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Beta radiation induced luminescence of polycrystalline Cu-doped $Li_2B_4O_7$

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ABSTRACT

Thermoluminescence (TL) and radioluminescence (RL) properties of polycrystalline lithium tetraborate ($Li_2B_4O_7$) doped with different concentrations of copper (0.25, 0.5, 1 wt %) under beta irradiation have been investigated. The feasibility of using this borate in radiation dosimetry at low doses has been evaluated. Tissue equivalent $Li_2B_4O_7$ was prepared by solid state reaction using mixing stoichiometric compositions of lithium carbonate (Li_2CO_3) and boric acid (H_3BO_3) and a solution of $CuCl_2$ as dopant. The glow curve of the most efficient copper doped borate ($Li_2B_4O_7$:Cu 0.5 wt %) shows a main stable peak centered at 225 °C and a second low temperature peak centered at 80 °C. The low temperature peak fades completely after 24 h of storage in darkness and at room temperature or after an annealing at 120 °C for 10 s. The main peak of the $Li_2B_4O_7$:Cu remains constant. The TL response of $Li_2B_4O_7$:Cu shows good linearity in the analyzed dose range. The stability and repeatability of RL signals of the borate have been studied and the $Li_2B_4O_7$:Cu (0.5 wt %) shows the higher RL emission and a stable and repetitive response. Results show that polycrystalline $Li_2B_4O_7$:Cu has prospects to be used in beta radiation dosimetry.

1. Introduction

The application of ionizing radiation sources in many fields of everyday life, namely, energy generation, radiation therapy, environment monitoring, sterilization, etc., has resulted in a continuous development of radiation detectors suitable to measure and control the dose or dose-rate in each particular case. In order to develop suitable sensors for achieving this goal, several physical radiation-induced phenomena have been studied. One of the most investigated is based on employing the luminescence observed in many materials, which is produced as a result of the absorption of energy from the radiation field. This luminescence can be observed either during irradiation, what is known as radioluminescence (RL) or after it when the irradiated material is stimulated by heating (thermoluminescence, TL). Generally, the luminescence yield is proportional to the dose-rate in the first case and to the dose in the second one, what can be used for dosimetry purposes [18].

In this context, lithium tetraborate $Li_2B_4O_7$ (LTB) compounds have attracted attention to be used as thermoluminescence detectors in personal and clinical radiation dosimetry due to their near human tissue equivalent absorption coefficient. Indeed, the effective atomic number (Z_{eff}) of LTB amounts to 7.3, so matching acceptably that of soft tissue (7.4) [23,29]. Another advantage is that borate dosimeters can be prepared easily because of having good heat stability and low melting temperature [1].

In order to increase their TL efficiency LTB compounds have been doped with different transition metal cations. In particular, Mn doped LTB has shown to be a highly efficient TL phosphor. The first studies on this borate were made in 1967 by Schulman et al. [26] and this material is still being studied [7,9], Guarneros-Aguilar et al. [2013] [11]. However, its peak emission wavelength does not suit very well the spectral response of photomultipliers tubes usually employed in TL readers [2]. On the other hand, Cu-doped LTB overcomes this problem without resigning luminescence efficiency

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because in general, the main emission of this compound is a broad band located between 300 and 500 nm. Besides, most recent research demonstrates that LTB:Cu exhibits good thermal stability, good post-irradiation storage stability, low cost and relatively easy preparation [3].

The TL of Cu singly-doped LTB irradiated with different sources has been reported [10,11,16,22,27,28,5]. In all cases, these investigations were conducted on gamma and/or X-ray irradiated samples. However, there are only a few studies focusing on the TL of Cu singly-doped LTB irradiated with beta particles. Faramawy et al. [8] employed a Sr-90 beta source to irradiate a LTB:Cu polycrystalline sample with low doses between 43 μGy and 1290 μGy founding that the response is linear within the mentioned range. Babita et al. [4] and Kelemen et al. [14] studied the beta response of LTB:Cu at higher doses but they focused on single crystal samples grown by Czochralski method.

