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Optically stimulated luminescence of CaF_2:Ce

C.C. Lopes[a], V.S.M. Barros[a,*], V.K. Asfora[a], M.E. Yamamoto[a], H.J. Khoury[a], P. Guzzo[b]

[a] Nuclear Energy Department, Universidade Federal de Pernambuco, Av. Professor Luiz Freire 1000, Recife, PE 50.740-545, Brazil
[b] Mine Engineering Departament, Universidade Federal de Pernambuco, Av. Moraes Rego s/n, 50670-901 Recife, PE, Brazil

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ABSTRACT

Optically Stimulated Luminescence (OSL) is the luminescence emitted from a previously irradiated with ionizing radiation material by exposure to light. The aim of this paper is to evaluate the Blue Stimulation Luminescence (BSL) and Infra-Red Stimulation Luminescence (IRSL) for CaF_2:Ce produced by the Solution Combustion Synthesis (SCS) method. The results showed that the OSL response of CaF_2:Ce is strongly influenced by post-combustion thermal sintering temperature and dopant concentration. OSL response to dose are of the same order of magnitude of Al_2O_3:C, indicating the possibility of use of this material for radiation dosimetry.

1. Introduction

Optically Stimulated Luminescence (OSL) is the dose-dependent luminescence emitted from a material in response to light of lower wavelength, previously exposed to ionizing radiation. The luminescence intensity is proportional to charge carriers trapped in appropriate sites, which in the band-gap model are represented by delocalized states within the semiconductor gap. This is the key feature that makes OSL a suitable technique for radiation dosimetry applications [1,2]. There are several advantages of OSL dosimetry over thermoluminescence (TL) dosimetry, such as: (a) the readout method is all optical, so there is no need to heat the sample; (b) possible thermal quenching of luminescence is avoided; (c) compact, simple, relatively inexpensive and low energy consuming components [3].

Research on several promising new OSL materials is underway in various laboratories around the world [4–6]. Pure calcium fluoride (CaF_2) is an example of one of these OSL materials that has been recently studied, predominantly in its natural form of fluorite [7–10]. The fluorite structure is interesting as it provides free space for small-sized impurities to modify several of the fluorite properties. However, the use of natural fluorite for dosimetry applications is difficult due to varying types of impurities and concentrations. For this reason, efforts were made to produce synthetic materials with controlled types of dopants and of concentrations.

Various methods have been employed to synthesize doped CaF_2, including sol-gel techniques [11], ion beam implantation [12], sonochemical preparation [13], solvent evaporation [14], electrochemical route [15] and combustion synthesis [6,16,17]. The Solution Combustion Synthesis (SCS) has already been used to investigate new dosimetric materials such as Al_2O_3 undoped or doped with different lanthanides [18–20]. In this technique, which is one of the most attractive due to its simplicity, high efficiency, energy saving and uniform morphology, the heat released from the highly exothermic redox reaction between nitrates and an organic fuel is used for sintering of the material.

The present work we investigate the OSL response of CaF_2:Ce, produced by the Solution Combustion Synthesis (SCS) method, for Blue (BSL) and Infra-red (IRSL) Stimulation Luminescence.

2. Experimental

CaF_2:Ce samples were produced via Solution Combustion Synthesis (SCS) method by mixing stoichiometric amounts of calcium nitrate Ca $(NO_3)_2$ and ammonium fluoride (NH_4F). Cerium nitrate ($CeNO_3$) in a concentration of 0.2 mol% respect to calcium as added as the dopant and urea ($CO(NH_2)_2$) was also added as a fuel. The mixture was placed in a beaker and heated in a hot plate for a few minutes until obtain a thick and transparent gel and then transferred to a muffle furnace (preheated to 565 °C), where spontaneously ignited after one to two minutes. The resulting powder was cold pressed in pellets with 6 mm diameter and 1 mm thickness.

The OSL response was evaluated was measured using an automated Lexsyg Smart OSL reader equipped with an internal $^{90}Sr/^{90}Y$ source with a dose rate of 100 mGy/min and a Hamamatsu H7360-02 bialkaline type photomultiplier tube. For blue light stimulation luminescence (BSL) measurements were acquired using constant illumination intensity mode (CW) with blue LEDs with peak emission at 458 nm and power set to 5 mW/cm^2. This LED power corresponds to 5% of the

* Corresponding author.
E-mail address: vsmdbarros@gmail.com (V.S.M. Barros).

