability and light weight, these systems have been commonly used (in bulk or fibers form) as low and middle energy radiation detectors. Nevertheless, significant drawbacks are their low light yield, due to a low transfer efficiency of excitation energy from the matrix to luminescence centres and their low radiation hardness. Both effects are due to the presence of many trapping sites in the glassy matrices, where charge carriers can be trapped, giving rise to a non-radiative recombination. To improve the energy transfer mechanism, the sensitization effect due to the trivalent gadolinium ion, discovered for crystals (e.g. PWO), is successfully performed, as confirmed by photoluminescence and decay kinetics measurements [41].

4.1 Ce$^{3+}$-doped heavy germanate glasses

Glass matrices with density higher than 5 g/cm$^3$ containing GeO$_2$, BaO, Gd$_2$O$_3$ and doped with 0.5% of CeO$_2$, were prepared by melting the glassy starting powder in air, inert atmosphere (N$_2$) and reducing atmosphere (N$_2$+graphite) [42]. The absorption edge of the glass melted in air is at longer wavelengths than that in reducing atmosphere: this behaviour can be explained because Ce$^{3+}$ ions are easily oxidised to Ce$^{4+}$ when exposed to air, causing the formation of broad absorption bands extending to the longer visible wavelength (figure 4) [43]. Ce$^{3+}$ ions significantly interact with the hosting matrix and exert the red-shift effect on the ultraviolet and visible absorption position due to the 4f-5d electronic transitions, as shown in figure 5. Unlike exhibiting the monotonous deterioration effect on the glass matrix, radiation plays the radiation protection role on Ce$^{3+}$-doped glasses, depending on the glass melting atmosphere and on the radiation dose: this phenomenon is explained by the radiation induced reducing and oxidising mechanism due to the ability of Ce$^{3+}$ and/or Ce$^{4+}$ ions to capture both radiolytic holes and electrons [44]. The observed radiation induced effects seem to be relevant to an optimal radiation dose beyond which opposite influences occur. This is most likely associated with the double roles that radiation plays on glasses: when a limited radiation dose is applied, reducing and/or oxidising effects on glasses are dominant; as the radiation dose increases, concentration of radiation induced colour centres becomes higher and it finally exceeds what cerium ions can suppress. As a result, the radiation damage increases [45] [46].

![Figure 4. Transmittance curves of germanate glasses melted in different atmospheric conditions [43].](image1)

![Figure 5. Transmittance curves of germanate glasses before and after gamma irradiation of undoped (inset) and Ce$^{3+}$-doped glasses [44].](image2)

4.2 Cerium and terbium doped silicate and phosphate glasses

Ce$^{3+}$ ion is widely used as an activator in scintillating crystalline and glassy matrices. Depending on the hosting glass composition, its emission properties can vary. For example, cerium doping gives rise to a fast luminescence, with a typical decay time of about 20 - 50 ns, peaked at around 410 nm in silicate glasses and at around 350 nm in phosphate matrices [41] [47] [48] [49]. Considering silicate
glasses, the increase of cerium doping (from 2% to 6%) induce a nearly negligible red-shift in the transmittance curves and very low modification after gamma irradiation up to 252 Gy in the range 360 - 470 nm (here not shown). The same matrix was also doped with 3% of Tb$^{3+}$ ions: in this case, evident modification of the sample is clear in terms of the transmittance, when compared to a broad absorption band up to 500 or 600 nm. The radiation induced absorption coefficient $\mu$ for Ce$^{3+}$ and Tb$^{3+}$-doped glasses monotonically decreases in the whole UV-VIS range and the cerium addition strongly improves the radiation hardness. This result is also confirmed comparing the $\mu$ value calculated at the emission wavelength correspondent to the single activator [49] [50] [51].