According with the radioluminescence of the Cu doped LTB, time resolved RL spectrum of a LTB:Cu single crystal was reported by Ignatovych et al. [13] and they found that maximum RL emission of this borate was centered around 370 nm. Their study was carried out in a LINAC facility. Several years later, Huy et al. [12] and Kobayashi et al. [15] reported similar results when samples of LTB:Cu was irradiated with X-ray and gamma radiation. To the best of our knowledge, to date has been not reported a RL study of Cu-doped LTB irradiated with beta radiation.

In this context and taking into account that polycrystalline phosphors are easier and cheaper to fabricate than single crystals which makes them more suitable for practical applications, the aim of this work is developed Cu singly-doped LTB polycrystalline samples and study their TL response under beta irradiation within a broad dose range. The structural characteristics of the synthesized samples have been investigated by X-ray diffraction and FTIR studies. Besides, the Cu concentration rendering the most efficient compound has been determined. Finally, the characteristics of the radioluminescence (RL) signal have been also investigated in order to determine the scintillation spectrum and the characteristic Cu transitions being responsible for the RL emission.

2. Materials and methods

Li_2CO_3 and H_3BO_3 were mixed and melted at 950 °C in air during 180 min in a ceramic crucible using a muffle furnace. The sample was slowly cooled down to room temperature (RT) and then reheated at 650 °C during 120 min to complete the crystallization. LTB samples were doped with different Cu concentrations (0.25, 0.5 and 1.0 wt %) by adding the LTB powder into a solution of $CuCl_2$ in acetone/alcohol, which was subsequently dried. The dried mixture was annealed at 900 °C in air during 60 min. The phosphors were ground and the powders were characterized by X-ray diffraction (XRD) using Cu-Kα (1.5406 Å) radiation in an X-Ray Diffractometer Panalytical X-Pert Pro MRD, operated at 40 kV and 20 mA. The slow scan was performed in the 2θ range from 15° to 80° with a scan step of 0.026°, to confirm the phase purity of the synthesized samples. Fourier Transform – Infrared – Attenuated Total Reflectance Spectroscopy (FT-IR-ATR) was used to study the vibrational modes of the materials by Perkin-Elmer Spectrum One 51394 FTIR Spectrometer, between wavenumber 4000–650 cm^{-1}.

For the thermoluminescence (TL) and radioluminescence (RL) measurements, the LTB:Cu samples were irradiated at RT with a 3.7×10^{-8} Bq ophthalmic ^{90}Sr beta-source rendering 0.022 $Gymin^{-1}$ dose rate at the sample position. TL glow curves were recorded from 50 up to 400 °C with a constant heating rate of 1.0 $K\,s^{-1}$ by using a Harshaw–Bicron 3500 TL reader featuring a Hamamatsu R6094 photomultiplier tube. RL curves were measured as a function of time during beta irradiation. All the samples were irradiated at RT with the ^{90}Sr beta-source mentioned above and the light emitted by the samples was collected by means of a $\varphi = 1$ mm communication grade optical fiber and projected onto a Sens-Tech P25PC-02 photon counting photomultiplier tube. RL spectra were recorded by means of an Acton Research SP-2155 0.150 m monochromator featuring a Sens-Tech P25PC-02 photomultiplier tube. Spectra were measured within the wavelength range of 300–700 nm and at a rate of 1 nm seg^{-1}. The sample was placed at the entrance slit and irradiated with the aforementioned beta-source, which was situated 1 cm away from the sample. A resolution of approximately 5 nm was attained by setting the entrance and exit slits width at 3 mm during the measurements.