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maximum available power on the Lexsyg reader, since a higher power triggered an overload of the light collection system, which reflects the very high sensitivity of this material. The BSL curves were acquired under constant illumination intensity mode (CW) using the "380 nm filter pack" of the Lexsyg. The "TL-380" filter pack used comprised the BP365-50, LF101581 and KG3 filters. For Infra-red (IR) light stimulation luminescence the "Wide-Band-Blue" filter pack was used composed the BG39, BG25 and KG3 filters.

2.1. Dopant concentration

To evaluate the effect of the Ce concentration in the OSL response of the materials, samples were prepared as described above with dopant concentrations of 0.15, 0.2, 0.4, 0.75 and 1.0 mol%. A fixed irradiation dose of 100 mGy ($^{90}Sr/^{90}Y$ beta source) was used for all measurements, which were made in both IR and Blue stimulations.

2.2. OSL dependence on particle size

Samples were produced using a fixed concentration at 0.2 mol% of Ce and the resulting powder was divided in aliquots according to grain size. Sieves were used in order to select particles with four different grain size ranges: smaller than 75 µm; between 75 and 150 µm; in the 150–180 µm range and above 180 µm. The five aliquots were subjected to Particle Size Analysis (PSA), which were conducted using a Malvern Mastersizer 2000E laser particle size analyzer with a Hidro 2000MU pump accessory of the Mineral Technology Laboratory (LTM-UFPE). Pellets from each grain size range were then prepared for OSL. Again, a fixed irradiation dose of 100 mGy ($^{90}Sr/^{90}Y$ beta source) was used for all measurements, which were made in both IR and Blue stimulations.

2.3. Post-combustion thermal sintering

A new batch of CaF_2:Ce powder was produced by SCS with dopant concentration fixed at 0.20 mol%. The resulting powder was subjected to Differential Thermal Analysis/Thermal Gravimetric Analysis (DTA/TGA). The objective of TGA is to record mass changes while DTA aims to record the endothermic and exothermic peaks by comparison with an inert reference sample during temperature increase at a constant rate. The analysis were carried out using a DTG-60H Simultaneous TG/DTA detector of the Mineral Technology Laboratory (LTM-UFPE) in a temperature range of 20–900 °C, a heating rate of 10 °C/min, with nitrogen flow. The analysis of the DTA-DTG curves was used to aid in establishing, non-randomly, appropriate sintering temperature intervals. As shown in Fig. 1 the TGA curve presents one major weight loss inflection in the 380–600 °C range. DTA analysis exhibits two endothermic peaks occurring at the temperatures of 516 and 808 °C. Based on the results, sintering temperatures of 0, 100, 200, 300, 400, 600 and 750 °C were selected for further studies of OSL response as a function of heat treatment temperature of CaF_2:Ce. All the pellets were irradiated at 100 mGy ($^{90}Sr/^{90}Y$ beta source). OSL was measured in both IR and Blue stimulations.

2.4. Dose response and residual TL after OSL

For dose response comparison with a well-established OSL dosimeter, two carbon doped α-alumina single crystals dosimeters were measured using the same experimental parameters. Samples were irradiated at the same dose of 500 mGy ($^{90}Sr/^{90}Y$ beta source) for comparison. For readout both IR and Blue stimulation was used under the same parameters already described.

Residual thermoluminescent (TL) glow curves were recorded after BSL acquired after different stimulation times from 1 to 10 s. Temperature was increased from 50° to 350 °C at a heating rate of 2.0 °C/s, channel time was set to 1 s and a Wide-Band-Blue filter pack was used for all TL measurements. For the residual TL after IRSL, glow curves were acquired after optical stimulation times from 3 to 30 s. The TL parameters were the same as those used for BSL. The dose was fixed at 500 mGy ($^{90}Sr/^{90}Y$ beta source) for all measurement cycles.

