LaAlO$_3$:Pr$^{3+}$ as photon radiotherapy dosimeter

A A Barrera-Angeles$^1$, M A Ugalde$^4$, D Nolasco$^1$, J G Gutiérrez-Márquez$^2$, A Morales-Hernández$^3$, J Zarate-Medina$^4$ and T Rivera-Montalvo$^1$

$^1$ CICATA-Legaria del IPN, 694 Av. Legaria, 11500 Ciudad de México, México
$^2$ CMN-Siglo XXI, 330 Av. Cuauhtemoc, 06720 Ciudad de México, México
$^3$ TNM-ITM, 1500 Av. Tecnológico, 58120, Morelia Mich. México
$^4$ IIMM-UMSNH, Edificio “U”, CU, 58060, Morelia Mich. México

E-mail: abalba1@hotmail.com

Abstract. The intention of radiotherapy is to control and cure tumor while avoiding late effects caused by radiation. High energy photon beam dose can be determined by different modalities. In this paper, dosimetric properties of praseodymium doped lanthanum aluminate exited by X-ray beams are reported. LaAlO$_3$:Pr$^{3+}$ powders samples were prepared using modified Pechinis’s method. The formations of the obtained samples were confirmed by an X-ray diffraction patterns. TL glow curve and dosimetric characteristics of LaAlO$_3$:Pr$^{3+}$ powder samples were investigated under X-ray irradiation effects. All TL measurements were made using an automated Harshaw TL reader 5500. TL glow curves were obtained using a constant heating rate 10 °C/s from room temperature up to 350°C in a nitrogen atmosphere. The dose response and minimum detectable dose (MDD) values of the samples were determined. Dosimetric characteristics of the samples were carefully analyzed. Experimental results of TL dosimetric characteristics of the powder samples appear to have potential application for high energy photon beam dose measurements.

1. Introduction
Thermoluminescence (TL) is the thermally stimulated emission of light from a semiconductor or insulator, following the previous absorption of energy from ionizing radiation such as X-rays, gamma rays, high energy electron beam, etc. Thermoluminescent materials exhibit differences in dose response between sparsely ionizing radiation (high energy photons like X-rays and gamma rays) [1]. Thermally stimulated luminescence or better known as thermoluminescence (TL) is one of the most used techniques extensively used for ionizing radiation dosimetry, which makes use of materials commonly divided in two groups (the first one includes tissue equivalent phosphors) which generally exhibit low sensitivity to ionizing radiation whereas the second one is formed by systems with high sensitivity but poor equivalence to organic tissue [2]. For many years the most commonly used phosphor was LiF detector doped with Mg and Ti. LiF has been used as quality assurance program dosimeter and other investigations have been reported some characteristics of TLDs irradiated with 6 MV X-ray beams [3, 4]. Other papers report experimental results of some phosphors suggested as using on different application in radiation therapy dosimetry [5, 6]. Recently in our group has been born the idea to develop new materials to determine the quantity of energy per unit mass of material that has been absorbed during the exposition this is in order to propose as radiation dosimeter in different application such as environmental and personal

1 abalba1@hotmail.com
dosimetry, as well as quality control device. In this order several materials as well as ceramics have been suggested to these purposes.

One of the most attractive materials constituted on perovskite type is the lanthanum aluminates (LaAlO$_3$). LaAlO$_3$ crystalline is a class of materials whose cubic crystalline structure follows the general formula ABO$_3$. The main applications of LaAlO$_3$ crystalline are mostly related to their mechanical and electrical properties [7, 8]. TL properties of LaAlO$_3$ applied to radiation dosimetry have been recently studied [9, 10]. Meanwhile, other studies focused on thermoluminescent characteristics of RE doped LaAlO$_3$ powders under ultraviolet radiation effect have been reported [11–13]. But in the literature LaAlO$_3$:Pr$^{3+}$ has not been observed as ionizing radiation dosimetry.

