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CARBON DOPED LANTHANUM ALUMINATE ($LaAlO_3$:C) SYNTHESIZED BY SOLID STATE REACTION FOR APPLICATION IN UV THERMOLUMINESCENT DOSIMETRY

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ABSTRACT

In this work we discuss the TL output for $LaAlO_3$:C crystals grown by using three different combinations of Al_2O_3, La_2O_3 and carbon atoms during the synthesis process. Recently, $LaAlO_3$ single crystals, co-doped with Ce^{3+} and Dy^{3+} rare earth trivalent ions and grown under hydrothermal conditions, have been reported to show high thermoluminescent response (TL) when exposed to low levels of ultraviolet radiation (UVR). However, undoped $LaAlO_3$ synthesized by solid state reaction method from the 1:1 mixture of aluminum and lanthanum oxide under reducing atmosphere revealed to have still higher thermoluminescent sensitivity to UV photon fields than the co-doped with Ce^{3+} and Dy^{3+}. It is well known that carbon doped aluminum oxide monocrystals have excellent TL and photoluminescent response properties for X-rays, UV and gamma radiation fields. Thus, we conducted three different syntheses of $LaAlO_3$ by this solid state reaction method, doping the mixture with carbon. The lanthanum aluminate polycrystals were synthesized from the 1:1 mixture of aluminum and lanthanum oxide, adding 0.1wt.% carbon and annealed at 1700°C for two hours in hydrogen atmosphere. The X-ray diffraction analysis revealed the formation of rhombohedral $LaAlO_3$ crystallographic phase, however a small percentage (15%) of Al_2O_3 has been also identified. The UV-Vis absorbance spectra were obtained and F and F^+- center were ascribed. The UV irradiations were carried out using a commercial 8W UV lamp. Thermoluminescence measurements were performed at a Harshaw 4500 TL reader. All compositions investigated have shown high TL sensitivity to UVR.

1. INTRODUCTION

The thermoluminescence (TL) effect has been suggested for the evaluation of ionizing radiation doses since 1953 [1]. 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 [2]. 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 [3].

Lanthanum aluminate is a ceramic compound that has a perovskite-like crystalline structure. Materials with these properties are utilized for 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 [4; 5]. Perovskite-type ceramics (ABO_3) have received much attention because this unique crystalline structure can accommodate a large distribution range of cation sizes in their sublattices [6]. Oxygen vacancies can be generated to compensate the charge of substituting ions, enabling the aliovalent cations to be distributed in both A and B site cation sublattices. The oxygen vacancies concentration are directly related to the enhancement of TL sensibility, because these vacancies result in charge trapping [7; 8].

The first investigation concerned to the TL properties of $LaAlO_3$ applied to radiation dosimetry have been recently reported [9]. The investigation revealed that $LaAlO_3$: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. Al_2O_3:C and ZrO_2 crystals. On the other hand, lanthanum oxide (La_2O_3) was suggested as a new ultraviolet radiation dosimeter for the first time in 2010. It presented very closely some of the ideal criteria for a TL dosimetric material [10].

It is well known that carbon doped aluminum oxide monocrystals have excellent TL and photoluminescent response properties for X-rays, UV and gamma radiation fields. Thus, we conducted three different syntheses of $LaAlO_3$ by this solid state reaction method, doping the mixture with carbon. In the present study we have synthesized and investigated the TL properties of polycrystalline $LaAlO_3$ doped with 0.1 wt. % of carbon atoms. The samples were synthesized by the solid state reaction method under high reducing atmosphere. We discuss the TL output for $LaAlO_3$:C crystals grown by using three different combinations of Al_2O_3, La_2O_3 and carbon atoms during the synthesis process

2. EXPERIMENTAL PROCEDURE

2.1. Lanthanum aluminate

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. In order to investigate the influence of the mixing methodology in the TL output of carbon doped lanthanum aluminate, the samples were produced using three different combinations of Al_2O_3, La_2O_3 and carbon atoms on the synthesis process. After the

synthesis final stage 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) [3].