3. Results and discussion

3.1. Dopant Concentration

The influence of the Ce concentration on the sensitivity of samples irradiated with 100 mGy is shown in Fig. 2. A dopant concentration of 0.2 mol% maximizes the luminescent intensity and is similar to the optimal concentration (0.15 mol%) found for Tm doped CaF_2 for both TL [17] and OSL [16] techniques. Lower OSL responses at concentrations higher than 0.2 mol% are probably related to rare-earth concentration quenching.

3.2. OSL response versus particle size analysis

Particle Size Analysis (PSA) distributions are shown in Fig. 3 for non-sieved (yellow) and sieved samples with resulting particle sizes: (a) smaller than 75 µm; (b) between 75 and 150 µm; (c) in the 150–180 µm range and (d) above 180 µm. The non-sieved samples show a wide distribution from ~20 to ~830 µm with maxima at ~360 µm.

The OSL response for each particle size range and for IRSL and BSL was measured. From each particle size range (a-d) pellets were produced and the OSL response was defined as the integrated area under the decay curve from 0 to 60 s. Both BSL and IRSL intensities were maximized for the 150–180 µm range (Vol. Weight. Mean = 158 µm)

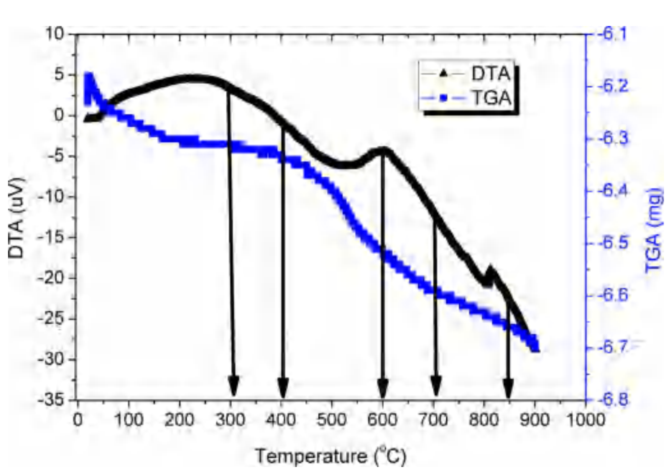

Fig. 1. DTA/TGA curves obtained for Cerium 0.2% doped CaF2.

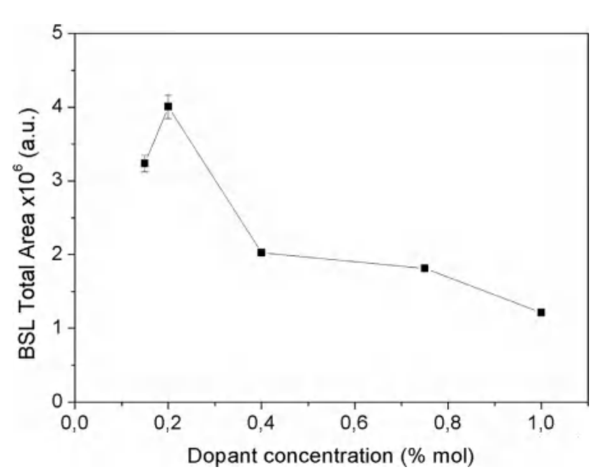

Fig. 2. Effect of different Ce dopant concentrations on the BSL response.

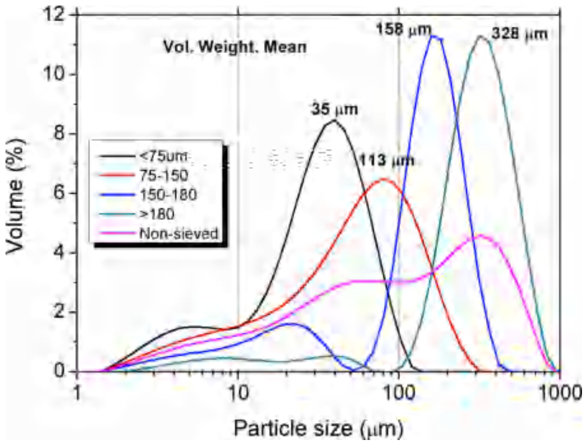

Fig. 3. Particle Size Analysis (PSA) for CaF2: Ce.

