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Thermoluminescence and radioluminescence properties of tissue equivalent Cu -doped $Li_2B_4O_7$ for radiation dosimetry

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Abstract

Thermoluminescence (TL) and radioluminescence (RL) properties of lithium tetraborate ($Li_2B_4O_7$) doped with different concentration of copper (0.25, 0.5, 1 wt %) under gamma and beta irradiation has 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 80ºC. The low temperature peak disappears completely after 24 hours of storage in darkness and at room temperature or after an annealing at 120°C for 10 seconds. 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 %) shown the higher RL emission and a stable and repetitive response. Results show that $Li_2B_4O_7$:Cu has prospects to be used in gamma and beta radiation dosimetry.

Keywords: Thermoluminescence, radioluminescence, lithium tetraborate, dosimeter.

1.- INTRODUCTION

Lithium tetraborate, $Li_2B_4O_7$, it is a material with broad applications in piezotechnology, acoustoelectronics, nonlinear optics, environmental, personal, and clinical radiation. An important feature is their near human tissue equivalent absorption coefficient with an effective atomic number (Z_{eff}) of 7.3, almost similar to that of tissue of human body (7.4) [Zhigadlo *et al.*, 2001, Ranjan Singh *et al.*, 2012].

A large number of materials exhibit thermoluminescence (TL) property, however, a lack of low Z_{eff} phosphors are suitable for use in radiation dosimetry. Then it is important to synthesize and study the luminescence properties of lithium tetraborate, this material gains more importance from the clinical dosimetry because accurate estimation of the dose absorbed by the tissue is required. Although $Li_2B_4O_7$ doped with manganese was the first TL material commercialized, this higher emission wavelength does not suit the spectral response of common photomultiplier tubes, $Li_2B_4O_7$:Cu showed TL emission at lower wavelength compared to $Li_2B_4O_7$:Mn and hence resulted in enhanced TL sensitivity, since this transition metal ion provides electron and hole traps that significantly increase the light output in photoluminescence (PL) and thermoluminescence experiments, its emission lies in the near UV region that is suitable for using with normal TL readers [Kelemen *et al*. 2007, Kelemen *et al*. 2012, Mehmet Kayhan *et al.*, 2011, Annalakshmi *et al.*, 2013].

Another important characteristic is that the borate compounds has higher sensitivity, good thermal stability, good post-irradiation storage stability, low cost and relatively easy preparation. In this work, thermoluminescence and radioluminescence (RL) studies of $Li_2B_4O_7$:Cu doped with different concentration were carried out to evaluate the feasibility of using this borate in radiation dosimetry at low doses, in previous analyses, the material show some desirable features for TL in terms of linearity and storage and many of the earlier problems of fading, light sensitivity and poor humidity behavior have been avoided, the synthesized materials are promising for dosimetric applications and as radiation proof material for optical devices [Guarneros-Aguilar *et al.*, 2013].

2.- MATERIALS AND METHODS

Li_2CO_3 and H_3BO_3 were mixed and melted at 950°C in air during 180 minutes in a ceramic crucible using a muffle furnace. The sample was slowly cooling to room temperature and then reheated at 650°C during 120 minutes to complete the crystallization. $Li_2B_4O_7$ obtained was doped with different Cu concentrations (0.25, 0.5 and 1.0 wt %) adding the $Li_2B_4O_7$ powder into a solution of $CuCl_2$ in acetone/alcohol and subsequently dried. The dried mixture was treated at 900°C in air during 60 minutes. 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 Bruker D8 Discover Diffractometer, operated at 40 kV and 40 mA, the slow scan was performed in the 2θ range from 10–80° with a scan step of 0.026°, to corroborate the phase purity of the samples synthesized. 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 thermoluminescence (TL) and radioluminescence (RL) measurements, the Cu doped lithium tetraborate samples were irradiated at room temperature (RT) with a 3.7 x 10^{-8} Bq ophthalmic ^{90}Sr beta-source rendering 0.022 $Gymin^{-1}$ dose rate at the sample position. TL glow curves from the samples 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 (PMT). Radioluminescence curves were measured as a function of time during beta irradiation. All the samples were irradiated at RT with the same ^{90}Sr beta-source and the light emitted by the samples was collected by means of a φ=1 mm communication grade optical fiber and projected onto a Sens-Tech P25PC-02 photon counting PMT. RL spectra were recorded by means of an Acton Research SP-2155 0.150 m monochromator featuring the same Sens-Tech P25PC-02 PMT. 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 obtained by setting the entrance and exit slits width at 3 mm during the measurements.

