Radiation Measurements 125 (2019) 29–33

Contents lists available at ScienceDirect

Radiation Measurements

journal homepage: www.elsevier.com/locate/radmeas

Investigations on luminescence properties of erbium-doped phosphate glass produced at Juiz de Fora Federal University

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A R T I C L E I N F O

Keywords:
Erbium-doped phosphate glass
TL dosimetry
OSL dosimetry
Beta radiation

A B S T R A C T

Rare Earth doped-phosphate glasses have received a great deal of attention on research because of their applications in biomaterial engineering, however, little to no attention has been given to potential luminescent properties from "heating" these materials when exposed to ionizing radiation. This paper aims to presents results on investigations of Thermoluminescent (TL) and Optically Stimulated Luminescence (OSL) properties of the Er^{3+}-doped phosphate glasses produced at the Physics Department of Federal University of Juiz de Fora on a characterization for beta radiation dosimetry. It was used a RISØ TL/OSL reader and its coupled $^{90}Sr/^{90}Y$ beta source. The experimental findings indicate that the material presents linear responses of thermo (TL) and optically stimulated luminescence (OSL) over the absorbed dose range of 2 to 20Gy. Its emitted TL and OSL signal is more intense and with extended linearity range compared with undoped phosphate glass, probably caused by two absorption bands on 350–380 nm from Er^{3+}. Further investigations are being carried out on its applications to other types and qualities of radiation.

1. Introduction

In the past few years, phosphate-based glasses belonging to promising laser glass hosts were extensively studied and their crystallographic structure and optical properties were characterized using different spectroscopic techniques (Babu et al., 2007; Song et al., 1998; Pugliese et al., 2016). Recently, glasses doped with rare-earth ions have attracted much attention due to their potential applications in solid-state lasers, optical amplifiers and three-dimensional displays (Hraiech et al., 2017). Erbium is a very used rare earth ion and a lot of work has been done on the spectroscopic properties of Er^{3+} doped phosphate glasses (Pugliese et al., 2016; Hraiech et al., 2017; Langar et al., 2014; Sdiri et al., 2012; Desirena et al., 2006; Sardar et al., 2003), however, little to no attention has been given to potential luminescent properties from "heating" the material and its behavior after being exposed to ionizing radiation.

Thermoluminescence (TL) dosimetry has been actively developed in the past years due to its reliability, sensitivity and commercial availability and is currently in use with different commercial dosimeters, such as TLD-100 and $CaSO_4$:Dy, for personal and environmental dosimetry (Morato et al., 1982; Campos and Lima, 1986; McKeever et al., 1995). Nowadays, TL dosimeters are also being applied to dose measurements in radiation therapy and diagnostic radiology (Nunes and Campos, 2008; Bravim et al., 2011; Kron, 1999; Villani et al., 2017).

The optically stimulated luminescence (OSL) technique is also a very important tool for radiation dosimetry and have recently gained popularity, since it utilizes materials and electronic processes similar to TL but evaluation of the absorbed dose is performed by light instead of heat. It has been used as tool for medical dosimetry, both at diagnostic and therapeutic levels (Kron, 1999; Villani et al., 2017; McKeever, 2001; Akselrod et al., 2006; Sanchez et al., 2014).

The Dosimetric Materials Laboratory of the Instituto de Pesquisas Energéticas e Nucleares – LMD/IPEN has tradition in research related to TL and OSL materials and its applications. Since borate glasses, specially alkaline earth borates and aluminoborates are reported to have high TL properties and successful dosimetry applications (Fukuda and Takeuchi, 1989; Sabharwal et al., 2004; Nakauchi et al., 2016; Rojas et al., 2006), this paper aims to present the results on investigations of TL and OSL properties of the Erbium-doped phosphate glasses produced by Physics Department of Federal University of Juiz de Fora on a characterization for beta radiation dosimetry.