Similar investigation was carried out on Ce$^{3+}$ and Tb$^{3+}$ doped phosphate matrices containing 30 mol.% of Gd$^{3+}$. The comparison of the initial transmittance curves of phosphate glasses containing Ce$^{3+}$, shows a strong red-shift of the absorption band-edge with an increase of Ce$^{3+}$ concentration, ranging from 325 nm for 3% of Ce$^{3+}$ to 370 nm for 5% and 410 nm for 10% of Ce$^{3+}$. Such phenomenon limits the Ce$^{3+}$ concentration that can be introduced in the glass matrix (3 - 4 mol.%), because it gives rise to a re-absorption of Ce$^{3+}$ scintillating light (emitted at 350 nm), lowering the potential usage of these glasses as scintillating detectors. The transmittance curves before and after irradiation (10 Gy), in the case of cerium activated glasses show a slight transmittance decrease in the UV region of the spectrum, while an extended reduction from 250 to 550 nm of terbium is present. Finally, the comparison of $\mu$ coefficient for singly Gd$^{3+}$-doped and co-doped phosphate glasses with Ce$^{3+}$ and Tb$^{3+}$ shows that at the dopant proper emission wavelength the most radiation resistant sample is the terbium activated one (figure 6). In conclusion, these results indicate that doped-glasses radiation damage is strictly dependent on the matrices [48] [50] [51] [52].

![Figure 6](image_url)

**Figure 6.** Radiation induced absorption coefficient plots for singly Gd$^{3+}$-doped and co-doped phosphate glasses with Ce$^{3+}$ and Tb$^{3+}$ [50].

### 4.3 Mixed oxide glasses containing ZnO as emission centre

Glassy matrices containing zinc oxide are studied for their luminescence properties and for applications as scintillating materials [53]. Interesting results were obtained by adding a high concentration (around 60 mol%) of ZnO in borosilicate glasses, without deteriorating the glass-forming ability, and investigating the thermal treatment effects on the photoluminescence emission spectra [54]. Despite the high concentration of zinc oxide, XRD spectra (here not shown) show that only ZnO crystalline aggregates are formed avoiding the ZnO bulk phase [54]. This evidence is also confirmed by the excitation and emission spectra reported in figure 7(a). When excited at the wavelength $\lambda_{ex}=262$ nm, the glass samples show a broad emission band at around 396 nm, while the emission band of ZnO bulk (range 500 - 600 nm) is absent. The emission band position is related to trapped excitons localized at the ZnO aggregate interface with the glass host. Compared with the untreated sample, the emission intensity of the heated glasses is sensibly modified (figure 7(b)), giving the most enhanced results for the glass treated at 350°C. This behaviour is reasonably explained with an energy transfer from the host glassy matrix to the luminescence ZnO aggregates.

The gamma irradiation effect was also investigated in a ZnO-based silicate matrix. In this system, SiO$_2$ acts as the network formers, BaO as network modifier leading to the formation of non-bridging oxygens, and Al$_2$O$_3$ (if present) as donors and glass network intermediate, having a tendency to substitute Si$^{4+}$ with charge balance realized by Ba$^{2+}$ atoms [55]. The ability of Al$^{3+}$ ions dopant to increase the charged carrier concentration in the conduction band and broadening the band gap in the glassy matrix, is evident by the UV-shift of the cut-off wavelength in the transmission spectra. When
aluminium oxide modifies the glass network, the non-bridging oxygens, which are known to be responsible for the colour centre formation, are bonded again, strengthening the glass structure and reducing the concentration radiation induced defects precursors in the matrix. The latter effect sensibly improves the radiation resistance of the glasses, as evident by the radiation induced absorption coefficient trends, after irradiation up to 262 Gy. While the matrix without aluminium shows a monotonic decrease of $\mu$, the doped samples present a band peaked at around 380 nm.

**Figure 7.** (a) Excitation (I) and emission (II) spectra of ZnO-borosilicate glasses heated at 350°C [54]; (b) Emission spectra of as prepared and heated ZnO-borosilicate glasses [54].

The same SiO$_2$-ZnO-BaO glassy matrix was also modified by the addition of barium fluoride, to investigate the effect of p-type F$^-$ ions dopant on the luminescence and optical properties [53] [56] [57]. The BaF$_2$-free samples show an emission band centered at about 430 nm, as reported in figure 8. With the addition of F$^-$, the dominant emission band moves to shorter wavelengths at around 396 nm, approaching the excitonic peak emission of ZnO bulk (380 nm). A possible explanation is based on the possibility for F$^-$ to replace the O$^{2-}$ bonded to Zn$^{2+}$ or some non-bridging oxygen, introduced by BaF$_2$, forming positive charged centres that allow the glass emission intensity increase.

