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Thermoluminescence of aluminum oxide co-doped with terbium and thulium obtained via combustion synthesis

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ABSTRACT

In this work thermoluminescent properties of α-Al_2O_3 samples doped with Tb^{3+} and Tm^{3+}, prepared by the combustion synthesis route, were studied. Samples were prepared by mixing stoichiometric amounts of aluminum nitrate, urea and dopants with different amounts of terbium and thulium nitrates varying from 0 to 0.15 mol%. The mixture was ignited in a muffle furnace at low temperature (500 °C). After the combustion, the samples were sintered at 1400 °C for 4 h in order to obtain the pure α-phase crystalline structure. The TL response of these samples for Co-60 gamma radiation was evaluated. It was observed a TL glow peak around 220 °C and a linear response for doses in studied range of 0.1–1 Gy. It was observed that the 0.1 mol% concentrations of both dopants present the highest TL sensitivity. The sensitivity of the co-doped (0.10 mol%) samples is 5 times higher than the 0.1 mol% Tm-only doped Al_2O_3 and 40 times higher than the sample doped only with 0.1 mol% of Tb. These results strongly suggest that the Al_2O_3:Tm–Tb, prepared through the combustion method, is a potential material for TL radiation dosimetry.

1. Introduction

Doped aluminum oxide (α-Al_2O_3) has been widely used as luminescent dosimeter for ionizing radiation. The most common and efficient of these materials uses carbon as dopant (Akselrod et al., 1990). Conventional fabrication processes of these dosimeters utilize Czochralsky or Vernuil crystal growth techniques, which involve the use of high temperatures (>2000 °C) and highly reducing atmospheres (Summers, 1984).

As an alternative route to synthesize carbon doped TL materials, nanoporous aluminum oxide has been prepared through electrochemical oxidation of aluminum in organic acids with subsequent thermal treatment (Azevedo et al., 2006; Barros et al., 2007), which shown quite interesting results. Due to the increasing necessity to obtain more efficient dosimeters, rare-earth (RE) elements have been chosen as dopants. The interest in RE doped aluminum oxide materials is their potential use in photonic applications. For that reason, these materials have been synthesized by sol–gel techniques (Kaplyanskii et al., 1998), ion beam implantation (Can et al., 1995), sonochemical preparation (Gedanken et al., 2000), solvent evaporation (Azorín et al., 2002), electrochemical route (Azevedo et al., 2004) and combustion synthesis (Hirata et al., 2005; Barros et al., 2008, 2010).

Amongst these techniques, the combustion synthesis (CS) is particularly attractive because of its low cost, high yield and the ability to achieve high purity single phase complex oxide powders at low processing temperatures and short reaction times (García et al., 2001). In this technique, the heat released from the highly exothermic reduction-oxidation reaction between nitrates (the "basis" and dopant materials) and an organic fuel is used for sintering of the material (Patil et al., 2002). It also has the possibility of production of materials with varying dopant species and concentrations.

In order to find a new alternative process to prepare doped aluminum oxide materials for dosimetric application purposes, this work presents results of the thermoluminescence (TL) study of aluminum oxide co-doped with Tb^{3+} and Tm^{3+}, prepared using different concentrations, through the CS route.

2. Materials and methods

The aluminum oxide samples used in this work were prepared by mixing appropriate amounts of aluminum nitrate ($Al(NO_3)_3.9H_2O$) as oxidant, urea ($CO(NH_2)_2$) as fuel and a dopant material. Terbium nitrate ($Tb(NO_3)_3.9H_2O$), thulium nitrate

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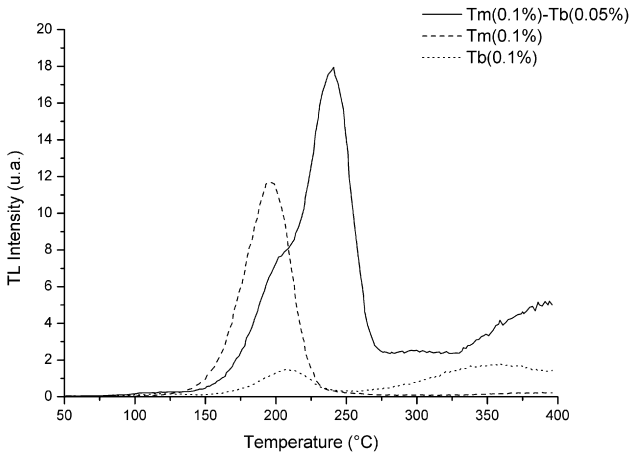

