



Thermoluminescent properties of $\text{LaAlO}_3\text{:C}$ crystals synthesized by solid state reaction applied to UV Dosimetry

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ABSTRACT

In this work, the thermoluminescent (TL) response of carbon doped lanthanum aluminate crystals grown by solid state reaction method was investigated. Three syntheses using different combinations of Al_2O_3 , La_2O_3 and 0.1 wt % of carbon atoms were conducted. The 1:1 mixture of aluminum and lanthanum oxide was mixed with 0.1wt.% carbon and annealed at 1700°C for two hours in a hydrogen atmosphere. The X-ray diffraction analysis revealed the formation of the rhombohedral LaAlO_3 crystallographic phase. Ultraviolet-visible spectroscopies were obtained and F and F^+ centers were identified ascribed. Fourier transform infrared spectroscopic data show higher and lower frequencies assigned to AlO_6 octahedra in LaAlO_3 . The UV irradiations were carried out using a commercial 8W UV lamp. Thermoluminescence measurements were performed at a Harshaw 4500 TL reader. The three syntheses were very efficient to obtain carbon doped LaAlO_3 crystals with high thermoluminescent output, for low exposure rates of UVR fields.

Keywords: Lanthanum aluminate, thermoluminescence, ultraviolet radiation.

1. INTRODUCTION

Lanthanum aluminate is a ceramic compound that has a perovskite-like crystalline structure. Materials with these properties find use in several technological applications due to their special electrical and magnetic properties. These include insulators and superconductors, ferroelectric crystals and the use as a substrate for superconductors of high critical temperature, among others [1; 2]. Perovskite-type ceramics (ABO_3) have received much attention because of its unique crystalline structure. It may accommodate a large distribution range of cation sizes in their sublattices [3]. Oxygen vacancies may be generated in order to compensate the charge of substituting ions, enabling the aliovalent cations to be distributed in both A and B sites cation sublattices. The oxygen vacancies concentrations are directly related to the enhancement of TL sensibility, because these vacancies result in charge trapping [4; 5].

Exposure to ultraviolet radiation (UVR), in particular from the sun's rays, is a significant public health hazard and may increase with further depletion of the ozone layer. The possible health hazards range from short term effects, such as sunburn and eye damage, to chronic effects, such as skin cancer and melanoma or cataracts. Exposure to sunlight is the major cause of UVR exposure, but there are few artificial sources that result in human exposure to UVR greater than that from the sun. The spectrum of the UVR emitted from artificial sources varies from one source to another [6].

Ultraviolet radiation measurement using thermoluminescent materials has been suggested by many authors [7; 8; 9]. The interest in the synthesis of new TL materials has been increasing, mainly because of their reading easiness when compared to other techniques [10].

The thermoluminescence (TL) effect has been suggested for the evaluation of ionizing radiation doses since 1953[11]. A considerable number of various chemical compositions have been investigated since then, in order to find the explanation of mechanisms for this effect and to discover promising TL phosphors for different dosimetry purposes. In TL materials, energy from radiation is stored in their crystal lattice by the trapping of released free electrons and holes. The electron and hole traps are due to lattice defects in the material [12]. Normally thermoluminescence is obtained by doping the crystal lattice of ionic crystals with impure atoms that in turn behave as electronic

traps. When the TL material is exposed to ionizing radiation, electrons are released from the valence band becoming free to move through the crystal lattice. Most of these free electrons recombine immediately with the ionized atoms in the valence band. However, a small amount is captured in the electronic traps, being after released when a constant heating rate is supplied to the material, emitting light when they return to the valence band. The amount of emitted light is then proportional to the radiation dose [2]. The main goal of dosimetric devices is to determine the quantity of energy per unit mass of material (dose) that has been absorbed during the irradiation, thereby leading to applications such as personal and environmental dosimetry, diagnostic imaging and computed radiography [13].

