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TL and OSL study of $Li_2B_4O_7$:Cu,Ag synthesized by combustion and solid-state reactions

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ABSTRACT

The aim of this work was to investigate the Thermoluminescence (TL) and the Optically Stimulated Luminescence (OSL) responses of Li_2B4O_7:Cu,Ag synthesized using two methods: a) solid-state and b) liquid combustion. In both procedures, 0.4% mol of $CuN_2O_6.3H_2O$ and 0.1%mol of $AgNO_3$ were used as dopants. The techniques of X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used for structural and morphological characterization. The results showed that the samples synthesized using the combustion method are mostly formed by $Li_2B_4O_7$:Cu,Ag, while those produced by the solid-state method showed the presence of $LiBO_2$. This fact affects the luminescence response of the samples, those produced by combustion have higher TL and OSL sensitivities. The Infrared stimulation luminescence (IRSL) response was not observed for both sample batches for the reading conditions used in this work. Future studies will be carried out to evaluate the use of $Li_2B_4O_7$:Cu,Ag synthesized by solid-state route for high dose dosimetry.

Keywords: **lithium tetraborate, optically stimulated luminescence, thermoluminescence.**

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1. INTRODUCTION

Thermoluminescence (TL) and, more recently, optically stimulated luminescence (OSL) are the most used luminescence techniques for radiation dosimetry in medical applications. There are few materials that present adequate properties for OSL dosimetry [1]. Currently, the Brazilian laboratories dedicated to personnel radiation monitoring using TL use lithium fluoride doped with Mg and Ti (LiF:Mg,Ti) and/or calcium sulfate doped with dysprosium ($CaSO_4$:Dy). This later is used as a tandem system side by with almost energy independent LiF:Mg,Ti (Z_{eff} =7.3). In the field of OSL dosimetry, Al_2O_3:C and BeO are practically the only commercial OSL dosimeters used for medical, environmental, and personnel dosimetry [2,3]. Therefore, there is a current interest in the scientific community in novel synthesis methods for materials used in radiation dosimetry [4].

Lithium tetraborate ($Li_2B_4O_7$) (LTB) has attracted the attention of researchers for application in radiation dosimetry due to its effective atomic number - Z_{eff} (7.3), which is close to that of the human tissue [5,6,7]. This is an important characteristic for dosimetry of medical applications of ionizing radiation [8]. The luminescence response of this material has been investigated using powders and glass or crystal chips [9,10]. It is also a promising material for neutron dosimetry since ^{6}Li and ^{10}B have high capture cross-sections for thermal neutrons [11]. Studies on the TL properties of $Li_2B_4O_7$ doped with different materials such as Mn, Cu, and Ag have been suggested in recent years by different research groups [12,13]. It was observed that the luminescence intensity is strongly influenced by the preparation method, the manufacturer of the chemicals that are used, the sintering temperature, activator and co-activator concentration, particle size, etc. [14]. Therefore, the aim of this work was to produce lithium tetraborate co-doped with Cu and Ag by liquid combustion and solid-state reactions and to evaluate the TL and OSL response of these materials.

2. MATERIALS AND METHODS

2.1. Preparation of the $Li_2B_4O_7$:Cu,Ag

Samples were synthesized by the combustion method (method 1) and by the solid-state technique (method 2). In both method, 0,4 mol% Cu and 0,1 mol% Ag (relative to Li^+) were used as dopants. Several batches were produced, but for the characterization of the TL and OSL response of the $Li_2B_4O_7$:Cu,Ag the samples were produced by only one batch for each route method. The sensitivity of the samples was also evaluated by irradiation all of them at the same dose and radiation conditions and a sensibility factor was used to correct the differences between the samples. The stoichiometric calculations to prepare the samples were made with the Mathcad software 14 [15].