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https://doi.org/10.1016/j.radmeas.2019.04.005
Received 22 October 2018; Received in revised form 21 February 2019; Accepted 4 April 2019
Available online 09 April 2019
1350-4487/

2. Material and methods

2.1. Synthesis of 3 mol% erbium-doped phosphate glass

Starting materials for the glass system are obtained in reagent grade quality (Sigma-Aldrich). The dopant material Er_2O_3 has purity better than 99.99%. The samples were prepared on the basis of 30 g. Series of four glass samples of the form (40-x)P_2O_5-(3-x)SiO_2-(13-x)CaO-(13-x) MgO-(13-x)Na_2O-(13-x)ZnO-(5-x)Al_2O_3-xEr_2O_3 with 3.0 mol% were prepared using melt-quenching technique. The ingredients of the glass were weighed with 0.0001% accuracy. After the reagents were chosen, they were separated, weighed and mixed in an alumina mortar in order to homogenize the mixture. Soon after this procedure, it was taken to Mufla Logen 1800 where the mixture was melted at 1200–1250 °C for 4 h, enough time to ensure complete homogeneity.

Then the melt was poured into high-purity stainless steel mold giving the shock which guarantees rapid cooling. The samples received a heat treatment with temperatures between 50 and 100 °C, below the transition temperature to remove internal stress for 2 h and then cooled inside the furnace down to room temperature. Finally, the samples were polished and cut in aliquots with approximate dimensions of 2 mm o thickness, 5 mm height and 5 mm length then used for measurements.

2.2. Optical absorption measurements

Optical absorption measurements using a Cary 5000 UV-Vis-NIR spectrophotometer were performed to investigate and compare the matrix differences between the undoped and doped glasses signals. Measurements were performed in a light-sealed environment for absorption bands ranging from 200 to 800 nm.

2.3. TL/OSL reading system

The investigations were performed on a TL/OSL-DA-20 model RISØ reader equipped with bialkali EMI 9235QB photomultiplier tube (PMT). For the TL investigations, the reader was programed to perform a linear heat from 0 °C to 450 °C with constant heating hate of 10 °C.s^{-1} at N_2 atmosphere. For the OSL investigations it was used continuous-wave (CW-OSL) mode of illumination of the NICHIA Blue LED array NSPB-500AS-type. It is consisted of four groups of 7 blue LEDs resulting in 80 nW cm^{-2} of total power, with emission peak ~470 nm and full width at half maximum (FWHM) of 20 nm (RISØ TL/OSL User Manual; Yukihara et al., 2011). For the measurements, it was used 90% of power and stimulation time of 60 s. Hoya U-340 detection filter (transmission ~290–390 nm) was coupled to the reader system in order to avoid the stimulation light to interfere into the emitted signal from the samples.

2.4. Irradiations

The investigations regarding of the TL and OSL responses of the material to beta radiation were performed using the coupled $^{90}Sr/^{90}Y$ source from the integrated irradiation system of the reader, with initial dose rate of 0.1 Gy s^{-1} (calibrated in 06/10/2010) in terms of air kerma. Prior to any irradiation, aliquots of the 3 mol% Er-doped aliquots (Fig. 1) were subjected to a heat stimulation of 450 °C to release any residual background signal. A dosimetric characterization was obtained in order to analyze the emitted TL and OSL signal in function of the absorbed dose from the $^{90}Sr/^{90}Y$ beta source. The obtained results were compared with aliquots of a undoped phosphate glass sample. The presented experimental results of the absorbed doses are the average of three aliquots measurements and the error bars, when visible over the size of the data points, are the standard deviation the mean.

Fig. 1. Aliquots of 3 mol% Er-doped phosphate glass used in this study.