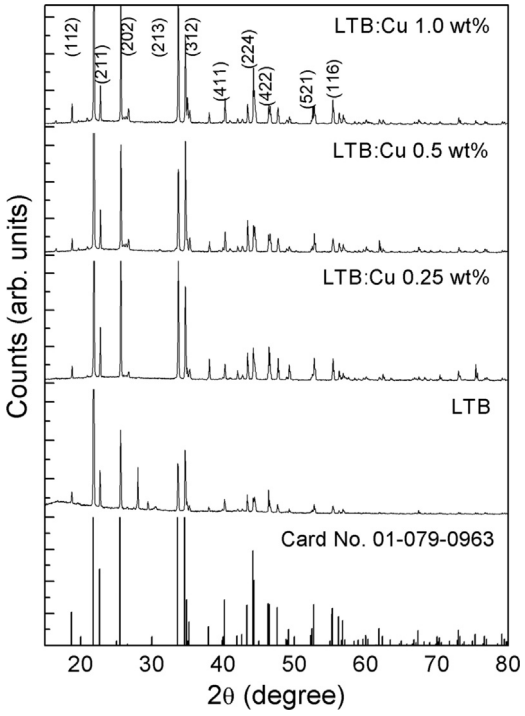

Fig. 1. X-ray diffraction pattern of LTB and LTB:Cu doped with different Cu concentrations (0.25, 0.5, and 1.0 wt %) matched with the standard data (card no. 01-079-0963).

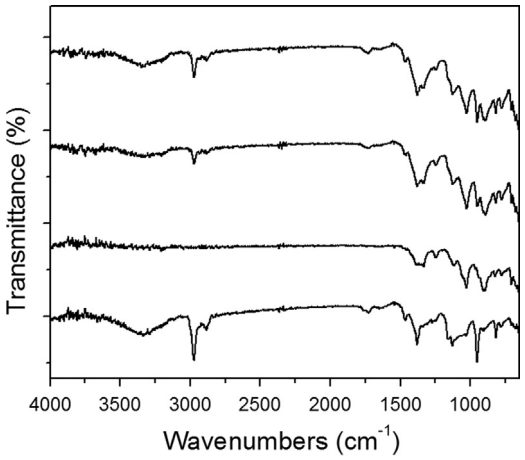

Fig. 2. The FT-IR-ATR spectra of nominally pure LTB and LTB doped with 0.25, 0.5, and 1.0 wt % of copper, from bottom to top, respectively.

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of the Cu-doped and nominally pure LTB. The *hkl* values of the most relevant peaks are indicated. The XRD pattern obtained for the undoped LTB samples was matched with the standard data available (card no. 01-079-0963). As expected, it corresponds to body-centered tetragonal structure with space group $I4_1cd$ (C_{4v}^{12}) and point group 4 mm being the cell parameters $\boldsymbol{a}=\boldsymbol{b}=9.47900$, $\boldsymbol{c}=10.29$. The diffraction peak showing up at 28° in the pure sample XRD pattern corresponds to boric acid plane [002] (card no. 01-073-2158). This peak is absent in the doped samples due to the second thermal treatment, which allows the remnants to react completely. It can be concluded that the dopant inclusion does not affect with the LTB crystal structure [21,4].

FT-IR-ATR spectra for the solid state synthetized undoped LTB and the doped phosphor with different copper concentrations are presented in Fig. 2. According to [21] the common vibrational modes expected in LTB are located in 900–865 cm^{-1} for stretching vibrations of tetrahedral $(BO_4)^{-4}$, stretching vibration $(BO_3)^{-3}$ in 1246–1807 cm^{-1}, and the stretching vibrations of B–O of trigonal $(BO_3)^{-3}$ units in 1343–1248 cm^{-1} [21]. The infrared bands between 600 and 800 cm^{-1} observed are mainly due to B–O bending [29]. The vibrational modes of the synthetized samples are summarized in Table 1. It is apparent from the figure that the principal bands corresponding to borate groups are present in the FT-IR-ATR spectra of the samples, which confirms the quality of the fabrication process.

As in the case of XRD analyses, the dopant ion added does not interfere significantly with the vibrational modes of lithium tetraborate structure. However, it is observed that the bands located at 890–910 cm^{-1} are more intense in the doped sample than in the undoped one (Fig. 3).

Table 1
FT-IR-ATR vibrational modes observed in doped and undoped LTB.