The first investigation, concerned to the TL properties of LaAlO_3 applied to radiation dosimetry, has been recently reported [14; 15]. The $\text{LaAlO}_3:\text{Ce,Dy}$ crystals present high TL output for UV radiation fields, comparable to the TL output of the best dosimeters ever reported in literature, i.e. $\text{Al}_2\text{O}_3:\text{C}$ and ZrO_2 crystals [15]. It is well known that carbon doped aluminum oxide single crystals have excellent TL and photoluminescent response properties for X-rays, UV and gamma radiation fields [12; 16]. Thus, we conducted three different syntheses of LaAlO_3 by the solid state reaction method, doping the mixture with 0.1 wt% of carbon atoms. In the present study we have investigated the TL properties of polycrystalline $\text{LaAlO}_3:\text{C}$ exposed to UV fields.

2. MATERIALS AND METHODS

Lanthanum aluminate polycrystals were synthesized by solid state reaction method by mixing equimolar ratios of aluminum oxide (Vetec, 99.99%) and lanthanum oxide (Alfa, 99.98%). The mixed powder was weighed and, then, manually grinded in agate mortar with 0.1 wt. % of carbon atoms. The schematic diagrams illustrating the mixing and sintering procedures are shown in Fig. 1. The first methodology used is presented in Fig. 1(a), where aluminum oxide and lanthanum oxide were grounding in an agate mortar together with 0.1 wt.% of graphite and, then, the mixture was sintered in hydrogen atmosphere at 1770 °C for 2 hours. In the second methodology, schematized in Fig. 1(b), Al_2O_3 powder was mixed with 0.1 wt.% of carbon and sintered for 2 hs at 1770 °C. The

resulting powder was reground with La_2O_3 and sintered for 2 hours again at 1770°C . The third methodology, shown in Fig. 1(c), La_2O_3 powder was mixed with 0.1 wt.% of carbon and sintered at the same conditions above. The resulting powder was reground with Al_2O_3 and sintered again. The samples obtained using the methodology depicted on the diagrams were denominated according to Table 1.

Figure 1. Schematic diagrams illustrating the mixing and sintering procedures used to produce different $\text{LaAlO}_3:\text{C}$ polycrystals samples.

