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Combustion synthesis: A suitable method to prepare Al_2O_3 doped materials for thermoluminescent dosimetry

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Abstract

In this work we present an alternative route to synthesize rare-earth doped aluminum oxide materials for thermoluminescent (TL) dosimetry using the combustion synthesis (CS) technique. The samples were prepared by mixing aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$), urea ($CO(NH_2)_2$), and europium nitrate ($Eu(NO_3)_3$), terbium nitrate ($Tb(NO_3)_3$) and tetra-ethyl-ortho-silicate (TEOS, $C_8H_{20}O_4Si$) in appropriate amounts as dopants in an aqueous solution. 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 ignited spontaneously within a few seconds. The TL glow curve of the irradiated samples showed an isolated peak at around 200 °C for the Eu doped sample which is suitable for radiation dosimetry. The europium concentration was varied from 0.005% to 7% in order to study the effect of the dopant concentration on the TL response and the optimum concentration was found to be 0.5%. The effect of different annealing temperatures of the sample on the TL response was also studied and the results showed a broad TL peak for 600 and 800 °C and a well defined peak for a 1000 °C annealing temperature. From these results it is possible to conclude that the CS method is a very suitable technique to prepare doped aluminum oxide materials. The technique is fast, low cost and produces well defined materials that can be used for dosimetric applications. Further work is still under way in order to optimize sensitivity for low dose measurements.
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Keywords: Combustion synthesis; Aluminum oxide; Rare-earth doping

1. Introduction

Single crystal aluminum oxide dosimeters ($\alpha-Al_2O_3\colon C$) shows a high thermoluminescent (TL) sensitivity to ionizing radiation, 50–60 times higher than LiF:Mg,Ti (Akselrod et al., 1990). Conventionally, these dosimeters are prepared by crystal growth techniques, which require sophisticated laboratory infrastructure equipment, high temperatures (2050 °C) processing and highly reducing atmospheres. 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). Recently, there has been increased interest in rare-earth (RE) doped aluminum oxide materials, and the reason seems to be their potential use in photonic applications. 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), by electrochemical route (Azevedo et al., 2004) and combustion synthesis (CS) (Hirata et al., 2005). In particular, the CS method is an excellent technique for preparing crystalline materials because of its low cost, high yield and the ability to achieve high purity single or multiphase complex oxide powders in the as-synthesized state at low processing temperatures, and in a short reaction times (∼s) (García et al., 2001). The CS process is based on the use of the heat released from the redox chemical reaction, instead of the use of intensive high-temperature furnaces, to supply the energy necessary for the synthesis.

In order to find a new alternative process to prepare doped aluminum oxide materials for dosimetric application purposes, in this work, we present the synthesis process and the TL response of $Al_2O_3\colon X$ (where $X = Eu^{3+}$, Tb^{3+} and Si) oxide materials obtained by the CS method.

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2. Materials and method

The samples were prepared by mixing aluminum nitrate ($Al(NO_3)_3.9H_2O$) as oxidant, urea ($CO(NH_2)_2$) as fuel and a dopant material in distilled water. The europium nitrate ($Eu(NO_3)_3$), terbium nitrate ($Tb(NO_3)_3$) and TEOS ($C_8H_{20}O_4Si$), in appropriate amounts, where used as dopants. The excess water of the mixture was evaporated on a hot plate until a gelatinous mixture was formed, which was then transferred to a muffle furnace pre-heated to 500 °C where it ignited spontaneously within a few seconds. The resulting aluminum doped oxide powder was pelleted and annealed at the temperatures of 600, 800 or 1000 °C for 2 h.

In this work, three types of samples were prepared and nalyzed: Al_2O_3: Tb, Si, Al_2O_3: Eu, Si and Al_2O_3: Eu. For the first and second samples the ratio X:Al concentration was fixed to be 5% (X = Tb, Si or Eu), whereas for the last type of sample, the Eu:Al ratio was varied from 0.005% to 7% in order to observe the effect of dopant concentration on the TL sensitivity, defined in this work as the TL response for a 1.5 Gy Co-60 gamma dose, normalized by the response of the 0.5% Eu sample.

The prepared samples were irradiated with Co-60 gamma radiation at dose ranges from 100 mGy to 70 Gy, and the TL response was measured using a Harshaw-Bicron 3500 TLD reader.

3. Results

Fig. 1 shows the TL glow curve, obtained for the aluminum oxide sample doped with Tb–Si, Eu–Si and Eu. The highest sensitivity was found for the samples Al_2O_3: Tb, Si obtained by CS technique. This sample presented a TL response 5000 times higher than the undoped Al_2O_3. Comparing the TL response for the three prepared samples we observe that the Al_2O_3: Eu doped samples show an isolated and well defined peak at around 200 °C, which seems well suited for radiation dosimetry, even though this sample presents a less sensible response than the Tb doped sample. Therefore, for these samples we also investigated the effect of the dopant concentration on the TL sensitivity and the effect of the thermal annealing on the shape of the TL glow curve.