Occurrence	LTB	LTB:Cu 0.25 wt%	LTB:Cu 0.5 wt%	LTB:Cu 1.0 wt%
Stretching vibrations of tetrahedral $(BO_4)^{-4}$ (cm^{-1})	896.8	896.9	894	893
Stretching vibration of $(BO_3)^{-3}$ (cm^{-1})	1379.4	1379.4	1386.4	1379.4
B–O of trigonal $(BO_3)^{-3}(cm^{-1})$	1251, 1273.9, 1311.3, 1341.5	1245.8, 1333	1245.8, 1275, 1332	1246.9, 1275, 1339

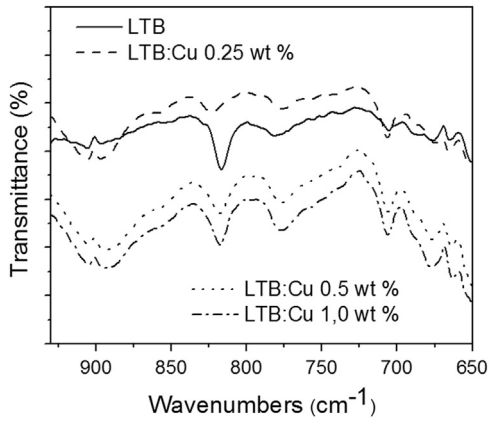

Fig. 3. The FT-IR-ATR spectra of LTB and LTB:Cu doped with 0.25, 0.5 and 1.0 wt %.

Fig. 4 shows the TL glow curve of LTB doped with different concentration of copper. It can be seen from the figure that among the Cu doped lithium tetraborate samples, the concentration of 0.5 wt % yields the highest TL response under beta radiation.

The shape of glow curve of the most efficient copper doped borate (0.5 wt % Cu) shows a main stable peak centered at 225 °C and a minor low temperature peak centered at 80 °C (Fig. 4). The glow curves corresponding to the less efficient LTB:Cu samples, say, the samples doped with 1 wt % and 0.25 wt % Cu, show a similar structure. However, it is apparent from the figure that each of the mentioned peaks is actually a band of overlapping peaks. Differences in the relative intensity of the overlapping peaks result in the differences observed in the shape of each band. It was observed that the maximum temperature of the low temperature glow peaks shifts (Fig. 4) depending on the copper doping concentration. The low temperature peak also appears at 83 °C in the sample doped with 1 wt % and at 94 °C in the sample doped with 0.25 wt %. Although a deeper study should be necessary in order to guess a reason for this observation, it could be ascribed in principle to the copper aggregation in the lattice, which modifies the trap depth and consequently the peak maximum. For the three doped samples, this low temperature peak disappears completely after 16 h of storage in darkness and at RT. For this reason, the low temperature peak could be related to shallow traps.

On the other hand, the peaks located between 150 and 350 °C for the other two concentrations, namely, 1 and 0.25 wt % Cu, appear to be considerably less intense than that of the most efficient copper doped borate and even less than the low temperate peak of each curve. Besides, it is evident from the figure that for the 1 wt % of copper, this peak is the sum of at least two overlapping peaks. For the case of the 0.25 wt % Cu doped sample, this

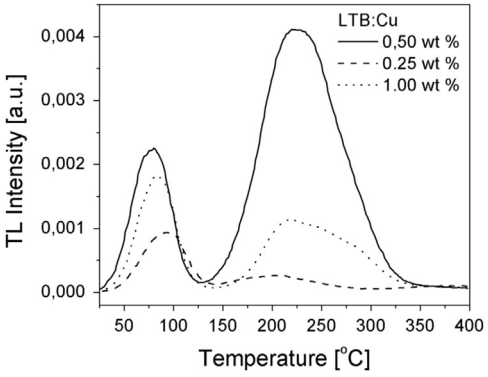

Fig. 4. TL glow curves of LTB doped with different concentrations of copper.

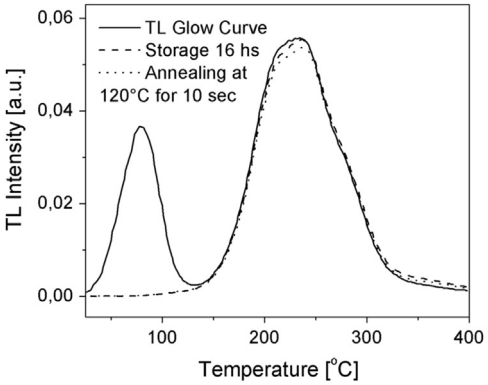

Fig. 5. TL glow curve of LTB:Cu (0.5 wt %) measured immediately after irradiation (solid), after 16 h of storage in darkness and at RT (dash) and after an annealing at 120 °C for 10 s (dot), respectively.