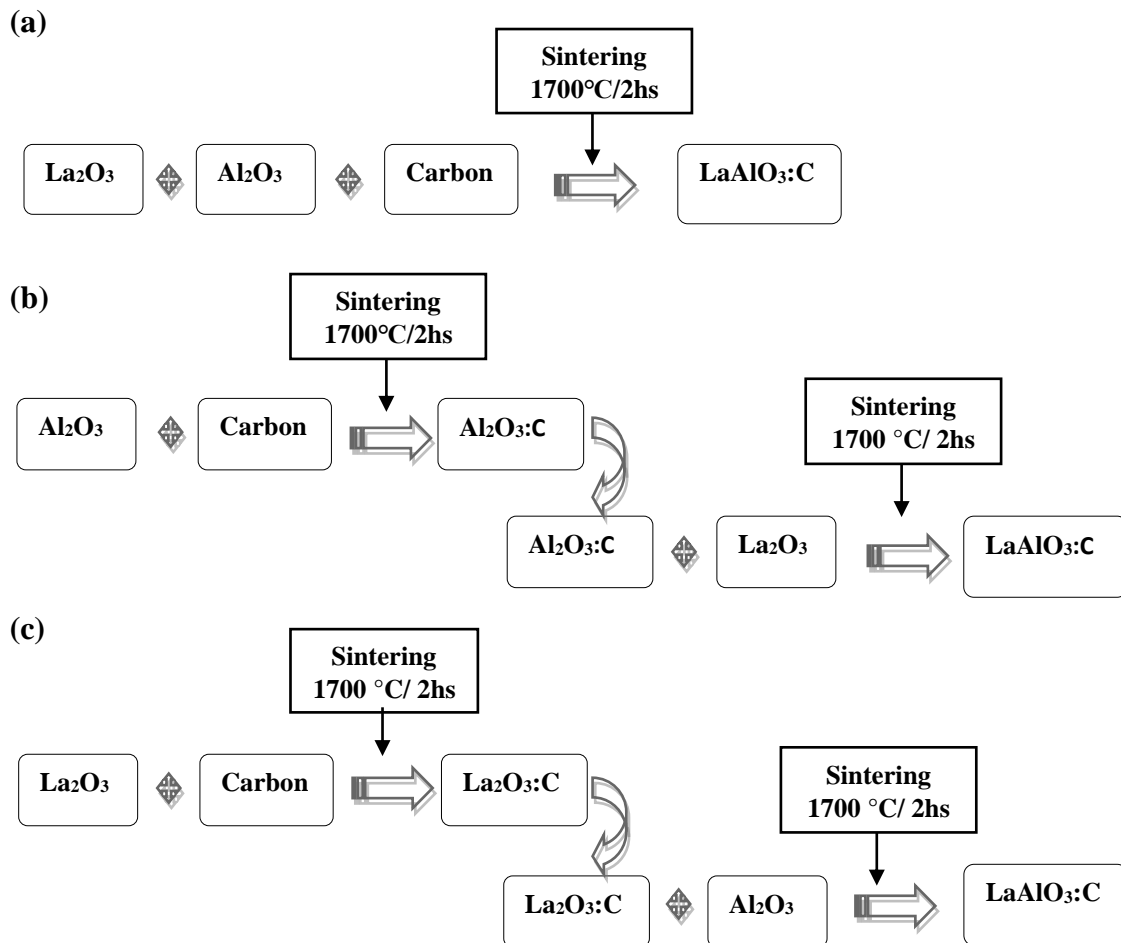


Table 1: Synthesis methodology and sample denomination.

| Sample Denomination | Methodology | Resulting Crystal |
|---------------------|--|-----------------------|
| SA | La ₂ O ₃ + Al ₂ O ₃ + Carbon | LaAlO ₃ :C |
| SB | Al ₂ O ₃ :Carbon + La ₂ O ₃ | LaAlO ₃ :C |
| SC | La ₂ O ₃ :Carbon + Al ₂ O ₃ | LaAlO ₃ :C |

All samples were annealed at 950 °C for 30 minutes, in order to remove captured charge carriers from trap centers, as suggested by LARSEN, N. A. (1999) [13]. In order to confirm the formation of the LaAlO₃ phase, the samples crystalline structure was analyzed by using Regaku D/Max ÚLTIMA X-ray diffractometer. The CuK α radiation was used and the scanning rate was set at 0.02 °/s at 2 θ ranging from 4 and 80°. The absorption spectra of carbon doped LaAlO₃ were taken in a SHIMADZU spectrophotometer model UV–2401pc, in the 190-900 nm wavelength range. All measurements were performed at room temperature. The FTIR spectra were collected by using a Bomem 100 spectrometer and the readout was performed with spectral resolution of 4 cm⁻¹ and 32 scans, for wavenumbers ranging from 400 to 4000 cm⁻¹. The powder samples were pressed with KBr in order to be analyzed. The UV irradiation was performed using a commercial 8W UV fluorescent lamp. The spectral irradiance at the lamp surface was 2.98 mJ/cm², measured using a calibrated radiometer UVX100 E-22476 with a 254 nm sensor. The thermoluminescent analysis was performed using a Harshaw TLD-4500 TL reader. The glow curves were taken using a heating rate of 15 °C/s with maximum temperature of 300 °C.