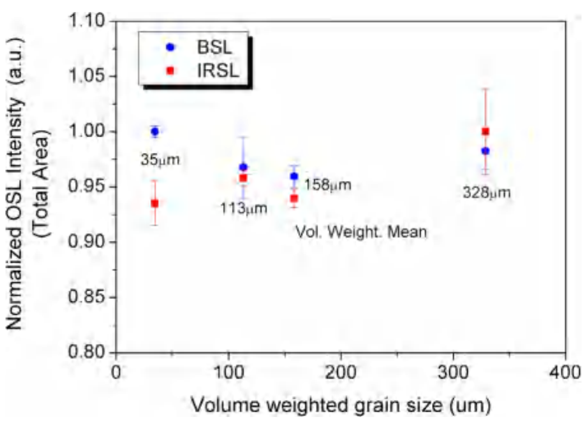

Fig. 4. Effect of particle size on the OSL response.

and varies − 10% to − 20% for smaller and larger grain sizes (Fig. 4). The Volume Weighted Mean, calculated from each distribution shown in Fig. 3, was used to correlate to the OSL response.

3.3. OSL response after thermal sintering

Fig. 5 shows the BSL and IRSL Ce 0.2% doped CaF_2 samples. The luminescent responses for both BSL and IRSL, as a function of the sintering temperature, showed a higher OSL sensibility when the sample was treated at 200 °C. For temperatures at approximately 400 °C, the sensitivity of the sample decays, and for higher temperatures, the sample loses its luminescent response. This loss in sensitivity is not observed in CaF_2 doped with other RE materials [6,17] but has been reported for natural fluorite materials [21] where Ce is a commonly found impurity and is responsible for a high OSL response.

3.4. OSL dose response and Residual TL

BSL Dose Response curves of CaF_2:Ce and α-Al_2O_3:C are shown in Fig. 6a for BSL and in Fig. 6b for IRSL. The BSL sensitivity was found to be higher than IRSL for these samples. In dosimetry, the total area is frequently used to relate the reference radiation quantity (eg. kerma, personal dose equivalent Hp(d) etc.) to the response of the material. Therefore, the results indicate that both IR and blue LED stimulation could be used in dosimetry applications. The comparison between blue and IR is not straight forward since: (a) the filter packs used in front of the PMT tube depend on the wavelength of the LEDs so that the stimulation light does not directly excite the PMT; (b) a change in filter pack changes the amount of dose dependent-light collected from the sample; (c) the maximum power of available IR LED array on the Lexsyg

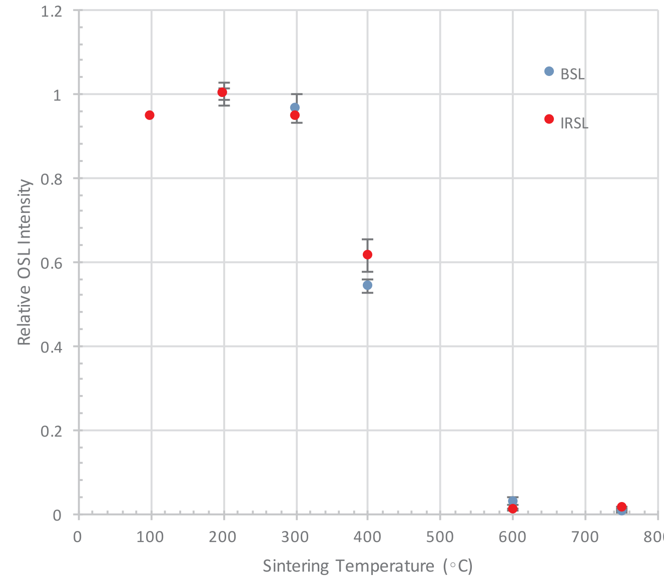

Fig. 5. Effect of the post combustion sintering temperature on the OSL response.