**Figure 8.** Emission spectra of SiO$_2$-ZnO-BaO (F1: 40SiO$_2$-30ZnO-30BaO; F2: 40SiO$_2$-35ZnO-25BaO) and SiO$_2$-ZnO-BaO-BaF$_2$: (F3: 40SiO$_2$-30ZnO-25BaO-5BaF$_2$; F4: 40SiO$_2$-30ZnO-20BaO-10BaF$_2$) glassy matrices [53].

5. Glass-Ceramics

Glass-ceramics are fine microstructured polycrystalline materials produced by heat treatment that induces a controlled crystallization (ceramization) of certain glass with specific composition. These materials are characterized by a high density (up to 99.5%) of small crystals embedded in a residual glassy phase. The starting glass (namely parent glass, formed by a standard glass-manufacturing process) and the final glass-ceramic do not present the same chemical composition and the ceramization process is usually rather critical to the attainment of acceptable and reproducible products. By designing the glass-ceramics composition, controlling the ceramization treatment and the resulting microstructure, an array of glass-ceramics materials with interesting and sometimes unusual combination of properties, are produced for several applications. Depending on their composition, glass-ceramics can combine a negative/zero/highly positive thermal expansion coefficient with optical transparency or opacity in the visible range, very high strength and toughness with translucency, chemical durability, biocompatibility and hardness for medical applications [58] [59]. Many glass-ceramics are also characterized by specific electric and magnetic features, low thermal conductivity, zero or very low porosity, thermal stability (400 - 1450°C) and mechanical properties [58] [60] [61].

The glass crystallization process, whose rate is temperature dependent, consists of reheating the parent glass above its transition temperature and occurs in two steps: a nucleation stage and a growth
stage. During nucleation, that may take several hours, an extremely high density \((10^{12} - 10^{15} \text{cm}^{-3})\) of small and stable crystalline phases nuclei are formed in preferred sites of the parent glass (interfaces within the parent glass or free surfaces). In most cases, nucleating agents (typically noble metals, fluorides, \(\text{ZrO}_2\), \(\text{Cr}_2\text{O}_3\), \(\text{Fe}_2\text{O}_3\), \(\text{TiO}_2\) or \(\text{P}_2\text{O}_5\)) are added to the parent glass composition to boost the nucleation process. The crystal-growth step involves the movement of atoms or molecules from the glass, across the glass-crystal interface, and into the crystals \([61] [62] [63]\). Several techniques allow the characterization of glass-ceramic materials. X-ray diffraction gives specific information regarding the crystallinity degree, the crystalline phases and sizes developed inside the glassy matrix and modified by heating. The distribution, composition and the dimension of the microcrystals are analyzed by the electron microscopy (SEM, TEM, EDX), while thermal analyses (DTA, DSC) allow us to determine the glass transition, crystallization and melting parameters as a function of the glassy system composition. Further characterization can be carried out by optical (UV-VIS, FTIR) and spectroscopic analyses (luminescence, ESR), physical measurements and mechanical tests.

An interesting investigation was carried out based on the results related to the \(\text{BaF}_2\) addition effect on the silicate glasses photoluminescence (previously described). A \(\text{SiO}_2\)-\(\text{ZnO}\)-\(\text{BaF}_2\) glassy matrix was studied as-prepared and after different heat treatments, with the aim to obtain the formation, inside the hosting matrix, of \(\text{ZnO}\) Quantum Dots (QDs). QDs consist of nanometer-sized particles and their electronic and optoelectronic properties can be tuned as a function of particle size and shape for a given composition. The emission peak of the parent glass, reported in figure 9(a), shows a maximum in the UV range at around 380 nm, when excited at 272 nm. If the sample is submitted to a different duration thermal treatment at \(580^\circ \text{C}\), the emission band shifts to longer wavelength, due to the increase of \(\text{ZnO}\) QDs size (figure 9(b)).

![Figure 9](image_url)  
**Figure 9.** Emission spectrum of \(\text{SiO}_2\)-\(\text{ZnO}\)-\(\text{BaF}_2\) parent glass: (a) as prepared; (b) after different thermal treatments \([56]\).

6. Conclusion
As discussed in this work, research activities performed on crystal and glassy matrices for hostile environments, such as nuclear plants, aerospace and High Energy Physics experiments, highlighted the importance of the choice of suitable doping ions to obtain specific optical and luminescence properties on materials. Radiation resistance improvement is also strictly dependent on the crystal and glassy hosting matrices composition.

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