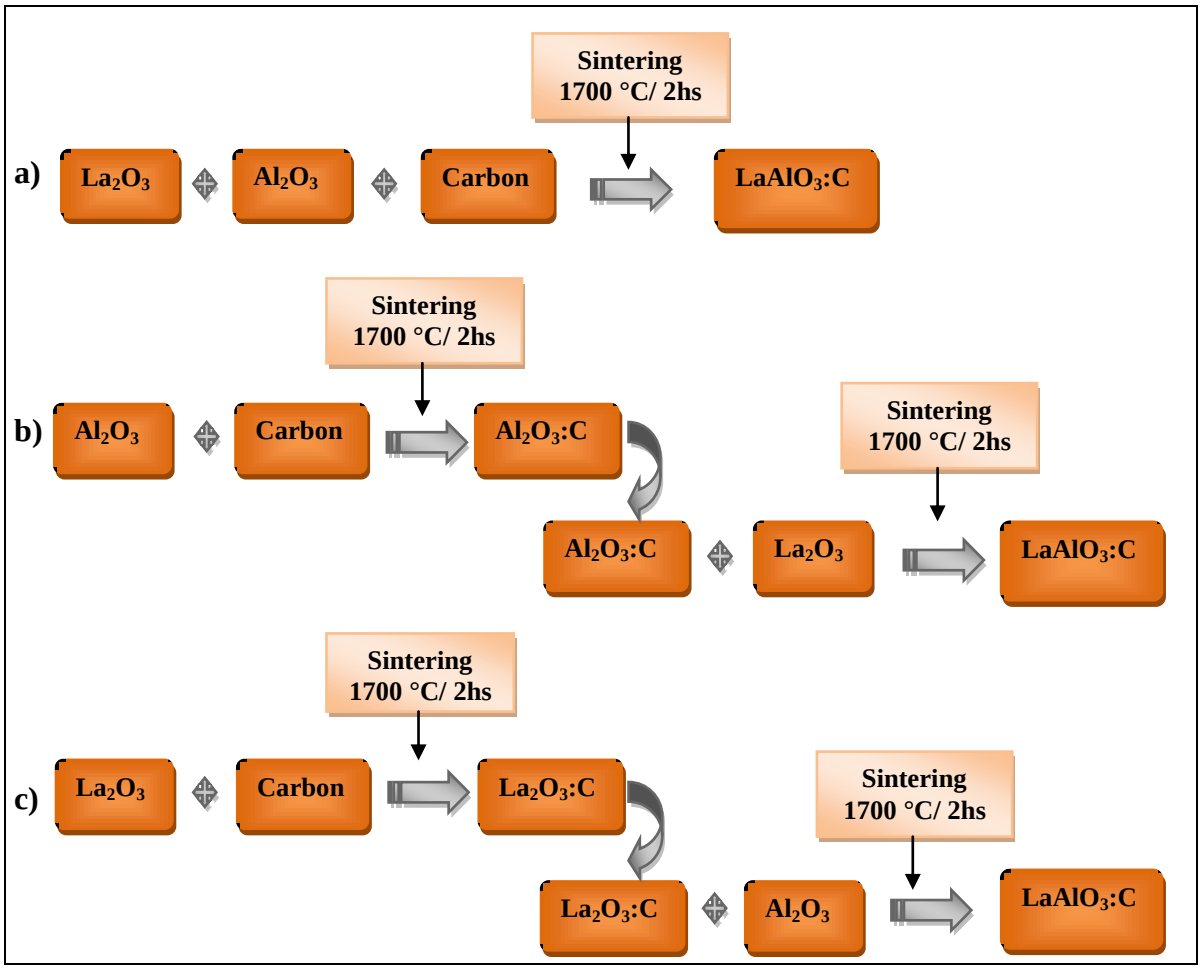

Figure 1: Schematic diagrams illustrating the mixing and sintering procedures used to produce the three types of $LaAlO_3$:C polycrystals.

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. The second methodology is shown in Fig. 1(b) where Al_2O_3 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 is shown in Fig. 1(c) where La_2O_3 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 above diagrams were denominated according to Table 1.

Table 1: Synthesis methodology and its sample denomination

Sample Denomination	Methodology
A	La_2O_3 + Al_2O_3 +Carbon
B	Al_2O_3:Carbon + La_2O_3
C	La_2O_3:Carbon + Al_2O_3

In order to confirm the formation of the $LaAlO_3$ phase, the crystal structure of the samples were analyzed using Regaku D/Max ÚLTIMA X-ray diffractometer. The CuKα radiation was used and the scanning rate was set at 0.02 °/s at 2θ ranging from 4 and 80°.