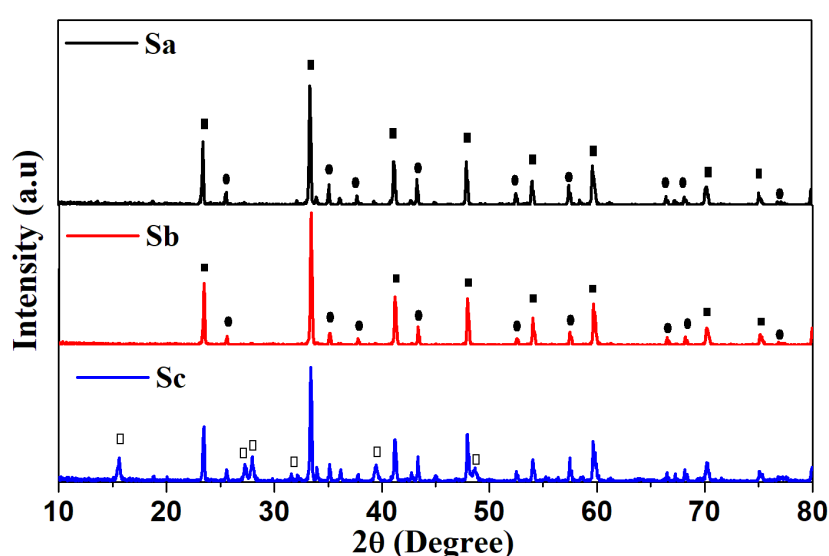
3. RESULTS AND DISCUSSION

The purpose of growing a crystalline material in reducing atmosphere is to induce a large concentration of oxygen vacancies into the crystal lattice. When these vacancies are occupied by strange atoms in the crystalline structure, some of them may create electronic trappers. At this point, they are directly related to the thermoluminescence sensitivity [4]. It is well known that oxygen vacan-

cies may form F^+ centers in Al_2O_3 by doping with carbon atoms during the crystal growth, in highly reducing atmosphere. This is due to the charge compensation of divalent carbon ion substituting trivalent Al^{3+} ions [16; 17]. Occupancy of an oxygen vacancy by two electrons gives rise to a neutral F center, whereas occupancy by one electron forms a positively charged center, with respect to the lattice (F^+ center). F and F^+ centers are known to play a key role in the high thermoluminescent output of Al_2O_3 . It was found that, increased F^+ centers concentration in $Al_2O_3:C$ causes significant increase in OSL and TL sensitivity [16; 18]. In order to enhance the oxygen vacancy production, the polycrystalline lanthanum aluminate was sintered at hydrogen atmosphere and doped with hyper-pure carbon, by mechanic mixture with 0.1 wt.%.

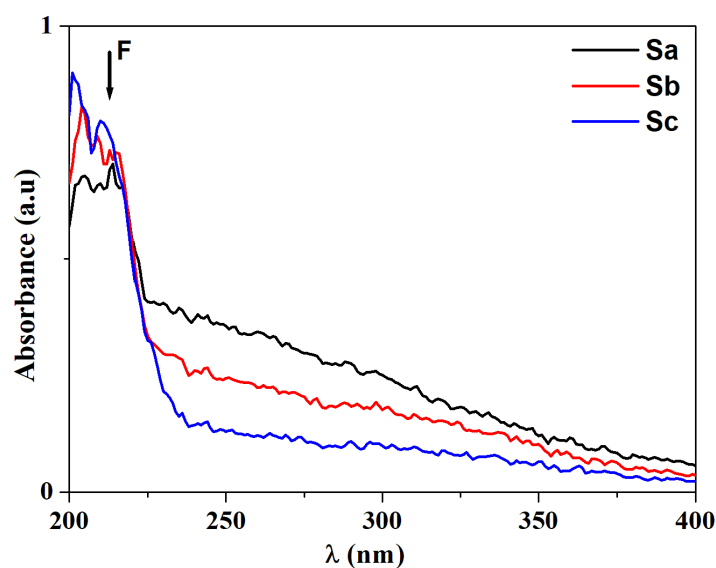
The XRD patterns diffractograms of samples produced by the three different synthesis are shown in Fig. 2. The X-ray diffraction analysis revealed the nucleation of rhombohedral $LaAlO_3$ (JCPDS 31-0022) crystallographic phase, however a small percentage (15%) of Al_2O_3 (JCPDS 10-0173) has been also identified in all compositions. One of them ("SC" sample) also presented peaks (17%) assigned to lanthanum hydroxide phase (JCPDS 36-1481) [19].

Figure 2: XRD patterns for the $LaAlO_3:C$ grown by different synthesis: (■) assigned to rhombohedral phase Lanthanum aluminate ($LaAlO_3$), (●) assigned for aluminum oxide (Al_2O_3) and (□) for lanthanum hydroxide ($La(OH)_3$).