To obtain of $Li_2B_4O_7$:Cu,Ag using method 1, all reagents (stoichiometric reaction: 18 $LiNO_3$ (aq) + 36 H_3BO_3 (aq) + 10 $C_2H_5NO_2$ = 9 $Li_2B_4O_7$ (s) + 20 CO_2 (g) + 14 N_2 (g) + 79 H_2O (g) were weighed on an analytical balance and then mixed in a beaker with water to ensure solubilization. Glycine ($C_2H_5NO_2$) was used as fuel. The mixture was heated on a hot plate for a few minutes for evaporation and then transferred to a muffle furnace at 450 °C where an intense flame type combustion occurred. The resulting powder was mixed in an agate mortar with the aid of a pestle and then heated at 800 °C for 1 h in a porcelain crucible to complete the synthesis.

The procedure used to prepare samples by method 2 followed the procedure described by Kar *et al.* (2014) [16]. All reagents (in mol% 29.9Li_2CO_3 – 69.6H_3BO_3 – 0.4$CuN_2O6.3H_2O$ –0.1$AgNO_3$) were weighed on an analytical scale and then mixed and homogenized in an agate mortar set for 1 h. The sample was synthesized at 400 °C for 3 h in an alumina crucible, using a resistive furnace (EDG type 3P – S) in an ambient atmosphere. The resulting powder was removed from the crucible and mixed in an agate mortar for 1 h, and then annealed at 600 °C for 10 h in an alumina crucible. The sample was cooled slowly and was only removed from the resistive furnace at room temperature. Through this process, the polycrystalline powder was obtained.

2.2. XRD and SEM studies

The identification of the crystalline phases in $Li_2B_4O_7$:Cu,Ag synthesized following liquid combustion and solid-state methods were performed by X-ray diffraction (XRD). The XRD powder patterns were obtained with a Bruker D2-Phaser diffractometer equipped with a Lynxeye one-dimensional detector, Cu-Kα radiation (30 kV, 10 mA; K_α wavelength 1.54060 Å), goniometer step of 0.0202 º/s, counting time 1 s and 2θ scanning from 4º to 80º with the tube operating at 30 kV and 10 mA. The experimental patterns were compared to the standard XRD patterns from the Inorganic Crystal Structure Database (ICSD). As a result, the patterns numbers 065930 and 200891 were selected.

The morphology of the powders obtained by method 1 and 2 was performed using scanning electron microscopy (Vega 3XM Tescan at accelerating voltage of 20 kV) equipped with secondary electrons (SE) and EDS (Energy Dispersed Spectroscopy) detectors. The powdered samples were entered on carbon strips and metallized with a thin gold layer to provide electrical conductivity for a scanning electron microscopy test. The micrographs were performed at magnifications of 500 and 5000 times in a low vacuum.

2.3. Sample pellets

The grains were classified in 75 x 150 μm particle size range using stainless steel sieves. The grains were blended with flocculated PTFE in the proportion of 0.8:0.2% by mass. A homogeneous mixture was pressed using a die manufactured with stainless steel. The compressive force (~10 kN) was applied during 10 s, using a SPECAC 15T hydraulic press. The dimensions of the pellets are 6 mm in diameter and 1 mm thick and the weight is approximately 50 mg.

2.4. TL and OSL measurements

The TL signals were measured in the pellets. In order to compare the sample TL signals of the samples produced by both methods, preliminary measurements were done using a Harshaw 3500 TL reader with a heating rate of 4 ºC/s. The samples were irradiated at doses of 5 Gy and 10 Gy using a ^{60}Co gamma cell irradiator with a dose rate of 1.7 kGy/h. Then, to acquire in addition to the TL response and the OSL response, it was used 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. In this case, the dosimeter was irradiated with the internal beta source and its OSL response was immediately obtained, followed by the residual TL signal. The same procedure was performed to obtain the TL response. Thus, the time between irradiation of the sample and obtaining its luminescence was the same for all samples.

The TL glow curves were recorded from 25 to 400 °C with a heating rate 2 °C.s^{-1} with a Wide-Band-Blue filter pack. Blue stimulation luminescence (BSL) was performed in continuous mode (CW-OSL) with blue LEDs (465 ± 5 nm) at room temperature using a 380 nm filter pack for 60 s and a channel time of 0.1 s and power set to 80 mW/cm². For Infrared Stimulation luminescence (IRSL), LEDs with an emission peak at 850 nm were used, a Wide-Band-Blue filter pack and power set to 250 mW/cm² and a total reading time of 60 s was selected, with a channel time of 0.1 s. From each type of method, three pellets were produced, and the coefficient variation for three cycles consisting of annealing, irradiation and readout was measured.