Fig. 1. TL glow curves for Al_2O_3 samples doped (and co-doped) with $Tb_{0.1}$ and $Tm_{0.1}$ irradiated with 1 Gy (Co-60).

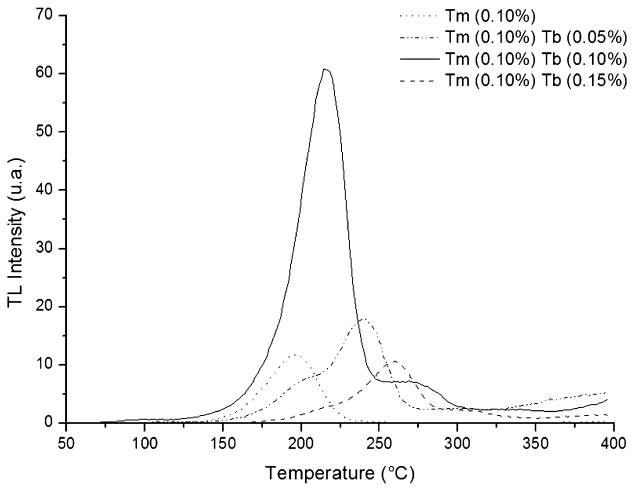

Fig. 3. TL glow curves for Al_2O_3:Tm–Tb samples with Tm concentration fixed at 0.1 mol% and Tb concentration varying from 0 to 0.15 mol%, irradiated with 1 Gy gamma dose.

($Tm(NO_3)_3.9H_2O$) or both were used as dopants. Samples of $Al_2O_3:Tm_{i\%}–Tb_{j\%}$ were prepared with different dopant concentrations, varied from [i,j] = 0, 0.05, 0.1 and 0.15 mol% with respect to the aluminum concentration, totalizing $4 \times 4 = 16$ different types of samples.

The excess water was evaporated on a hot plate to form a gelatinous mixture, which was then transferred to a muffle furnace (pre-heated to 500 °C), where it spontaneously ignited in less than a minute. The resulting powder was divided into two aliquots, pelletized and sintered at 1400 °C for 4 h with a 5 °C/min heating rate and allowed to cool inside the muffle. This heating treatment has been shown to eliminate excess of overlapping peaks and to decrease the FWHM of the main peak of the TL glow curve (Barros et al., 2010b). The pellets were made with 6 mm diameter and approximately 2 mm thick. Scanning Electron Microscopy (JEOL, model JSM-6460) micrographs showed that grain size of these powders are in the range of 500–1000 nm (Barros et al., 2010b).

To evaluate the TL response, samples with different concentrations were irradiated in a Co-60 irradiator (4.0 Gy/h at 12/2010) under electronic equilibrium. The TL measurements were carried out using a Harshaw–Bicron TL reader, model 3500, equipped with a Hamamatsu R6094 photomultiplier tube (maximum sensitivity centered at 420 nm) and a white filter. The glow curves were acquired at temperatures ranging from 50 to 400 °C with a heating rate of 5 °C/s. For annealing, the samples were treated at a two step annealing cycle of 400 °C at 1 h, followed 100 °C at 4 h, before each irradiation.