Therefore, it is anticipated that synthesized LaAlO$_3$:Pr$^{3+}$ can be used for ionizing radiation dosimetry purposes by means of thermoluminescence method. In the present work, lanthanum aluminates powders doped with trivalent praseodymium were characterized under high energy photon beams in order to use as out-of-field dosimeter in the future.

2. Experimental details

Lanthanum aluminates intrinsic and doped with trivalent praseodymium (LaAlO$_3$:Pr$^{3+}$) ion were obtained by sol-gel method using calcium nitrate tetrahydrated (Ca(NO$_3$)$_2$·4H$_2$O) and phosphorous pentoxide (P$_2$O$_5$), additionally, modified pechini’s method was used for powders drying as well as described in a previous paper [11, 12]. X-ray diffraction patterns were obtained using a Cu Kα radiation in the 2θ range of 20°-90° in a BRUKER Linxeye XE diffactometer.

Thermoluminescent analysis was carried out using a Harshaw 5500 TL analyzer coupled to a personal computer. The irradiation processes were made by mean of a clinical high energy photon beams using an accelerator ELEKTA model Synergy, at nominal energy 6 MV using a radiation field size of 10x10 cm$^2$. A solid water phantom (SWP) was used to maintain the TLD positioned at the center of the 10x10 cm$^2$ radiation field formed at the phantom (30x30x30cm) surface, located at 100 cm of the entrance surface dose, at the depth of maximum ionization, R$_{100}$, of the high energy, E, photon beam incident in the phantom material under standard practice dosimetry irradiation [14]. Calibration measurements were carried out using a Farmer cylindrical ionization chamber PTW30013; it was positioned according to the IAEA TRS 398 [15]. TL glow curve of LaAlO$_3$:Pr$^{3+}$ X-ray irradiated as well as other TL dosimetric characteristics were studied. The heating rate of the TL analyzer was kept at 10°C/s for all readings. The TL emission was integrated from room temperature (RT) up to 350°C. In order to reduce the thermal noise, resulting from the heating planchet of the TL reader, readings were made under nitrogen atmosphere.

3. Results and Discussion

Samples obtained by the modified Pechini’s method were characterized to confirm the presence of pure LaAlO$_3$ powders. Crystalline structure of undoped LaAlO$_3$ and trivalent Pr$^{3+}$ doped LaAlO$_3$ powders showed crystalline structure as reported in before work [10]. It shows the X-ray diffraction patterns of the calcinated powders at 1600°C for 5 hours in air. The diffraction patterns revealed that all observed diffraction peaks correspond to the rhombohedral LaAlO$_3$. The strongest peak appeared always at around angle 2θ = 32.98° corresponding to the (110) hexagonal reflection. Except for the peak at around 2θ = 32.98 the other peaks are relatively weak intensities, but all are described to the diffractions from the hexagonal structure. This is in good agreement with the PDF file PDF01-085-1071. In this figure trivalent praseodymium (Pr$^{3+}$) ions position have no noticeable effect; this result suggests that trivalent lanthanum ions are replaced by Pr$^{3+}$ ions.

The sensitivity of the TL glow curve was increasing as concentrations of Pr$^{3+}$ ion in LaAlO$_3$ was increased. The increase in glow peak sensitivity was increased up to 2% concentration of Pr$^{3+}$ ion (the maximum concentration used in this study was 5%). At this dopant concentration (2%) was favourable for future TL studies. The increase in the intensities of the glow peaks with increase of dopant concentration can be understood by the fact that more and more defects were created. After the maximum intensity (2 %), TL intensity was decreased as impurity concentration was increased. TL decreasing of the emission intensity can be attributed at the quenching concentration phenomena of dopant concentration. Therefore, we can conclude that
the distributions of traps produced by the irradiation of X-ray radiation can be altered greatly by the change in the concentrations of Pr$^{3+}$ ion doped in LaAlO$_3$ phosphor. Figure 1 shows TL intensity of LaAlO$_3$:Pr$^{3+}$ powders as a function trivalent ion dopant concentration.