The absorption spectra of carbon doped $LaAlO_3$ was measured using a SHIMADZU spectrophotometer model UV–2401pc in the 190-900 nm wavelength range. All measurements were performed at room temperature.

The UV irradiation was performed using a commercial UV fluorescent lamp of 8 W. The distance between lamp and sample was kept at 16 cm. The samples were irradiated and stored in dark ambient before the TL reading.

Thermoluminescent analysis was performed The TL glow curves of $LaAlO_3$:C were taken using a Harshaw TLD-4500 TL reader. The readings were performed with heating rate of 15 °C/s, maximum temperature of 300 °C and acquisition time of 26 seconds. Samples were annealed during the reading process.

3. RESULTS AND DISCUSSION

The purpose of growing a crystalline material in reducer atmosphere is to induce a large concentration of oxygen vacancies inside samples. 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 with thermoluminescence sensitivity [7]. It is well known that oxygen vacancies 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 trivalente Al^{3+}-ion [11]. Occupancy of an oxygen vacancy by two electrons gives rise to a neutral F-center, whereas occupancy by one electron forms a positively charged, with respect to the lattice (F^+- center). F and F^+-centers are known to play a key role in the high luminescent output of Al_2O_3. It was found that an increase in the concentration of F^+-centers in Al_2O_3:C causes significant increase in OSL and TL sensitivity [12]. In order to enhance oxygen vacancy production, the polycrystalline lanthanum aluminate was doped with hyperpure carbon by mechanic mixture initially with 0.1 wt.%. Amounts of La_2O_3 and Al_2O_3 were weight and sintered in hydrogen atmosphere at 1700 ºC.

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 also presented peaks (17%) assigned to lanthanum hydroxide phase (JCPDS 36-1481).

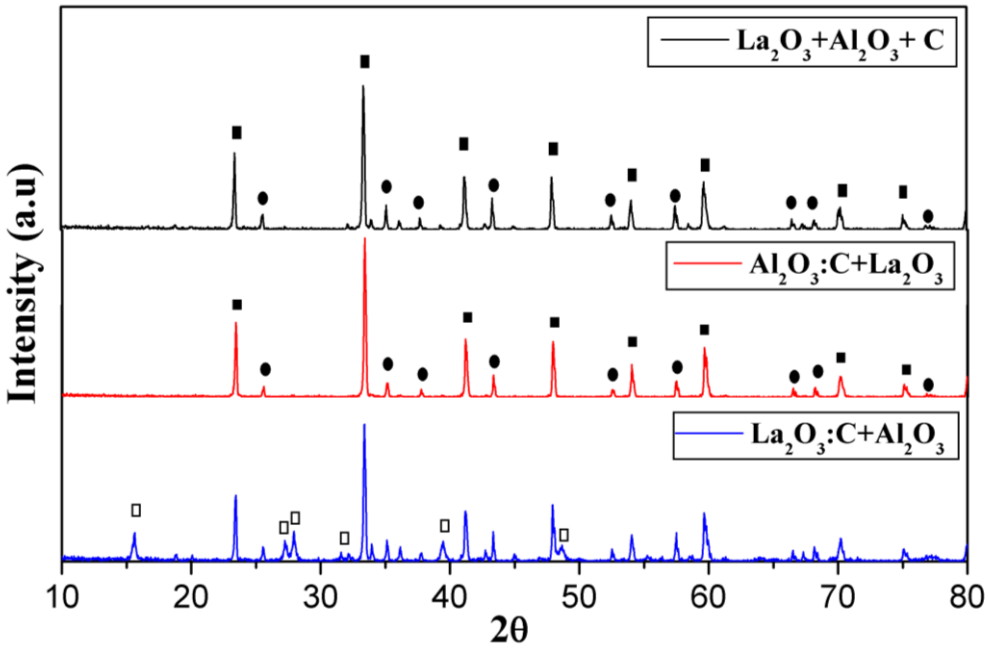

Figure 2: XRD patterns for the $LaAlO_3$:C grown by different synthesis. (■) assigned to rhombohedral phase Lanthanum aluminate ($LaAlO_3$), (●) assigned for aluminum oxide (Al_2O_3) and (□) for lanthanum hydroxide ($La(OH)_3$). The others peaks with less intensity are assigned for $LaAl_{11}O_{18}$, a secondary phase of Lanthanum aluminate.