3. RESULTS AND DISCUSSION

3.1 Crystalline phases and morphology

Figure 1 shows the XRD patterns of the powder obtained by method 1 and method 2. The peak positions of the compared to the ICSD 065930 (lithium tetraborate) and ICSD 20089 (lithium metaborate) reference patterns. The lithium tetraborate ($Li_2B_4O_7$) belongs to the tetragonal crystal system and the space group $I4_1cd$ with crystallographic parameters a = 9.4790 Å, b = 9.4790 Å, c= 10.2900 Å. The lithium metaborate (Li_2BO_2) belongs to the monoclinic crystal system and the space group P21/c with crystallographic parameters a = 5.8450 Å, b = 4.3530 Å, c= 6.4540 Å, α= 90°, β= 115 ° and γ= 90 °

The sample synthesized by method 1 shows the majority formation of $Li_2B_4O_7$. The XRD patterns showed identical crystalline structures and well-defined peaks, that are matched to the reference pattern, demonstrating that the synthesis was successful. On the other hand, the sample synthesized by method 2 has two crystalline phases. One phase is $Li_2B_4O_7$ and another phase is $LiBO_2$.

In future works, it is intended to determine the percentage of each phase obtained by the Rietveld refinement method [17].

Figures 2 (a) and 2 (b) show the SEM micrographs of the powders obtained by methods 1 and 2, respectively. In both cases, it is possible to see particles of micrometric order, which have irregular morphology. According to those micrographs, the $Li_2B_4O_7$:Cu,Ag powdered samples apparently form clusters. However, for method 1 the agglomeration of the particles is larger and more defined than the observed for the samples produced by method 2.

The aspect of particle morphology observed in Figure 2 (a) corroborates the tetragonal structure obtained by X-ray diffraction.

The images of the powder produced by method 2, and shown in Figure 2 (b), indicate that it is not possible to define the shape of the particles. The SEM micrographs present an irregular aspect, possibly due to the presence of the two phases present in their crystalline structure.

Figure 1: X-ray diffraction pattern of the powder obtained by method 1 and method 2, compared to the reference standards ICSD 065930 and ICSD 200891.