Results of the dependence of the TL sensitivity as a function of the europium concentration are shown in Fig. 2. From this result we conclude that the RE concentration that optimizes TL response is 0.5% of Eu^{3+} ions. The reason for this is until now unknown, however it may be associated with the crystallographic phase of the aluminum oxide that is formed, since it is already known that the α-phase formation is prevented as the concentration of the dopant ion is increased (Hirata et al., 2005).

Fig. 3 shows the TL response for the Al_2O_3: Eu^{3+} with different Eu concentration irradiated in the dose range from 5 mGy to 5 Gy. These results show a linear dose response for all samples, with the highest sensitivity for the 0.5% Eu concentration. For this sample, the minimum measurable dose, for a 90 mg pellet, was around 40 mGy.

Fig. 4 shows the effect of the thermal annealing temperature on the TL glow curve. This result shows that as the temperature increases the samples present a better defined TL peak. This effect may be related with the number of defects that are eliminated with the annealing temperature or related to the phase transition that happened in that temperature range. A phase transformation from amorphous to α-crystalline was also observed in the X-ray diffraction patterns of Al_2O_3: Eu^{3+}

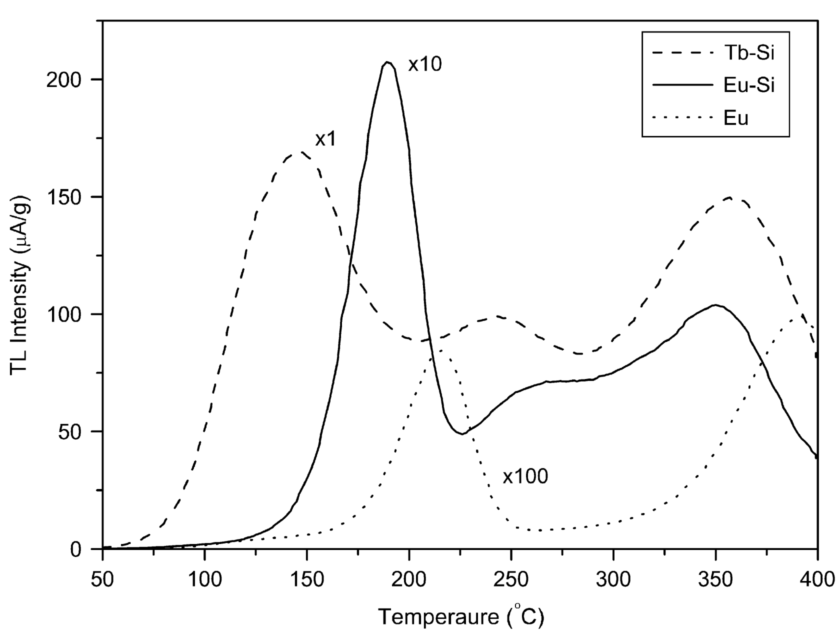

Fig. 1. Glow curves for Al_2O_3:Tb,Si prepared with 5% Tb and 5% Si, Al_2O_3: Eu,Si (x10) prepared with 5% Eu and 5% Si dopant concentration, and Al_2O_3: Eu (x100) prepared with 5% Eu dopant concentration.

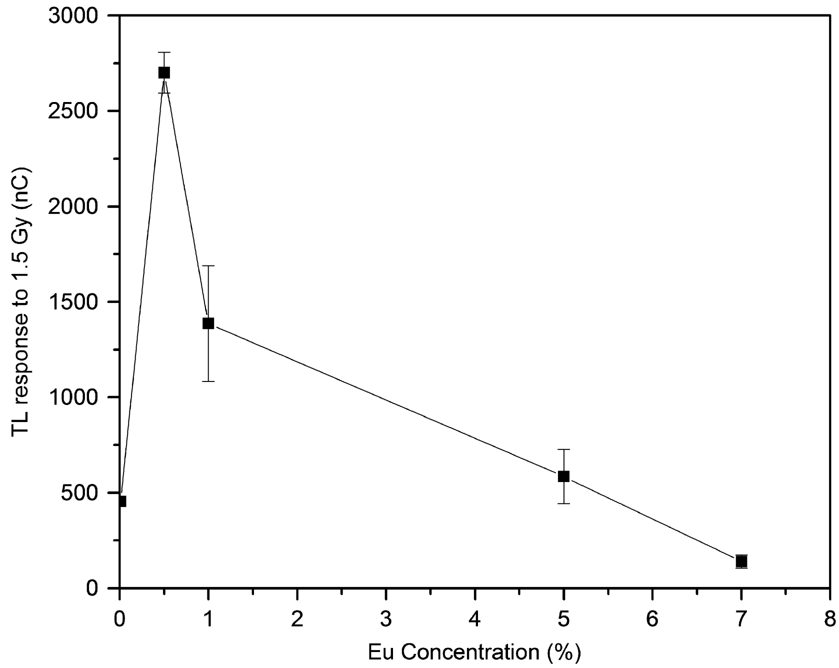

Fig. 2. Sensitivity of Al_2O_3: Eu as a function of Eu^+ ion concentration. Samples were prepared with dopant concentrations of 0.005%, 0.5%, 1%, 5% and 7%. Error bars correspond to 1 standard deviation.