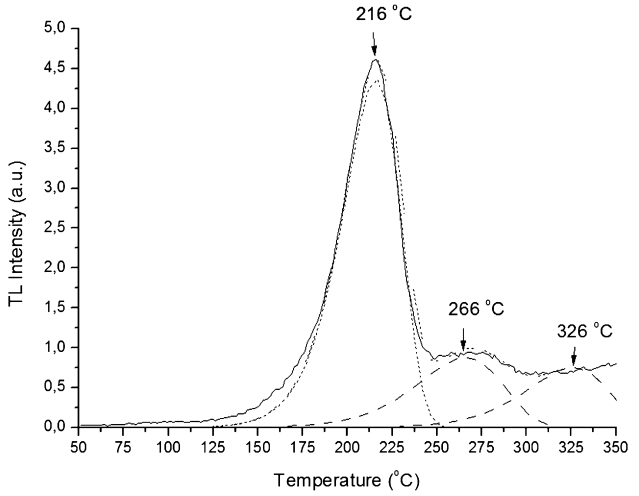

Fig. 2. TL glow curve deconvolution of $Al_2O_3:Tm_{0.1\%}$, $Tb_{0.1\%}$.

3. Results

Fig. 1 shows the TL glow curves for Al_2O_3 samples doped only with Tm at 0.1 mol% ($Al_2O_3:Tm_{0.1\%}$), with Tb at 0.1 mol% ($Al_2O_3:Tb_{0.1\%}$) and with the mixture of Tm at 0.1% and Tb at 0.05% ($Al_2O_3:Tm_{0.1\%}–Tb_{0.05\%}$), irradiated at the Co-60 gamma radiation dose of 1 Gy. The results show that the TL peak of $Al_2O_3:Tm_{0.1\%}$ sample is centered at 190–195 °C, approximately the same temperature as the main TL peak of commercial α-Al_2O_3:C.

With respect of the TL response of the sample with both dopants ($Al_2O_3:Tm_{0.1\%}–Tb_{j\%}$) the glow curve shows an additional peak. The deconvolution of the glow curve into first-order components shows that one peak is centered at approximately 215 °C, a second one at 265 °C and at least a third peak around 325 °C (Fig. 2). The trap unstable at 265 °C appears only for samples prepared with Tb–Tm dopation.

The influence of the Tb concentration in the glow curve of Al_2O_3 samples doped with fixed Tm concentration (0.10%) is shown in

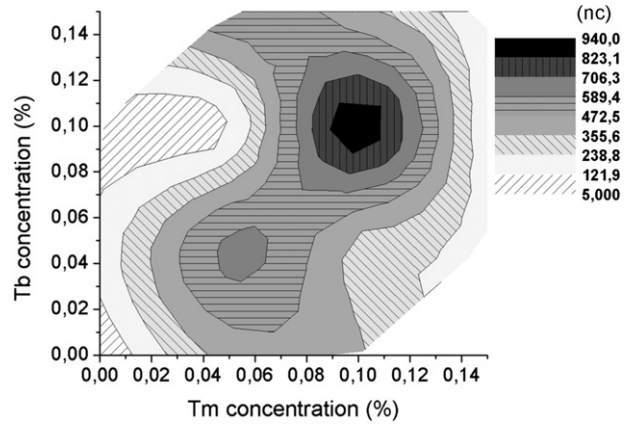

Fig. 4. Contour graph of Tm and Tb concentrations versus TL intensity, for Al_2O_3:Tm–Tb samples irradiated with 1 Gy gamma dose.

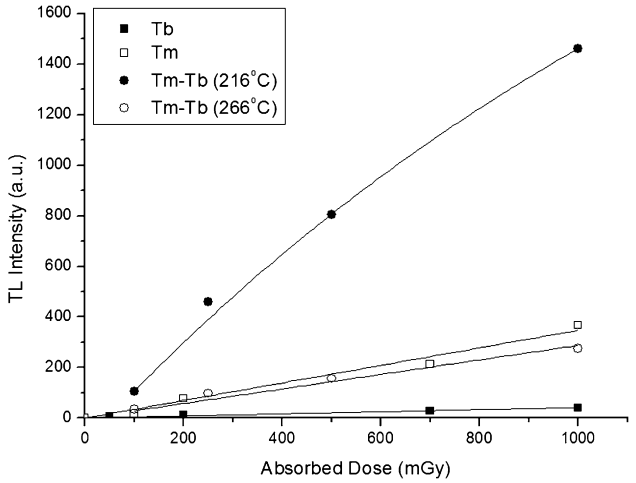

Fig. 5. TL response vs. gamma dose curve for the Tm^{3+} and Tb^{3+} doped and co-doped Al_2O_3 samples.