In Fig. 3, the absorption spectra of Carbon doped lanthanum aluminate grown by three different methodologies are plotted. An absorption band centered at 206 nm has been observed in all samples. In this context, we remark that it is well known that $LaAlO_3$ crystal have strong band-to-band absorptions for wavelengths ranging from 190 to 220 nm, which are assigned to F–Center formation. These centers are due to high concentrations of oxygen vacancies, just as it has been described for the production of Al_2O_3:C crystals [13; 14]. A large absorption band at 230-350 nm appeared on every sample, but with different intensities. We assigned this large band to F^+-Center.

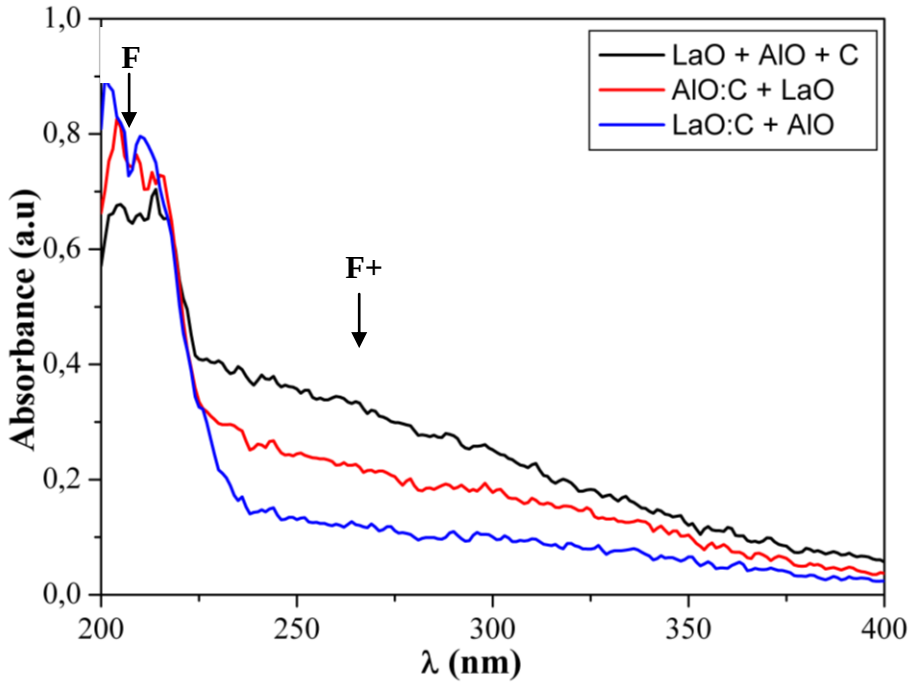

Figure 3: **The UV-Vis absorption spectra of unirradiated $LaAlO_3$:C polycrystals, indicating the absorption bands attributed to F and F^+ centers.**

As reported by LARSEN, N. A. (1999) [3], 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 thermal treatment process, the samples were irradiated using a commercial UV fluorescent lamp. Thus, the TL glow curves for samples produced by the three syntheses were collected.

In Figures 4(a), 4(c) and 4(e) we show the TL glow curves taken immediately after 30 seconds of irradiation together with the two individual TL peaks obtained by peak-fitting using Gaussian lines. The glow curve exhibited two peaks, the first at 145 °C and the second at 190 °C, which are common to the three methodologies tested. On the other hand, in Figures 4(b), 4(d) and 4(f) we show the TL glow curves collected 24 hours after UV irradiation, stored at room temperature. It is clear from these curves that the peak centered at 145 °C fads completely within the first 24 hours after exposuring. 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 with coefficient of determination r^2 = 0,99996. By comparing the three TL output intensities, it is possible to verify that the TL peaks are centered at the nearly at the same temperatures. However, it seems that the sample produced using LaO:C+AlO method show the higher TL output. This phenomenon can also be observed by comparing Figures 4(a), 4(c) and 4(e).