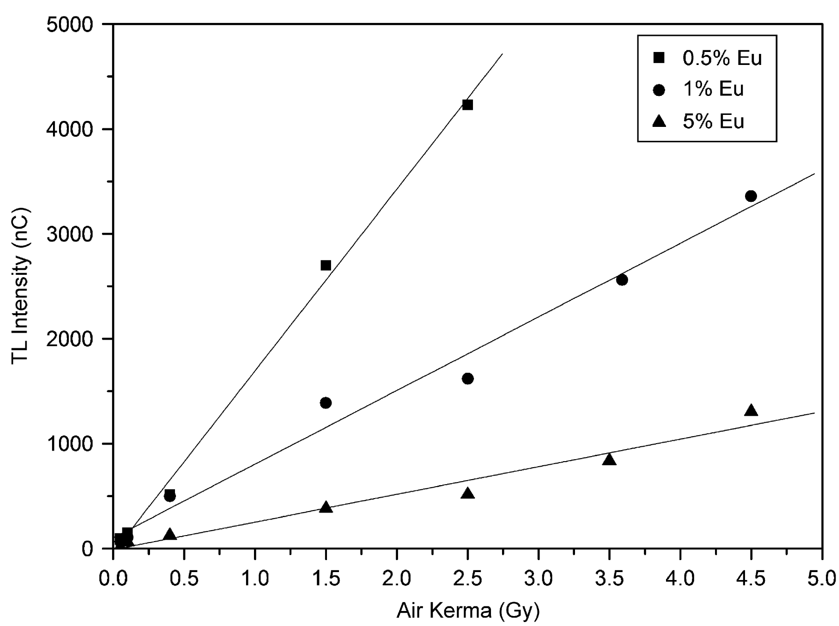

Fig. 3. Dose response for Al_2O_3: Eu with 0.5%, 1% and 5% Eu concentration.

by Hirata et al. (2005), where the α-phase forms at annealing temperatures around 1200 °C.

4. Conclusions

From the results above it is possible to conclude that the CS method is very suitable for the preparation of Al_2O_3 doped material for dosimetric applications. In particular, this technique seems to be very attractive due to its low cost and the extreme facility to prepare samples with well defined microstructures, at low processing temperatures and in a short reaction times (∼ s).

The concentration analysis shows that the Eu concentration that optimizes the TL response is 0.5% and, in order to obtain a well defined TL response peak for dosimetric applications, a thermal treatment at 1000 °C is necessary. Also for all studied samples a linear response with the dose was found. Work is under way to optimize sensitivity of the material for low dose measurements.

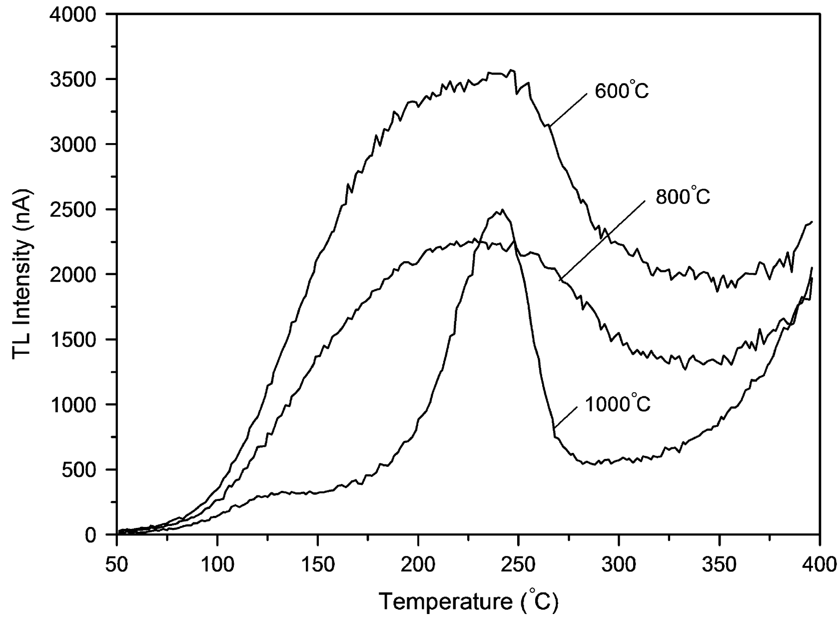

Fig. 4. TL glow curves of Al_2O_3: Eu with different thermal treatment temperatures, irradiated with a 10 Gy Co-60 gamma dose.

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