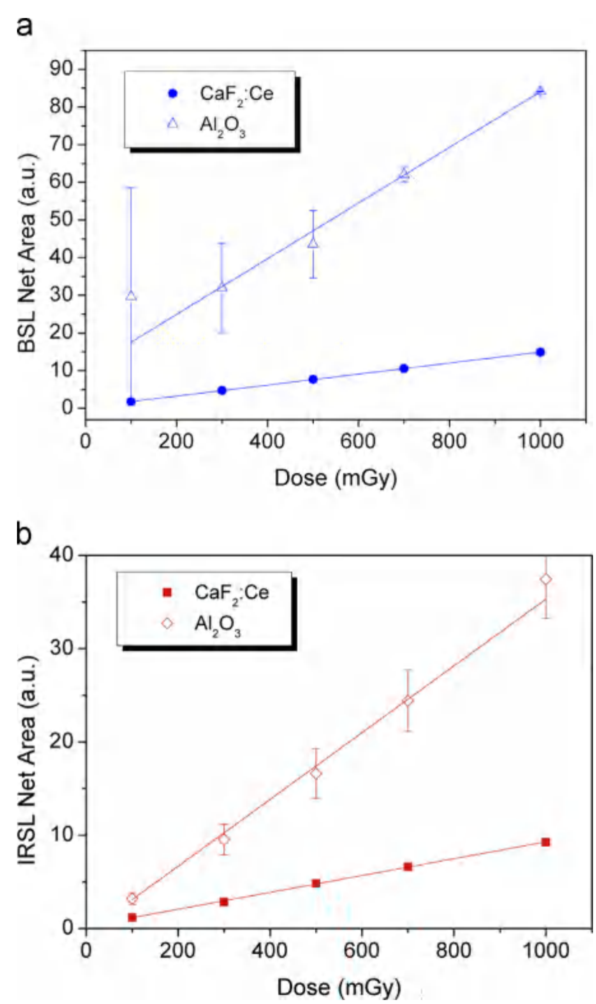

Fig. 6. Dose response of BSL and IRSL.

reader is also 2.5 times higher than for the blue array. These issues are more appropriately addressed in a later stage of the development of a dosimetric material when the minimum measurable dose (MMD) for

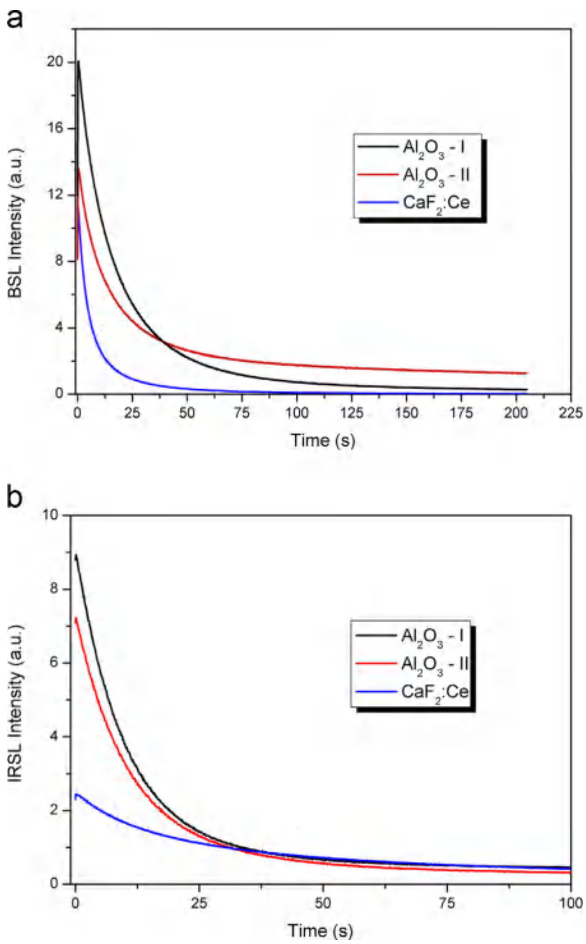

Fig. 7. (a) IRSL and (b) BSL decay curves for sintered CaF2:Ce and two different samples of α-Al2O3: C.