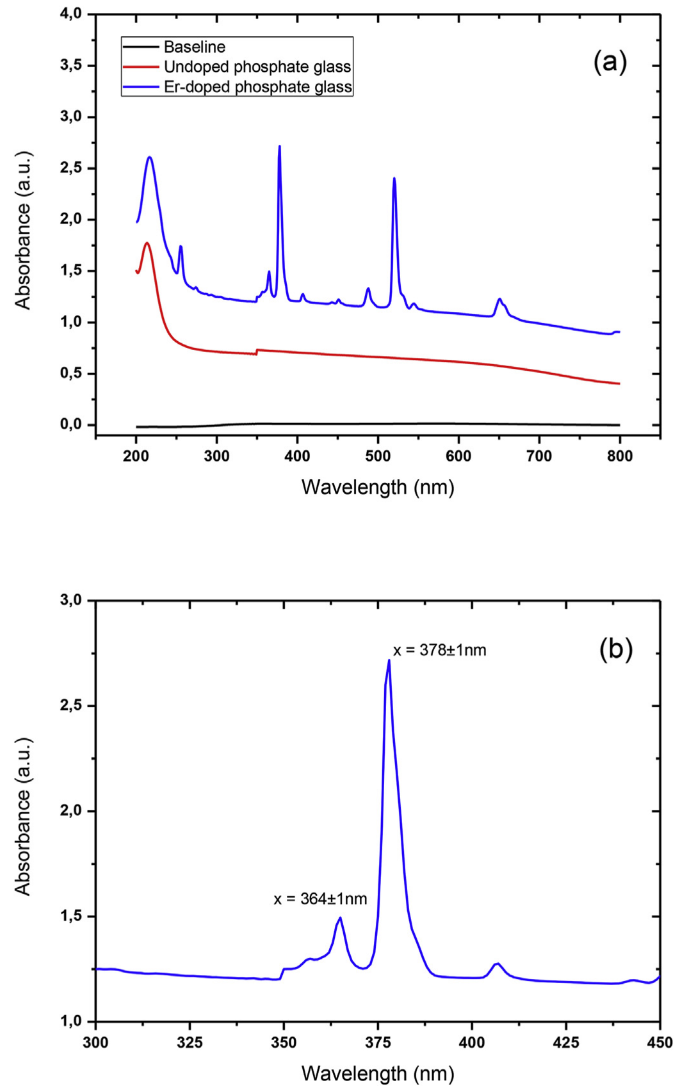

Fig. 2. Optical absorption of undoped phosphate glass and Er-doped phosphate glass. (a) Measurements ranging from 200 to 800 nm. (b) Detail on assigned bands from transitions $^4I_{15/2} \rightarrow {}^4G_{9/2}$ and $^4I_{15/2} \rightarrow {}^4G_{11/2}$ of Er^{3+}.

3. Results

3.1. Optical absorption measurements

Rare earth elements introduce assignment absorption bands into the phosphate matrix. Fig. 2a shows the experimental results of optical absorbance ranging from 200 to 800 nm. One can observe that absorption bands are created by the Er^{3+} compared with the undoped phosphate glass. Highlighted in Fig. 2b one can better observe two absorption bands given by Er^{3+} for transitions $^4I_{15/2} \rightarrow {}^4G_{9/2}$ and $^4I_{15/2} \rightarrow {}^4G_{11/2}$, with absorption peaks at 364 nm and 377 nm (Pisarski et al., 2014), which are probably responsible for the changes in the form and intensity of TL signals.