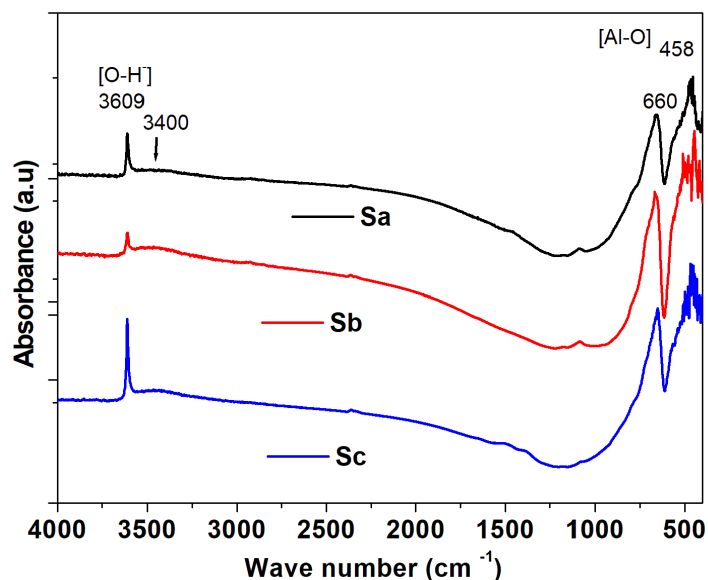


In Fig. 3, the correspondent absorption spectra of carbon doped lanthanum aluminate grown by three different methodologies are displayed. An absorption band centered at 206 nm has been observed in all samples. In this context, we remark that it is well known that LaAlO_3 crystals have strong band-to-band absorptions for wavelengths ranging from 190 to 220 nm [20]. This absorption region is assigned to F center formation. These bands are due to high concentrations of oxygen vacancies induced by high reducing atmosphere, just as it has been described for the production of $\text{Al}_2\text{O}_3:\text{C}$ crystals. [21; 22]. A large absorption band at 230-350 nm is observed for every sample, however with different intensities. In this Figure it isn't possible to clearly observe the bands associated to F^+ center.

Figure 3. The UV-Vis absorption spectra of unirradiated $\text{LaAlO}_3:\text{C}$ polycrystals. The absorption bands attributed to F centers are highlighted.