Figure 1. TL response of powders as a function of dopant concentration.

Figure 2 shows the TL glow curve of LaAlO$_3$:Pr$^{3+}$ powders exposed to high energy photon beam (6 MV) of LINAC. TL glow curve of the samples prior X-ray beam effect no glow curve peaks were observed. However, this TL glow curve is performed when the X-ray beam action was induced. This TL glow curve exhibited two peaks centered at 160 and 300°C respectively. The most intensity TL peak was centered at 160°C. The TL glow curve with two prominent peaks suggests the existence at least two distinct luminescent centers. The 160°C correspond shallow traps and the second one (300°C) indicates the existence of deeper traps. TL glow curve of the powders indicate that both type of traps is being activated within the particular temperature range with its own value of activation energy (E) and frequency factor (σ). The shape of the glow curve remains almost the same for different X-ray dose, but the height of the glow peak was increased as X-ray dose increasing.

The relationship between TL response of praseodymium ion doped lanthanum aluminate and X-ray dose is illustrated in figure 3, where the TL output (peak area corrected by background) is plotted against X-ray dose. Figure 3 shows TL intensity of LaAlO$_3$:Pr$^{3+}$ powders irradiated with 6 MV photon beams as a function of different values of the X-ray absorbed dose from 25 to 5000 cGy. The figure shows an increasing of TL response as X-ray dose was increased. As it can be seen in this figure, TL response of the samples exhibits a linear response over the dose range studied. This range was studied in order to use the material for high energy X-ray dosimetry or it can be also used as quality control meter device. Measurement of quality control high energy photon beams generated by a medical electron linear accelerator (LINAC) is required mainly to determine the appropriate beam-quality-correction factor for the radiotherapy treatments, which should be agreement with declare IEC 60977 [16] mandatory. Linearity of TL response of the powders suggest that the phosphors can be used as a complementary dosimeter for determining the absorbed dose in radiotherapy treatment where is used others dosimeter as well as diode in vivo dosimeter [17, 18].
Reusability is one of the most useful property that a sample should possess in order to find a place in any environmental or personal dosimetry application. If the sensitivity of a sample does not change after several cycles of exposures and readouts, then it is termed as a phosphor with good dosimetric characteristics. In order to assess the reusability of the X-ray dose measurements attainable using this material, samples were given exposure of 100 cGy X-ray dose and TL glow curve was recorded. 10 repeated cycles (annealing-irradiation-readout) under same experimental conditions were executed. The plot between TL readout cycles and TL sensitivities is shown in Fig. 4. The reproducibility of TL readings of Pr$^{3+}$ ions doped LaAlO$_3$ irradiated by 6 MV X-ray beams was ± 1.6%. This figure shows no significant change in the sensitivity of the glow peak.
Other TL characteristics is the fading, this is the TL response remaining in the phosphor at different post irradiation time. A group of set of powders were irradiated at an absorbed dose of 100 cGy with high energy photon beams and the readout procedure was performed each different day from 2 to up to 10 days after irradiation. Between irradiations, TLD samples were stored in dark conditions at room temperature between 25–27°C. After 10 days fading of the powders showed a fading value of 30% compared with that value obtained just after irradiation. This behavior indicates that the phosphors can be used for real time dosimetry or is good candidate to be used as QC meter. From the point of view of the dosimetric applications of this compound to TL dosimetry, it is of interest to investigate the fading of the TL information as a function of the storage time of each peak. Figure 5a shows the integrated TL response of 160°C peak as a function of storage time from 1 to 30 days. It can be seen from the figure that TL response presents a fading of approximately 30% after the first 10 days of storing. But the most interesting dosimetric peak is that located at 300°C one which its TL response remains almost constant as can be seen in figure 5b. For dosimetric applications TL response of 300°C peak can be used as candidate for dosimetric applications.