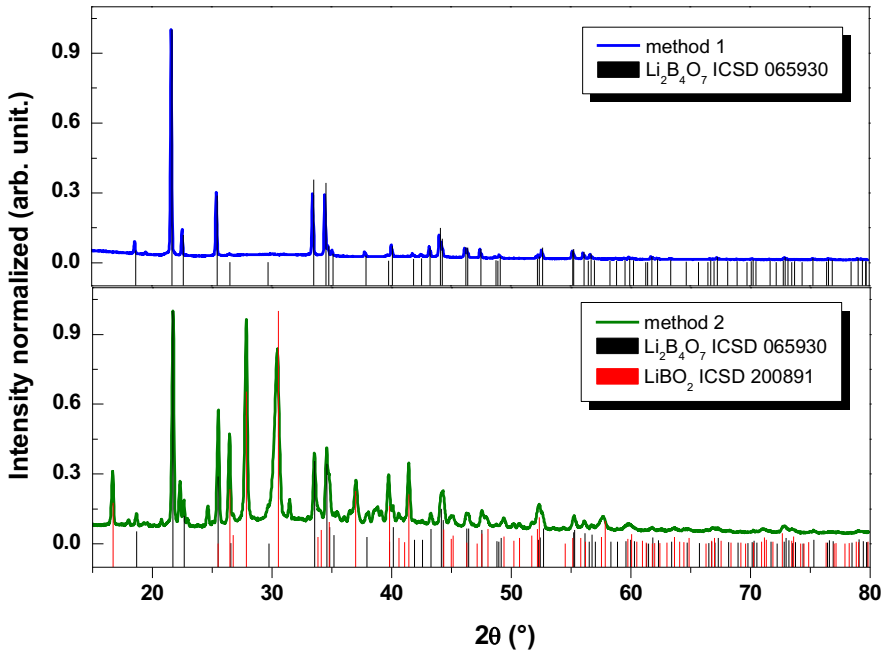
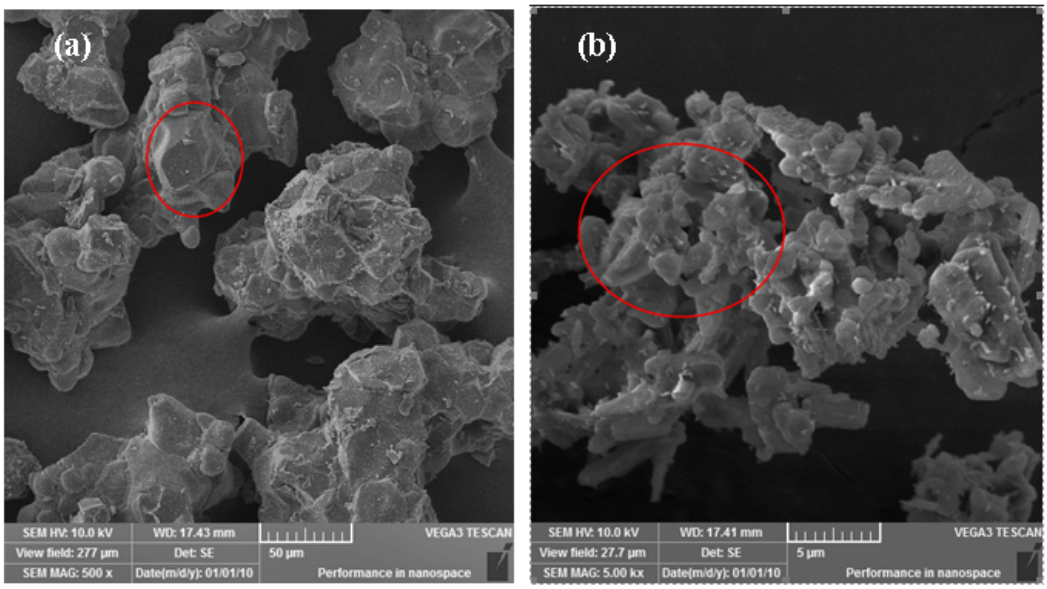


Figure 2: SEM micrographs of the powder samples obtained with different magnifications: (a) method 1 and (b) method 2.