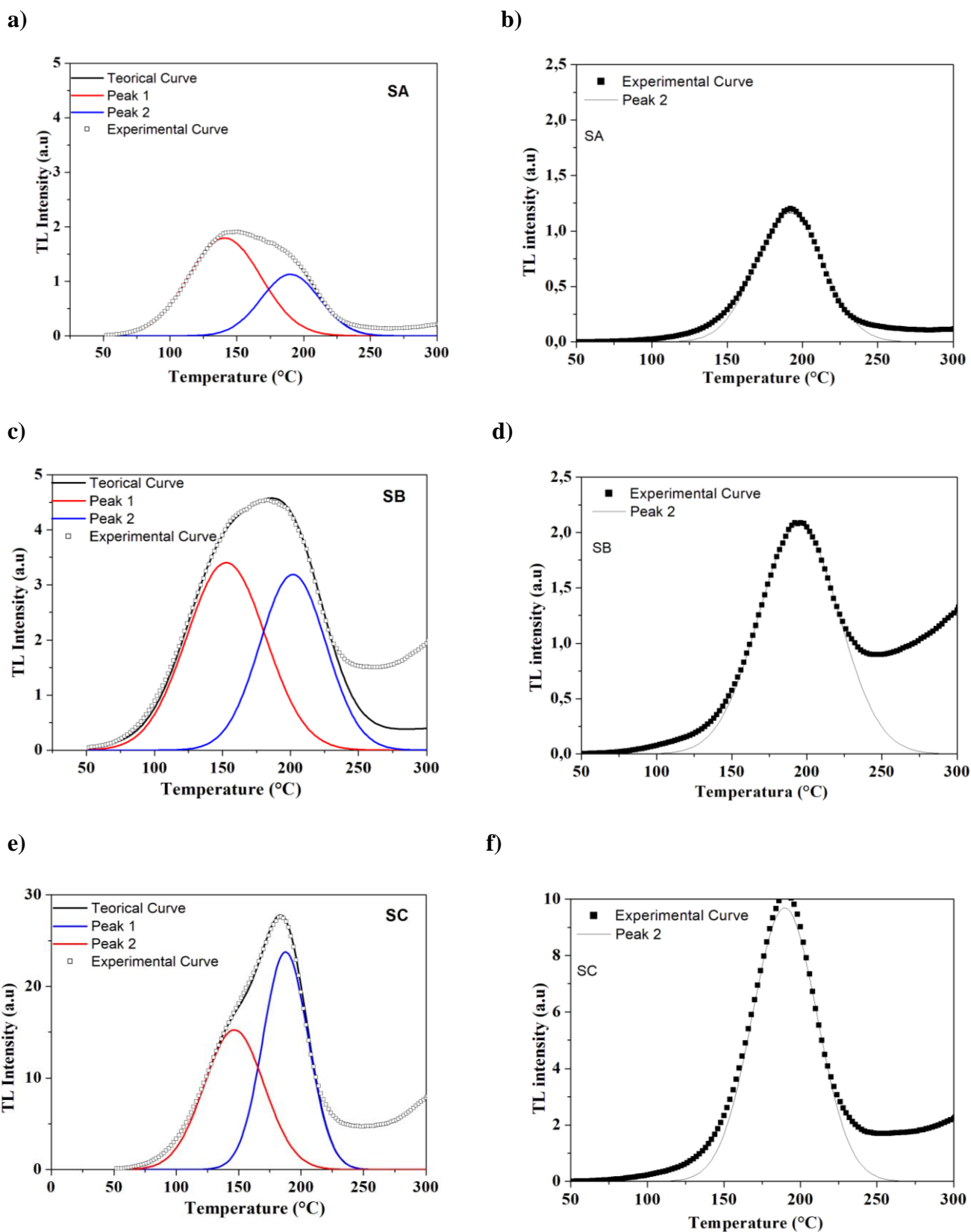


The FTIR spectra collected to all samples, for wavenumbers ranging from 400 to 4000 cm^{-1} , are shown in **Fig. 4**. In these spectra, it is possible to observe the specific absorption bands centered at 458, 660 and 3609 cm^{-1} . The two first bands are assigned to AlO_6 octahedra in LaAlO_3 [23]. The last one it is a stronger band, indicating the presence of $\text{La}(\text{OH})_3$ [24].

Figure 4. FTIR spectra for $\text{LaAlO}_3:\text{C}$ samples.

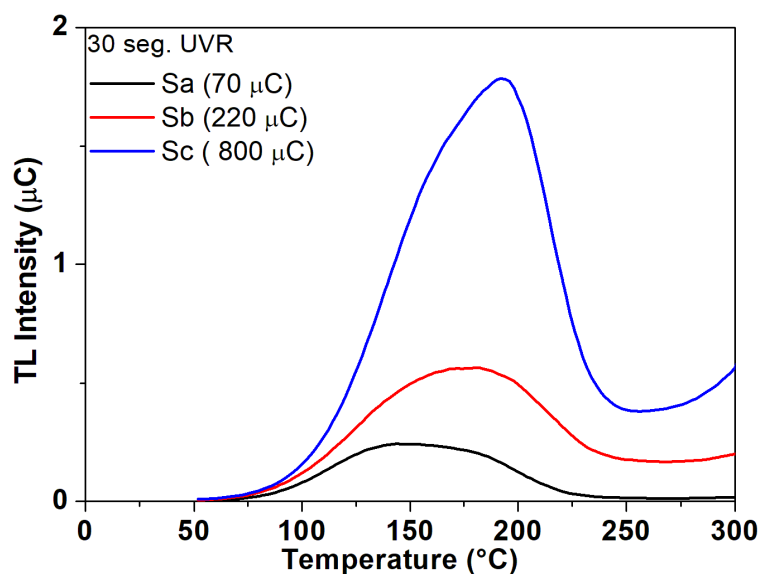
As reported by Larsen (1999) [13], before performing the irradiation and reading process, samples should be annealed with a thermal treatment at 950 °C for 30 minutes, in order to remove captured charge carriers from trap centers. After performing this annealing, the samples were irradiated using a commercial UV fluorescent lamp and, subsequently, the TL glow curves for samples produced by the three syntheses were collected. In Fig. 5.(a), 5.(c) and 5.(e) we see the TL glow curves taken immediately after 30 seconds of UV irradiation. Two individual TL peaks, the first at 145 °C and the second at 190 °C, obtained by peak-fitting using Gaussian lines are also shown in these figures. As it can be seen, the two peaks are common to the three methodologies tested. Although the shape of the glow curves is quite similar, it is possible to observe changes in the relative intensities of the individual peaks. On the other hand, in Fig. 5.(b), 5.(d) and 5.(f) we show the TL glow curves collected 24 hours after UV irradiation. It is clear from these curves that the peak centered at 145 °C fades completely within the first 24 hours after exposure radiation. Together with the experimental curves we have plotted the individual TL peak obtained after peak-fitting. This peak-fitting was performed using PeakFit® v.4, giving a correlation coefficient $r^2 = 0,99996$.