**Figure 4.** Repeatability of luminescence information of one sample after 10 times analyzing.

**Figure 5.** a) TL signal 160°C peak at different storage time in the interval (1-30 days), b) TL signal 160°C peak at different storage time in the interval (1-30 days)

4. Conclusion

Thermoluminescent properties of LaAlO$_3$ powders doped with Pr$^{3+}$ ions have been investigated for high energy photon beams dosimetry. Samples of LaAlO$_3$:Pr$^{3+}$ phosphor shows good TL properties. TL signal of LaAlO$_3$:Pr as a function of high energy X-ray dose show a TL glow curve with two peaks centered at 160 and 300oC respectively. The nature of the glow curve form in samples is attributed to at least two types of traps. Then, after experimental results LaAlO$_3$:Pr$^{3+}$ can be used as thermoluminescent material for high energy X-ray beam measurements.
Considering, the purpose of developing materials that is TL dosimetry of ionizing radiation, the LaAlO$_3$:Pr$^{3+}$ is useful in determining this type of radiation in the range studied (25-5000 cGy).

Finally, we conclude LaAlO$_3$:Pr$^{3+}$ powders with prominent TL characteristics can be used as good candidate as high energy photon beams measurements applications and it is also good candidate to be used as QC meter in 6 MV LINACs.

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**References**

[1] Chen, R and McKeever S W S 1997 Theory of Thermoluminescence and Related Phenomena, *World Scientific, Singapore.*

[2] S McKeever, Moscovitch M and Townsend P D 1995 Thermoluminescence Dosimetry Materials: Properties and Uses, *Nuclear Technology Publishing, Ashford, Kent.*

[3] Rivera T 2012 *Appl. Radiat. Isot.* **71** 30-34

[4] Rivera T, Espinoza A, Von S, Alvarez R snd Jiménez Y 2012 *Appl. Radiat. Isot.* **73** 1034-1036

[5] Rivera-Montalvo T. (2014). *Appl. Radiat. Isot.* **83** 204-209

[6] Rodríguez Cortés J, Rivera Montalvo T, Villaseñor Navarro L F, Flores López O, Roman J, Hernandez Oviedo J O 2012 *Appl. Radiat. Isot.* **71** 35-39.

[7] J Kaur, D Singh, V Dubey and N Suryanarayan 2014 *Res. Chem. Int.* **40** 2737-2771

[8] Li A D, Shao Q Y, Ling H Q, Cheng J B, Wu D, Liu Z G, Ming N B, Wang C, Zhou H and Nguyen B Y 2000 *Appl. Phys. Lett.* 83 3540–3542

[9] Alves N, Ferraz W B, Faria L O 2014 *Radiat. Meas.* **71** 90-94

[10] Rivera Montalvo T, Morales Hernández A, Barrera Angeles A A, Alvarez Romero R, Falcony C, Zarate Medina J 2017 *Radiat. Phys. Chem.* **140** 68-73.

[11] M de León Alfaro, Morales Hernández A, Román López J, Zarate Medina J, Rivera And Montalvo T 2018 *Appl. Radiat. Isot.* **132** 57-60

[12] Morales Hernández A, J Zarate Medina, M E Contreras García, J Azorín Nieto, T Rivera and Montalvo 2016 *Appl. Radiat. Isot.* **118** 12-17.

[13] Oliveira V H, Khaidukov N M, Faria L O 2011 *Rad. Meas.* **46** (10), 1173–1175

[14] P Almond, P Biggs, Hanson W F and M Huq 1999 *Med. Phys.* **26** 1847-70.

[15] Absorbed dose determination in external beam radiotherapy: An international code of practice for dosimetry based on absorbed dose to water 2008 *Tech. Report Series 398*

[16] International Electrotechnical Commission (IEC), Medical electrical equipment: Medical electron accelerators in the range 1 MeV to 50 MeV Guidelines for functional performance characteristics. 1989 *IEC 60977*

[17] Madrid González O A and Rivera Montalvo T 2014 *Appl. Radiat. Isot.* **83** 214-217

[18] National Council on Radiation Protection and Measurements (NCRP) 2015 *151*