Fig. 3. The results are for samples irradiated with the dose of 1 Gy of Co-60 gamma radiation. It can be observed that increasing the concentration of Tb from 0.05 to 0.1%, there is a significant enhancement of the TL peak, decreasing for higher concentrations (0.15%). This decrease in the TL efficiency is probably due to the blue absorption band of Tb^{3+} ions.

Fig. 4 shows the variation of TL intensity (z axis) versus Tb and Tm concentrations. The results show that the maximum TL sensitivity was found for Al_2O_3:$Tm_{i\%}$-$Tb_{j\%}$ with the concentrations i = j = 0.1 mol%, followed by the i = j = 0.05 mol% that, compared with the first one, has a relative sensitivity of 0.67. At dopant concentrations higher than 0.10 mol%, the TL intensity per unit dose decreased. A previous investigation by Barros et al. (2010) with aluminum oxide doped only by Tm or Tb also demonstrates that the highest TL sensitivity is obtained with a dopant concentration of 0.1%.

Fig. 5 shows the dose response for the TL peaks of Al_2O_3:$Tm_{0.1\%}$–$Tb_{0.1\%}$ centered at 215 and 265 °C, Al_2O_3:$Tm_{0.1\%}$ centered at 195 °C and Al_2O_3:$Tb_{0.1\%}$ peak at approximately 210 °C. Table 1 presents the angular coefficient of each dose response curve, the correlation coefficient and the relative sensitivity for the Tb/Tm doped samples, for pure Al_2O_3 and for TLD-100. The results show a linear dose response for the three samples irradiated with Co-60 gamma radiation in the studied dose range of 0.05–1.0 Gy. The highest TL sensitivity was found for the peak at 215 °C of Al_2O_3:$Tm_{0.1\%}$–$Tb_{0.1\%}$. For this peak a slight linear-sublinear evolution can be observed for doses in the 0.5–1.0 Gy region. The 265 °C of this sample has approximately the same relative TL sensitivity than the peak at 190 °C of Al_2O_3:$Tm_{0.1\%}$. It was found that the sensitivity of the $Tm_{0.1\%}$–$Tb_{0.1\%}$ doped sample for gamma radiation is 4 times higher than that of Al_2O_3:$Tm_{0.1}$, 30 times higher than the sensitivity of Al_2O_3:$Tb_{0.1\%}$ and 5.5 times lower than TLD-100.

Table 1
Linear regression coefficients and linear correlation coefficient (R^2) for each sample and the TL sensitivity in relation to the Tm–Tb doped sample.

Sample	Curve coefficient	R^2	Relative sensitivity
Al_2O_3:$Tm_{0.1}$–$Tb_{0.1}$ (216 °C)	1.48	0.99	1.00
Al_2O_3:$Tm_{0.1}$–$Tb_{0.1}$ (266 °C)	0.27	0.97	0.18
Al_2O_3:$Tm_{0.1}$	0.35	0.98	0.24
Al_2O_3:$Tb_{0.1}$	0.04	0.92	0.03
undoped Al_2O_3	0.011	0.99	0.01
TLD-100	8.1	0.99	5.5

4. Conclusions

It is possible to conclude that CS is a promising method to prepare α-Al_2O_3 doped with $Tm_{0.1\%}$-$Tb_{0.1\%}$ ions for dosimetric applications. This technique is particularly attractive due to its low cost, short reaction times, ability to produce pure products and straightforwardness to obtain samples with different dopants and concentrations. In summary, the results showed that a 0.1 mol% rare-earth concentration optimizes the TL sensitivity and that the thermal treatment at 1400 °C is necessary to obtain a well defined TL peak for dosimetric applications. The TL dose response curves of all samples presents a linear behavior within the studied dose range and doping with $Tm_{0.1\%}$-$Tb_{0.1\%}$ simultaneously produces a 4 times more sensitive material than with only one rare-earth ion. These results indicate that this material is suitable for dosimetric applications. More work is under way to optimize the sensitivity of the material to lower dose measurements and to characterize the material as a radiation dosimeter.

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