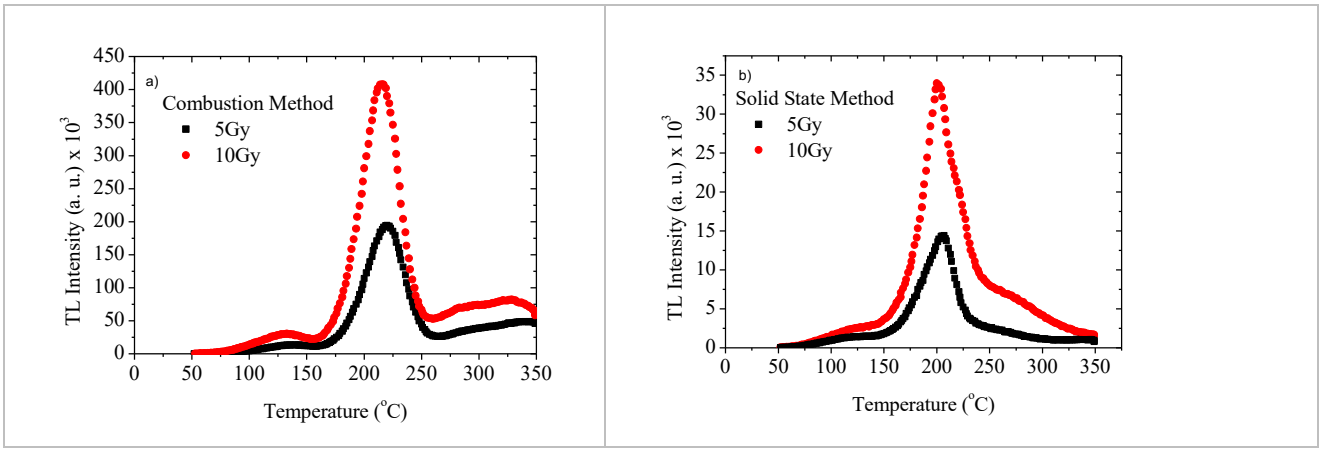


3.2 TL and OSL results

Figures 3 (a) and 3 (b) present the TL glow curves obtained with the $Li_2B_4O_7$:Cu,Ag pellets, produced by liquid combustion and solid-state methods, respectively. The results show that the TL response of the samples prepared by the solid-state method is around ten times lower than the signal obtained with the samples produced by the liquid combustion method. The TL glow curve of the samples produced by the combustion method shows three peaks, one at low temperature at about 120 °C, the main peak at about 210 °C and the third one at around 325 °C. Prokic [18] found that the glow curve of lithium tetraborate doped with copper and silver irradiated with gamma radiation from ^{60}Co presents a peak at 135 ^{0}C and a second peak at 185-190 ^{o}C. Same results were observed by Aydun et al. (2013) [19] when studied the TL of undoped and Cu-doped lithium tetraborate. They observed that the glow curve for pure $Li_2B_4O_7$ irradiated with beta radiation and 150 Gy shows only one peak at approximately 103 °C, while the samples of Cu-doped $Li_2B_4O_7$, irradiated at the same conditions, present two peaks, one at 115 °C and the second at 243 °C. Patra et al. (2016) [20], studying the TL glow curve of Ag doped $Li_2B_4O_7$ single crystals for neutron dosimetry, observed the main peak at 150 °C and a second peak at 250 °C. Mendoza-Anaya et al. [21] evaluate the TL response of $Li_2B_4O_7$:Cu,Ag,P (powder). They studied the TL glow curve of as a function

of the sintering temperature applied during two hours. The results showed that at (850 ºC) 1123 K sintering temperature is optimum as it results in a greater TL intensity. This sintering temperature is similar to that used in our work. The data indicates that there is some variability in the TL glow curves but they all have the TL peak at same temperature.

Figure 3 - TL glow curves of $Li_2B_4O_7$: Cu, Ag pellets prepared by two different methods and irradiated with 5 Gy and 10 Gy (a) Method 1 - Combustion method, (b) Method 2 - solid-state method



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The analysis of the glow curve of the samples prepared by solid-state methods shows the peak at a lower temperature, also observed in undoped $Li_2B_4O_7$, the main peak centered at 200 °C and the third peak at 270 °C, increasing the radiation dose it is possible to see that the main peak is overlapping with another peak, around 225 °C. These changes in the TL glow curve are probably associated with the presence of lithium metaborate that was identified by the XRD studies. The TL glow curve obtained with the samples prepared by solid-state methods requires the deconvolution of the peak for an adequate use for TL dosimetry.

The first peak, at a lower temperature, is not adequate to be used for TL dosimetry and it is possible to be eliminated by annealing. The main peak is adequate for TL dosimetry, but its shape and sensitivity for the samples prepared by combustion methods are better than for the samples prepared by the solid-state method.

Figure 4 presents the results of a CW-OSL signal obtained with blue LED stimulation, for samples irradiated with 1 Gy and with a blue stimulation time of 60 s. Figure 5 shows the result of the CW-OSL signal obtained with infrared LED stimulation. The analysis of the OSL curves indicates that $Li_2B_4O_7$:Cu,Ag synthesized by combustion method presents a BSL response while this response is poor for the samples synthesized by the solid-state method. The samples synthesized by both methods do not present an IRSL response for the studied dose range. There are few references in the literature about the OSL response of the $Li_2B_4O_7$:Cu,Ag.

Figure 4 - The BSL curves for $Li_2B_4O_7$:Cu,Ag irradiated with beta radiation with 1 Gy.