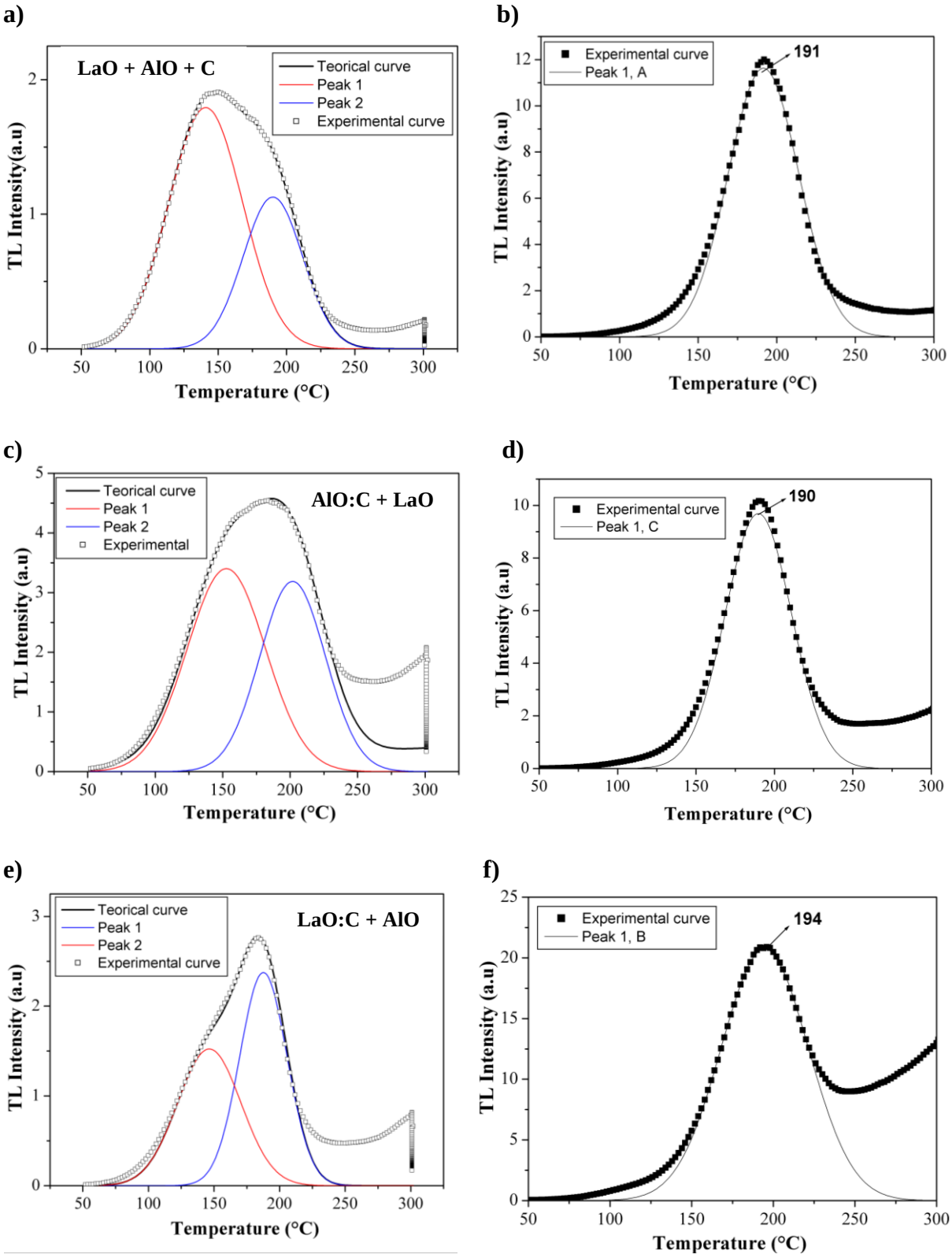

Figure 4: Figures 4(a), 4(c) and 4(e) : TL glow curves taken immediately after 30 seconds of UV irradiation and two individual TL peaks obtained by peak-fitting using Gaussian lines. Figures 4(b), 4(d) and 4(f): TL glow curves collected 24 hours after UV irradiation.

In fact, as shown in Figure 5, the electronic charge measured at the photomultiplier tube is 26, 94 and 266 μC for samples produced by the LaO+AlO+C, AlO:C+LaO and LaO:C+AlO methods, respectively. The higher TL output signal is presented for lanthanum aluminate identified how La_2O_3:C + Al_2O_3 sample (diagram C, Fig.1).