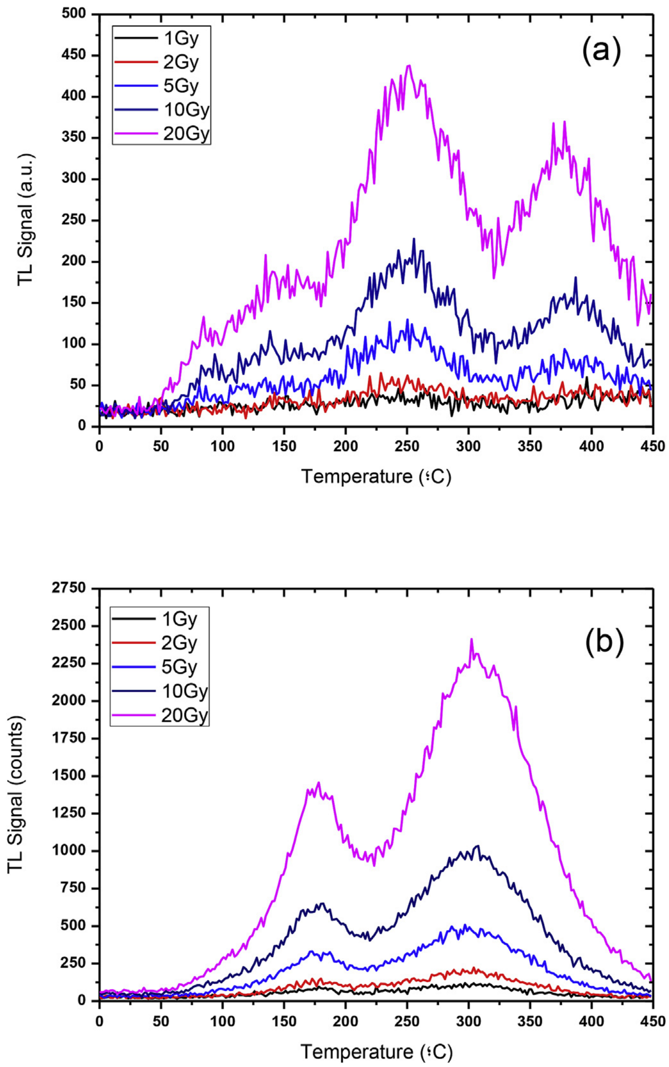

Fig. 3. TL glow curves obtained after $^{90}Sr/^{90}Y$ beta irradiations with absorbed doses ranging from 1 to 20 Gy (a) undoped phosphate glass (b) Er^{3+}-doped 3 mol% phosphate glass.

3.2. Thermoluminescent (TL) characterization

Fig. 3 *a* and *b* presents the TL glow curves for doses ranging from 1 up to 20 Gy for undoped phosphate glass and Er^{3+}-doped respectively. One can observe that the addition of the dopant element changes from a tree to a two peaks emission, given from the structural changes in the material. The deconvolution of the peaks (Fig. 4) shows that peak one is centered around 175 °C and peak two around 305 °C.

By the relation between the integrals of each glow curve with its respective irradiated dose, a function over the experimental data can be fitted to obtain the dose-response curves of the samples. As the aliquots used in the study show differences in size and mass, for statistical purposes the responses of each aliquot was normalized by its mass. Fig. 5 shows the dose-response curves for the Er^{3+}-doped and the undoped phosphate glasses.

The TL response of the material present linear behavior over the 2–20 Gy dose-range. The experimental calibration factor obtained with the linear fit of these data points for the Er^{3+}-doped samples is (9.16 ± 0.29) x 10^3 counts.Gy^{-1}, with reproducibility of measurements better than 3.2%. Undoped phosphate, as comparison, could have a linear fit and a lower detection limit of 5Gy.

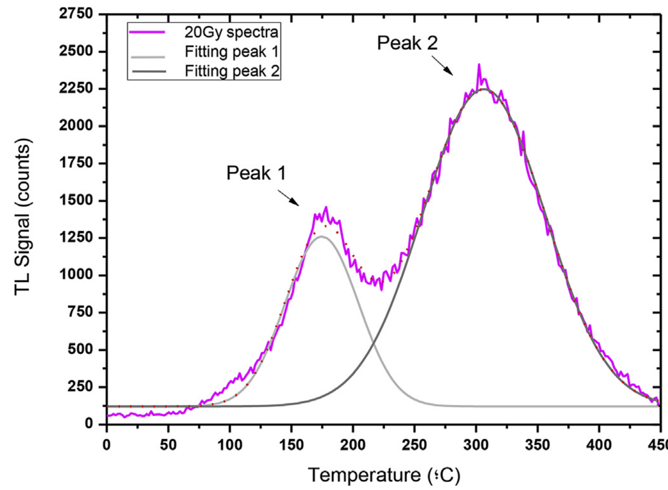

Fig. 4. Two peaks convolution from Er^{3+}-doped phosphate glass. First peak is centered around 175 ± 2 °C and second around 306 ± 3 °C.