Figure 5. Figures 5.(a), 5.(c) and 5.(e) : TL glow curves taken immediately after 30 seconds of UV irradiation and two individual TL peaks obtained by peak-fitting using Gaussian lines. Figures 5.(b), 5.(d) and 5.(f): TL glow curves collected 24 hours after UV irradiation.



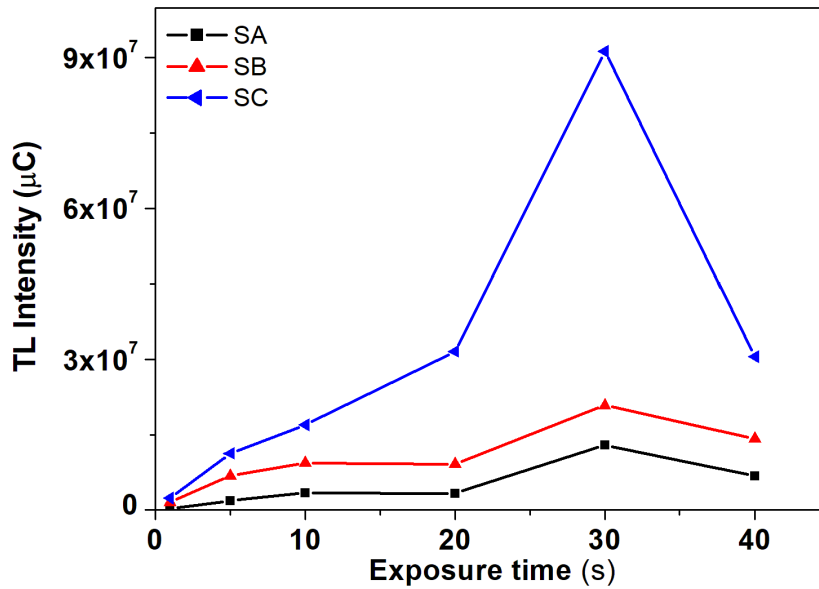
In Fig.6, the TL glow curves obtained immediately after the thirty seconds of UV irradiation are presented. The electronic charge measured by the photomultiplier tube was 70 and 220 μC for the samples SA and SB, respectively. These values are proportional to the area under the glow curve. The higher TL output signal is presented for SC sample with 800 μC . This sample was obtained by the methodology shown in diagram C on Fig. 1. We remark that the electric charge collected at the Photomultiplier Tube (PMT) per irradiance unit, for Sc sample, is $635\mu\text{C}/\text{mJ}\cdot\text{cm}^{-2}$. For comparison purposes, this rate measured for $\text{LaAlO}_3:\text{Ce},\text{Dy}$ single crystal is only $0.430\mu\text{C}/\text{mJ}\text{cm}^{-2}$ and $293\mu\text{C}/\text{mJ}\text{cm}^{-2}$ for undoped LaAlO_3 synthesized samples, irradiated at the same conditions and read at the same TL reader, after 30 seconds of exposition [15; 25]. We see that TL sensitivity to UV photons for $\text{LaAlO}_3:\text{C}$ from SC sample is much higher than those for $\text{LaAlO}_3:\text{Ce},\text{Dy}$ grown under hydrothermal conditions and for undoped LaAlO_3 synthesized under reducing atmosphere.