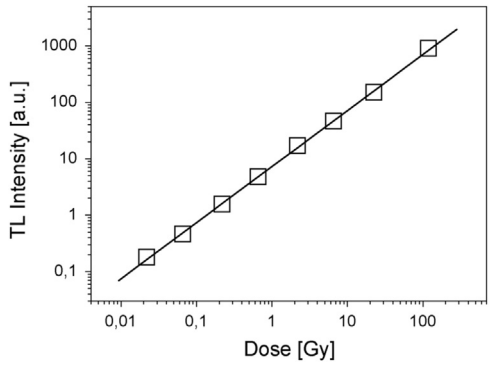

Fig. 6. Dose response of LTB:Cu (0.5 wt %) between 0.01 and 100 Gy. The solid line is a linear fit included for the eye guide. Error bars are smaller than the symbol size.

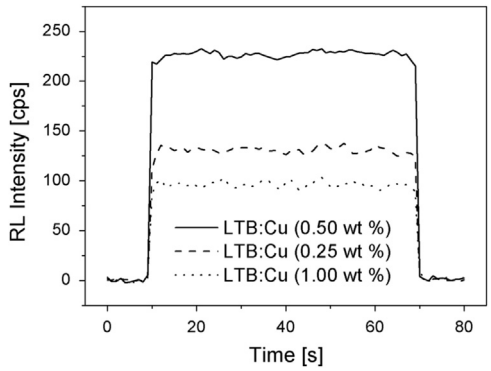

Fig. 7. RL response of LTB doped with three different concentrations of copper.

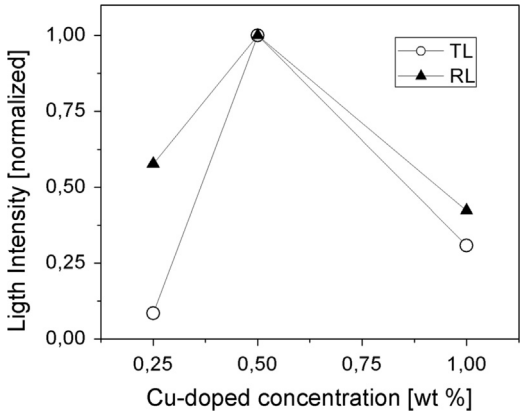

Fig. 8. RL and TL response normalized to the highest intensity in each case.

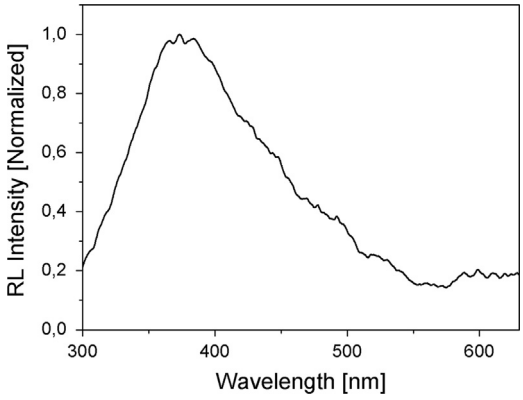

Fig. 9. RL spectrum of $Li_2B_4O_7$:Cu (0.5 wt %).

peak is almost negligible. The shape of the glow curves recorded in this work is slightly different to that found by other authors. For example, Faramawy et al. [8] showed a glow curve with the main and the secondary peaks centered at 178 and 120 °C respectively and, in the case of Babita et al. [4], the main and secondary glow peaks were centered at 220 and 104 °C, respectively. It should be mentioned that the heating rate employed by Faramawy et al. was 6 °C/s.

Returning to the most efficient copper doped borate, namely, LTB:Cu 0.5 wt %, a study of the fading of the signal was carried out and as it was mentioned in the previous paragraph, the low temperature glow peak disappears completely after 16 h of storage in darkness and at RT. The same result was observed if it is carried out an annealing at 120 °C for 10 s (see Fig. 5). On the other hand, the main peak remains constant in both cases.