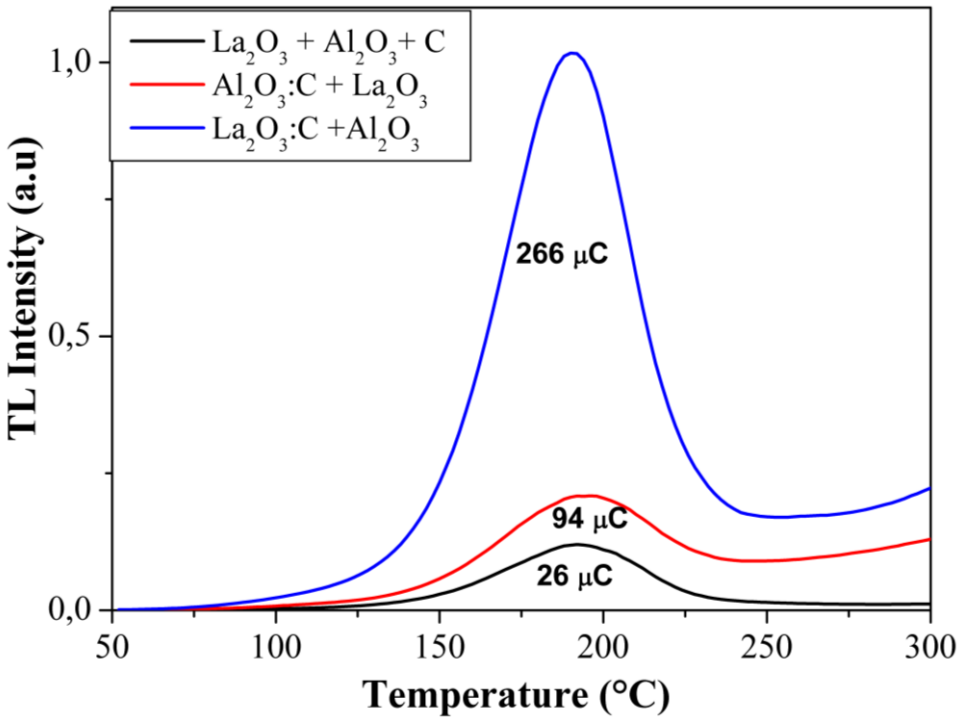

Figure 5: Thermoluminescent glow curves for $LaAlO_3:C_{0.1\%}$ exposed to 30 second UVR.

We believe the higher TL output for La_2O_3:C + Al_2O_3 sample is due to the lanthanum hydroxide presence. In this context, thermoluminescent sensitivity of La_2O_3 for UV radiation have been investigated and it is reported that La_2O_3 is very closely some of the ideal criteria for a TL dosimeter [10]. It is well known that La_2O_3 is hygroscopic in nature and quickly converts to lanthanum hydroxide ($La(OH)_3$) in the moist atmosphere. La_2O_3 converts back to pure $La(OH)_3$ if left open in the atmosphere for 24 hours [15] . We intent to explore more carefully these compositions making characterizations in order to obtain an ideal material for TL dosimetry induced by ultraviolet radiation.

Finally, we remark that the electric charge collected at the PMT per irradiance unit for La_2O_3:C + Al_2O_3 sample is 836 μC/mJ Cm^{-2}. For comparison purposes, this rate measured for $LaAlO_3$:Ce,Dy single crystal is only 0.430 μC/mJ Cm-2 and 293 μC/mJ Cm-2 for undoped LaAlO3 synthesized samples, irradiated at the same conditions and read at the same TL reader after 30 seconds of exposition [15;9]. We see that TL sensitivity to UV photons for La_2O_3:C + Al_2O_3 samples is much higher than those for $LaAlO_3$:Ce,Dy grown under hydrothermal conditions and undoped $LaAlO_3$ synthesized under reducing atmosphere.

3. CONCLUSIONS

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 carbon atoms during the synthesis process. Characterization of sintered powders by X ray diffraction and UV-Vis spectrophotometry has confirmed the $LaAlO_3$ phase.

According to the thermoluminescent investigation, the composition that have shown better TL output was lanthanum aluminate identified with La_2O_3:C + Al_2O_3 sample. The others compositions also have good TL response, but less than the previously mentioned.

We conclude that the synthesis were very efficient to obtain $LaAlO_3$:C crystals with high thermoluminescent intensities for low exposure rate UVR fields. We believe that carbon doped lanthanum aluminate has great potential for application in UV dosimetry.

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