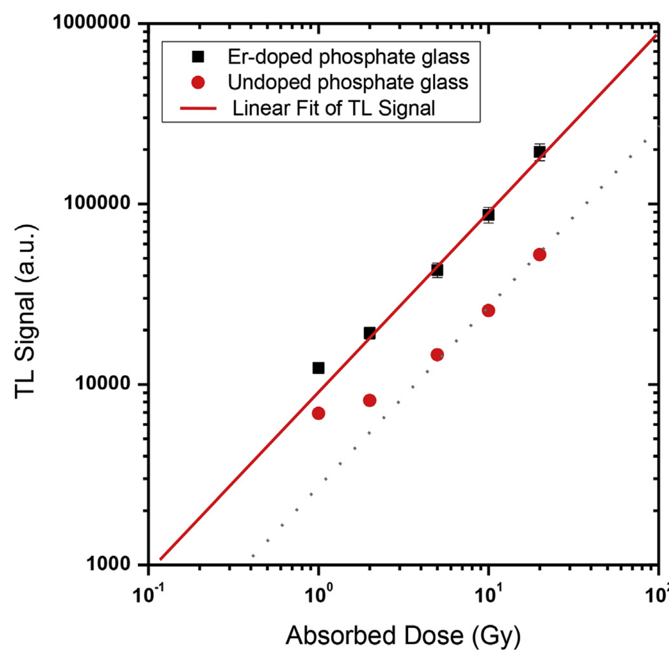

Fig. 5. Experimental TL dose-response curves for both Er^{3+}-doped and undoped phosphate glasses.

3.3. Optically stimulated luminescence (OSL) characterization

Since the TL investigations showed the higher performance on radiation detection using the Er^{3+}-doped glasses, the OSL measurements were not carried with the undoped aliquots. Fig. 6 presents the OSL decays from the aliquots for doses ranging from 1 up to 20 Gy. One can observe that the aliquots present OSL sensitivity higher than TL, with initial response of order of 10^3 counts. Using the same methodology, from the integration of the total area of the experimental OSL response and normalizing the emitted signal with the aliquot mass, a dose-response curve was obtained and presented in Fig. 7.

The OSL response of the material also present linear behavior over the 2–20 Gy dose-range. The experimental calibration factor obtained is (2.38 ± 0.11) x 10^4 counts.Gy^{-1} with reproducibility better than 5.0%. Again, this result show that the material presents higher OSL sensitivity.

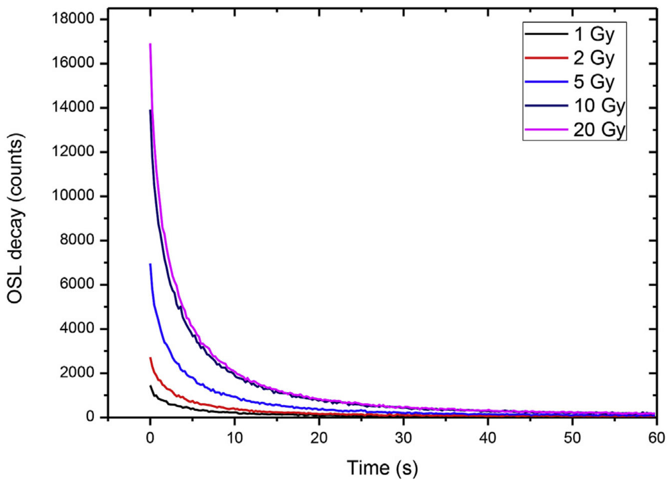

Fig. 6. OSL decay from the Er-doped samples irradiated with doses from 1 to 20 Gy.