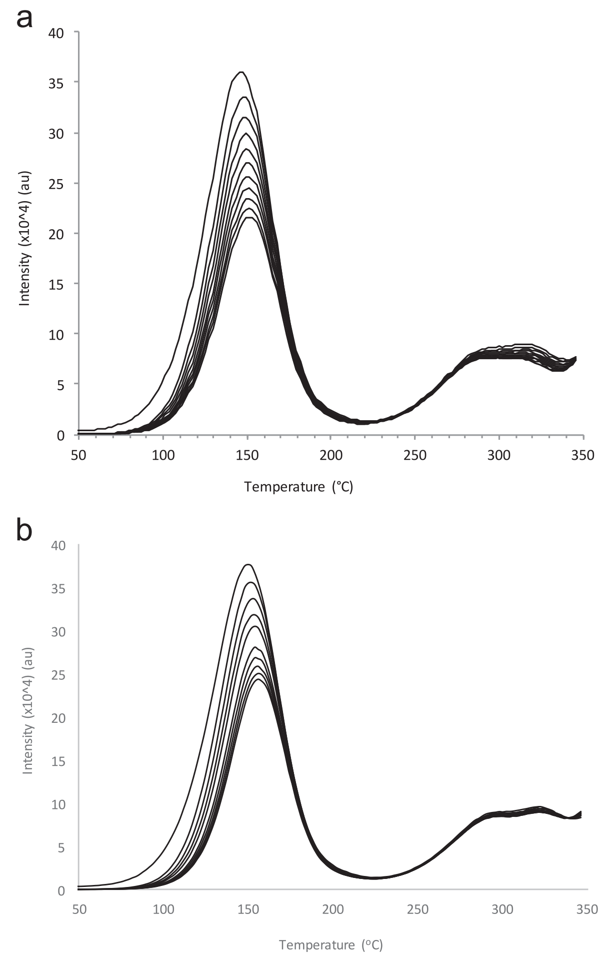

Fig. 8. (a) Residual TL after blue LED stimulation for 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 s, from top to the bottom for sintered CaF2: Ce. Beta irradiation dose was fixed at 100 mGy for all measurements; (b) Residual TL after IRSL stimulation for 3, 6, 9, 12, 15, 18, 21, 24, 27 and 30 s, from top to the bottom for sintered CaF2: Ce.

each illumination scheme are determined.

Studies were made in order to compare BSL and IRSL responses of CaF_2:Ce with decay curves for two different samples of czochralsky grown α-Al_2O_3:C crystal pellets. As shown in Fig. 7, the area under the exponential decay curve for α-Al_2O_3:C is slightly larger than for CaF_2:Ce. Shallow traps interference are more noticeable in α-Al_2O_3:C which is observable by the build–up of the OSL signal at the beginning of the emission and by a slow and hard-to-bleach component. Simpler decay curves are more desirable for dosimetry applications since the area below the curve is more easily defined. The effective area below the IRSL and BSL for CaF_2:Ce is around 9 times smaller when compared to α-Al_2O_3:C for BSL and around 5 times smaller for IRSL. However, as shown in Fig. 6, the influence of shallow traps is greater in α-Al_2O_3:C and therefore nonlinearities and higher uncertainties at low doses occur.

Residual TL measurements after BSL were performed with a fixed beta irradiation dose of 100 mGy, varying the LED stimulation time from 1 to 10 s. Beta irradiation dose was fixed at 100 mGy for all measurements. For the residual TL after IRSL, measurements were performed after stimulation of 3, 6, 9, 12, 15, 18, 21, 24, 27 and 30 s with a power set to 150 mW/cm^2 and the irradiation fixed at a dose of 100 mGy. TL glow curves are shown in Fig. 8-a for BSL and Fig. 8-b for IRSL, where it is observed the TL intensity reduction behavior over time only on the main dosimetric peak (centered around 150 °C). On the other hand, for peaks centered around 280–320 °C, increasing time practically does not change significantly the TL intensity. After 30 s of stimulation, the integration of Residual TL after IRSL gives a total area for sintered CaF_2:Ce approximately three times smaller than the area underneath the Residual TL after BSL curves.

4. Concluding remarks

Results suggests SCS-CaF_2:Ce has a good potential for OSL ionizing radiation dosimetry applications. Compared with the successful OSL dosimeter Al_2O_3:C, the CaF_2:Ce showed a similar response both for BSL and IRSL. A linear dose response for BSL stimulation was acquired and high OSL responses for both BSL and IRSL methods were also measured. Further dosimetric studies still have to be done in order to confirm the SCS-CaF_2:Ce material as a dosimeter.

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