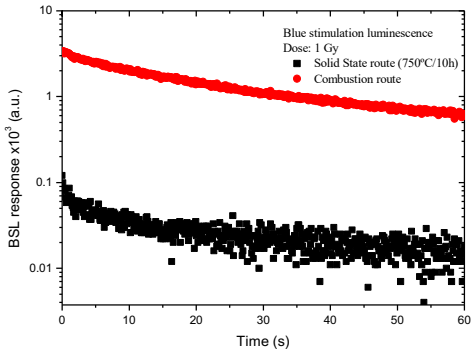
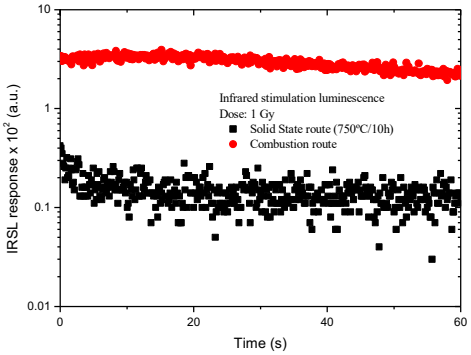


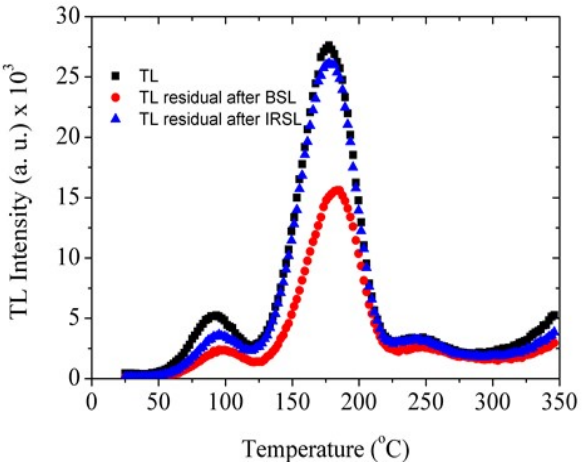
Figure 5 - IRSL curves obtained with samples of $Li_2B_4O_7$:Cu,Ag pellets prepared by combustion and solid-state methods and irradiated with 1 Gy of beta radiation.



The residual TL signal after BSL and IRSL were recorded, and the results are shown in Figure 6. The results show that after BSL read the first peak at about 100 °C and the second peak decreased, indicating that the contribution of the OSL signal is associated with the traps of these

peaks. The decay percentage of the first peak is higher than in the second peak, while the third peak is not affected by the stimulation with the blue LED. As the time between irradiation and reading is constant, both for TL and for IRSL and BSL; and as it is observed the decrease in the TL curve after optical stimulation (IRSL/BSL), probably there is an emission for optical stimulation (IRSL/BSL). However, it is not detected in this TL/OSL reader because the emission spectra is outside the detection region of the photomultiplier. Further investigations are important to evaluate the fading of the OSL signal and to evaluate the TL dosimetric proprieties of the third peak.

Figure 6 - Residual TL glow curve of samples synthesized by combustion method after BSL and IRSL measurements.



4. CONCLUNDING REMARKS

This work investigated the TL and OSL response of the $Li_2B_4O_7$:Cu,Ag synthesized by combustion and solid-state methods. It is possible to conclude that by the combustion method it is possible to produce $Li_2B_4O_7$:Cu,Ag samples with TL and BSL sensitivity higher than those produced by solid-state method. The XRD studies indicate samples synthesized by combustion are mostly formed by lithium tetraborate, while those produced by the solid-state showed the presence of lithium metaborate. This fact affects the luminescent response of the samples. The results show that the TL response of the samples prepared by the solid-state method is around ten times lower than that obtained with the samples produced by the combustion method. The

analysis of the OSL curves indicates that $Li_2B_4O_7$:Cu,Ag synthesized by combustion method presents a BSL response while this response is poor for the samples synthesized by the solid-state method. The samples synthesized by both methods do not present an IRSL response for available reading conditions in this work.

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