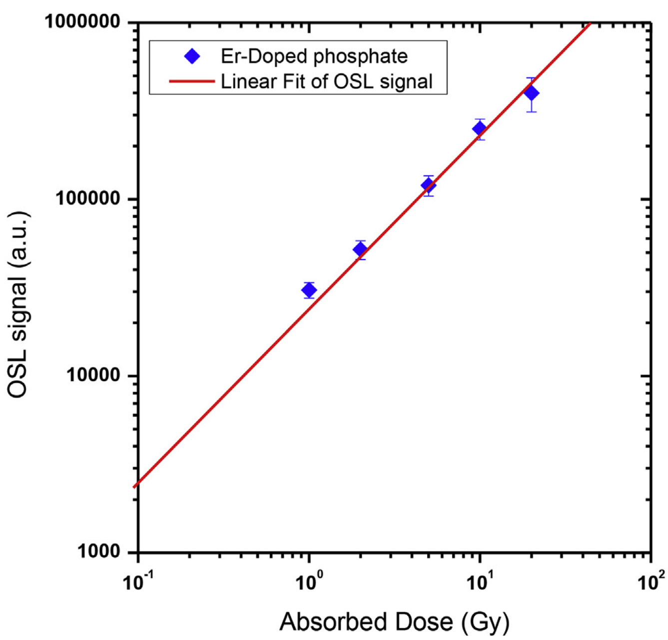

Fig. 7. Experimental OSL dose-response curves for Er^{3+}-doped phosphate glass.

3.4. Background signal and annealing cycles

The investigations of background (BG) signal of the samples and the residual signals after each irradiation cycle were evaluated. The signals emitted by the aliquots were measured in the following situations: before the first use and after being read and thermally treated at 450 °C for 15 min. Fig. 8 show the glow curves of BG, first and forth cycles (a); and the analysis of the integral of the BG glow curves throughout 4 cycles (b).

The experimental results show that samples presented some accumulated background signal. After each beta radiation investigation and annealing cycle, the analyzed residual signal remained stable, presenting no dependence to the previews absorbed dose up to 20 Gy.

3.5. TL/OSL intrinsic efficiency

The intrinsic efficiency (I_E) of the material for TL/OSL response for this type and quality of radiation over the linear dose-response range is calculated according to Eq. 1