By taking into account these results, prior to TL readout the samples were annealed at 120 °C for 10 s in order to obtain the dose response of this compound. As can be seen from Fig. 6, TL response (defined as the area under the glow curve) as a function of dose of this compound shows a good linearity in the dose range from 1 cGy up to 100 Gy. A linear regression performed on the experimental data has rendered a regression coefficient equal to 0.999, which indicates a very good linear TL response. This is an excellent result in the context of use this material in the field of beta radiation dosimetry.

Fig. 7 shows the RL response of LTB:Cu corresponding to each concentration of copper. It is evident from the figure that the highest emission intensity is obtained for 0.5 wt % concentration. Besides, no changes in RL sensitivity during irradiation and no afterglow with long decay time are observable from these lithium borates. Stable RL response and no long-lasting afterglow could be related to either a low concentration of shallow traps or rapid equilibrium attainment between charge-trapping and detrapping rates during irradiation [6].

It is worth mentioning that Santiago et al. [24] studied the RL of LTB doped with other dopants also exhibiting efficient direct transitions (Mg and Ag) from the point of view if their possible application as scintillating dosimeter. Although LTB:Mg was found to be more efficient than LTB:Cu, its RL signal shown strong dependence on accumulated dose and a long lasting afterglow. In this context, the stability of the RL signal of LTB;Cu as function of time and the absence of appreciable afterglow (see Fig. 7) make this phosphor an interesting material to be employed as scintillating dosimeter.

In Fig. 8, the RL intensity and TL integrated intensity normalized to the highest response for each Cu concentration is shown. The integrated TL intensity for LTB:Cu (0.5 wt %) is more than three times higher than that from any of the copper doped lithium tetraborate investigated in this work. The RL response of this concentration is almost twice higher than the other concentration of copper. The decrease of the efficiency at Cu concentrations higher than 0.5 wt % could be related to optical quenching effect, as widely observed in many phosphors [17,19,20].

Finally, the RL spectrum of LTB:Cu (0.5 wt %) under beta irradiation has been recorded (Fig. 9). This borate has a broad emission band between 300 and 500 nm with a maximum at 370 nm. This emission has been observed by several authors and it can be likely attributed to the Cu^+ emission due to the transition $3d^{10} <-> 3d^9–4s^1$ [24,25,4].

4. Conclusions

Lithium tetraborate was obtained by high temperature solid state reaction and doped with copper by $CuCl_2$ acetone/alcohol solution which was sintered subsequently. Powder XRD patterns

proved the formation of the lithium tetraborate phase and were found to match with the reported data, implying the synthesis of only the $Li_2B_4O_7$ body-centered tetragonal phase; with the dopant addition there was no change in the structure. FT-IR-ATR spectrum revealed that addition of the Cu activators caused no noticeable change in vibrational modes of borates and the bond structure within the material.

Of the three concentrations of doped studied in this work, LTB:Cu 0.5 wt % has shown the highest TL and RL response when it is irradiated with beta radiation. The TL response of this sample is nearly four times higher than that corresponding to samples doped at 0.25 and 1 wt % Cu. As to the RL efficiency, LTB:Cu 0.5 wt % is almost twice more efficient than LTB:Cu 0.25 and 1 wt %.

The TL dose response presents a very good linearity in the studied dose range from 0.01 up to 100 Gy and no fading is observed when an annealing at 120 °C for 10 s is carried out after irradiation. In the RL measurements, no changes in RL sensitivity during irradiation and no long-lasting afterglow are observed from these lithium borates, which could be related to a rapid equilibrium attainment between charge-trapping and detrapping rates during irradiation. These dosimetric properties make that these low cost and relatively easy preparation polycrystalline Cu-doped lithium tetraborates a good alternative to be used in beta radiation dosimetry.

Finally, the RL spectrum of the Cu doped lithium tetraborate has a broad emission band between 300 and 500 nm with a maximum at 370 nm and this emission could be attributed to the $3d^{10} <-> 3d^9–4s^1$ transition of Cu^+.

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