Figure 6. Thermoluminescent glow curves for $\text{LaAlO}_3:\text{C}_{0.1\%}$ exposed to 30 second UVR.



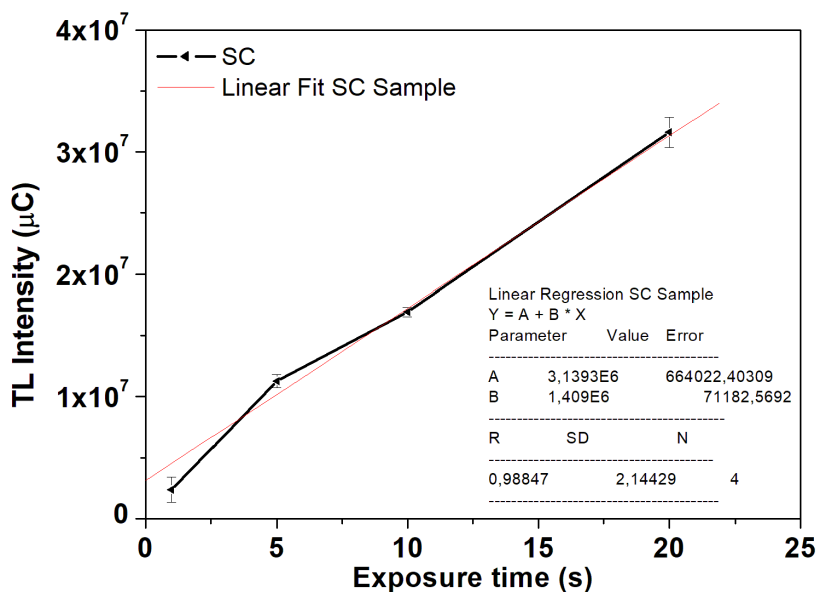
The thermoluminescence response of TL materials, commonly used in radiation dosimetry, is directly related to the amount of absorbed radiation dose. In order to check if there is a linear relationship between TL output and the irradiation exposure time, the samples were irradiated by different exposure times from 1 to 40 seconds. After 40 seconds of irradiation the maximum saturation is achieved. The corresponding TL intensities and exposure time are shown in Fig. 7.

Figure 7. Maximum TL response of samples $LaAlO_3:C_{1\%}$, as a function of the exposure time.



The best TL response for UV fields was found to SC sample. On the other hand, the corresponding linear fitting for the sample SC is shown in Fig. 8. The selected points in these curves are corresponding to 1, 5, 10 and 20 seconds, which provided a correlation coefficient equal to 0.98847.

Figure 8. TL output intensities for SC sample between 1 – 20 seconds of UV exposure, and the corresponding linear fitting (red line).



We believe the higher TL output for SC sample is due to the synthesis methodology and also to the presence of lanthanum hydroxide crystals into the sample. We intend to explore more carefully these compositions making some characterizations in order to obtain an ideal material for TL dosimetry in ultraviolet fields.

4. CONCLUSION

We report an investigation about synthesis of lanthanum aluminate powders. Crystals were grown via state solid reaction by three different combinations of Al_2O_3 , La_2O_3 and 0.1% of carbon atoms, during the synthesis process. According to the thermoluminescent investigation, the composition with the better TL output was lanthanum aluminate SC sample obtained by the La_2O_3 :Carbon + Al_2O_3 synthesis sequence, i.e. where La_2O_3 powder was mixed with 0.1 wt.% of carbon and sintered for 2 hs at 1700 °C, and the resulting powder was reground with Al_2O_3 and sintered for 2 hours again at 1770 °C. The others compositions also have good TL response, but less than the previously mentioned. We conclude that the synthesis was very efficient to obtain carbon doped LaAlO_3 crystals with high thermoluminescent intensities for low exposure rates of UVR fields. We believe that carbon doped lanthanum aluminate has great potential for application in UV dosimetry.

5. ACKNOWLEDGMENT

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