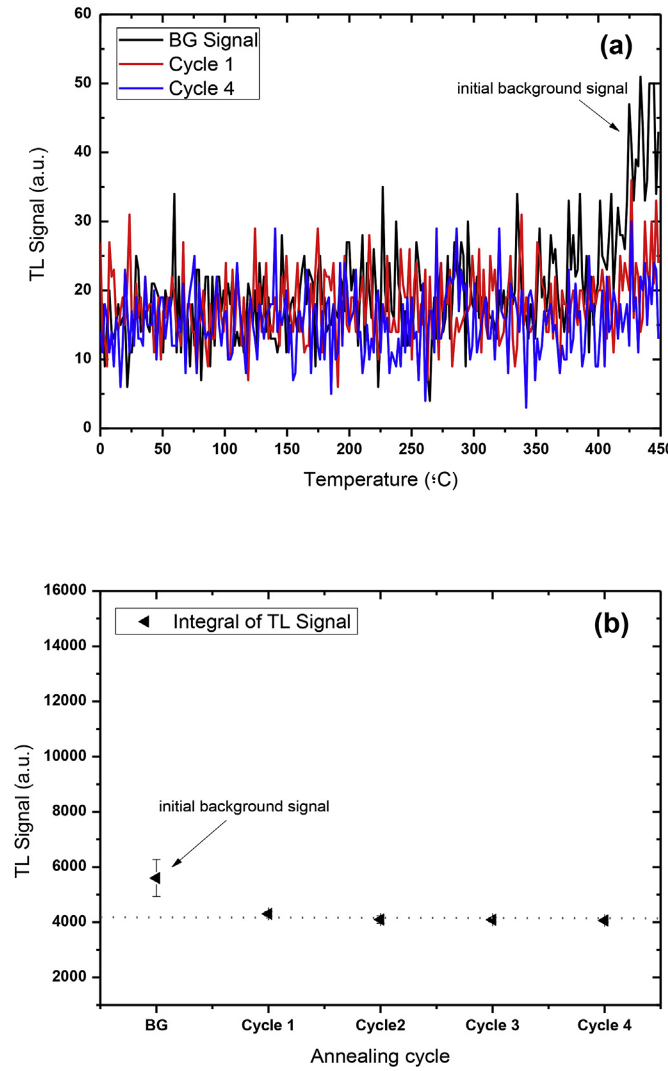

Fig. 8. Experimental OSL dose-response curves for Er-doped phosphate glass.

Table 1
Calculated intrinsic efficiency of the material to provide TL/OSL signal from $^{90}Sr/^{90}Y$ beta source.

Mass (mg)	$\bar{m}$ of 3 aliquots	$\bar{m}$ of 3 aliquots
	0.1188	0.1188
Absorbed Dose (Gy)	Average TL Intrinsic Efficiency (counts.Gy^{-1}.mg^{-1})	Average OSL Intrinsic Efficiency (counts.Gy^{-1}.mg^{-1})
1	1.04×10^5	2.58×10^5
2	8.10×10^4	2.18×10^5
5	7.25×10^4	2.02×10^5
10	7.33×10^4	2.11×10^5
20	8.18×10^4	1.68×10^5
Average[a]	$(7.71 \pm 0.25) \times 10^4$	$(2.00 \pm 0.22) \times 10^5$

[a] Average intrinsic efficiencies of the linear range of response (2–20Gy).

$$I_E = \frac{\bar{R}}{D.\ \bar{m}} \tag{1}$$

where $\bar{R}$ is the average TL/OSL response for an absorbed dose (D) of average mass $\bar{m}$ of the aliquots. The obtained results are presented in Table 1.

Since the calculated values of Intrinsic efficiencies are also normalized by the mass of the aliquots used for the measurements, the results indicate that the synthesized Er^{3+}-doped phosphate glass as a material and its efficiency on emitting TL and OSL signals. The Er^{3+}-doped aliquots presents intrinsic efficiencies of (7.71 ± 0.25) x 10^4 counts.Gy^{-1}.mg^{-1} for TL measurements and (2.00 ± 0.22) x 10^5 counts.Gy^{-1}.mg^{-1} for OSL measurements.

4. Discussion

Analyzing the results obtained with the phosphate glasses doped with erbium prepared at Juiz de For a University one can observe that the presence of Er^{3+} changes and intensifies the thermoluminescent emission of the samples (Figs. 2 and 3). This phenomenon probably should be associated with the two absorption bands of 364 and 377 nm assigned by Er^{3+} (Pisarski et al., 2014) incorporated in the phosphate matrix (Fig. 1). The TL characterization presents good repeatability and useful dose range interesting for clinical measurements. The OSL characterization, despite the repeatability being at 5%, it maintained the linearity range of response and presented higher signal amplitude and sensibility (Fig. 7).

Further investigation of annealing treatments can be performed, however the analysis of the background signal obtained after each 15-min-annealing cycle shows little to no residual signal (Fig. 8), independent of the previous dose absorbed by the material. Investigations are also being conducted to analyze the response of the material to gamma rays and its dosimetric applications for evaluations of clinical photons and electron beams.

5. Conclusions

The experimental findings of this work indicate that Erbium-doped phosphate glasses produced at Federal University of Juiz de Fora presents dosimetric properties for beta radiation and TL and OSL dosimetric characterization. Its emitted signal is more intense and with extended linearity range compared with undoped phosphate glass. Further investigations are being carried out in order to evaluate the TL/OSL responses to other types and qualities of radiation.

Acknowledgments

The authors would like to thank Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES (554/2018), Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq (5573659/2008-7) and Fundação de Amparo à Pesquisa do Estado de Minas Gerais - FAPEMIG for the financial support.

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