3.- RESULTS

Figure 1 shows the X-ray diffraction patterns of the successful synthesized samples with (hkl) values, the XRD pattern obtained for $Li_2B_4O_7$ was matched with the standard data available (card no. 01-079-0963) with body-centered tetragonal structure and cell parameters ***a*** = ***b*** = 9.47900, ***c*** = 10.29. At 28° is observed one peak which correspond to boric acid plane [002] (card no. 01-073-2158), but in $Li_2B_4O_7$:Cu samples there is not present due to the second thermal treatment, the remnants react completely. Then, the dopant added did not interfere with the crystal structure [Babita Tiwari *et al.*, 2010, Pekpaka *et al.*, 2011].

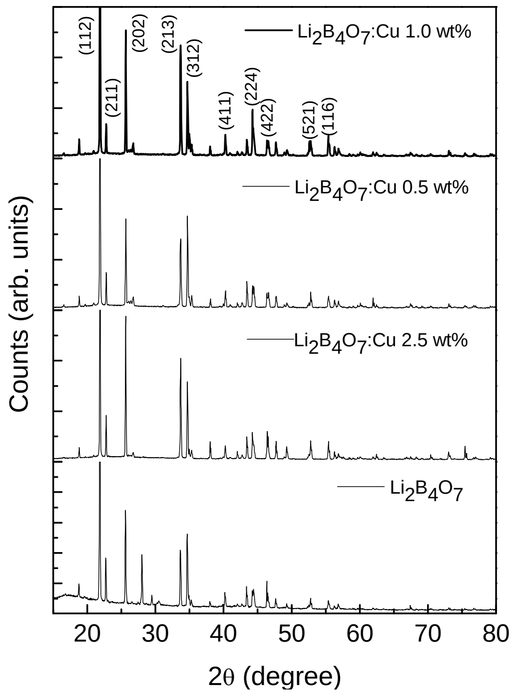

Figure 1. X-ray diffraction pattern of undoped lithium tetraborate and lithium tetraborate doped with copper (0.25, 0.5, and 1.0 wt %).

FT-IR-ATR spectra for the solid state synthetized undoped lithium tetraborate and the doped phosphor with different copper concentrations are presented in Figure 2. According to Pekpak *et al*. the common vibrational modes expected in $Li_2B_4O_7$ 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} [Pekpaka *et al.*, 2011]. The vibrational modes of the synthetized samples are resumed in Table 1, it can observed that the principal bands correspond to borate group are present.

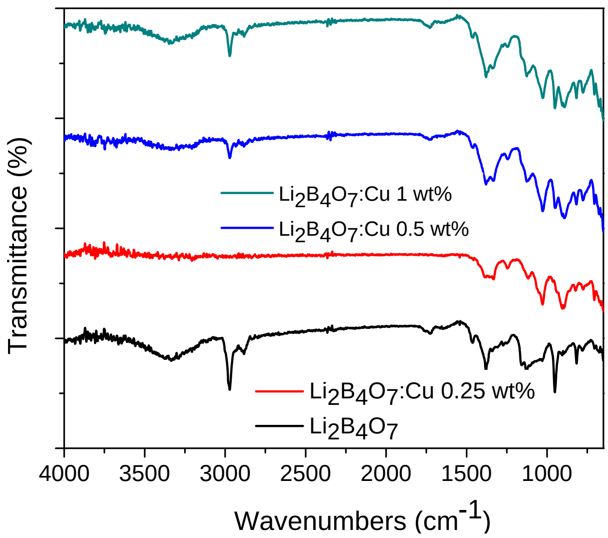

Figure 2. The FT-IR-ATR spectra of blank lithium tetraborate and lithium tetraborate doped with copper (0.25, 0.5, and 1.0 wt %).

Table 1.- FT-IR-ATR vibrations observed in doped and undoped $Li_2B_4O_7$.

Occurrence	$Li_2B_4O_7$	$Li_2B_4O_7$:Cu 0.25 wt%	$Li_2B_4O_7$:Cu 0.5 wt%	$Li_2B_4O_7$: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

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

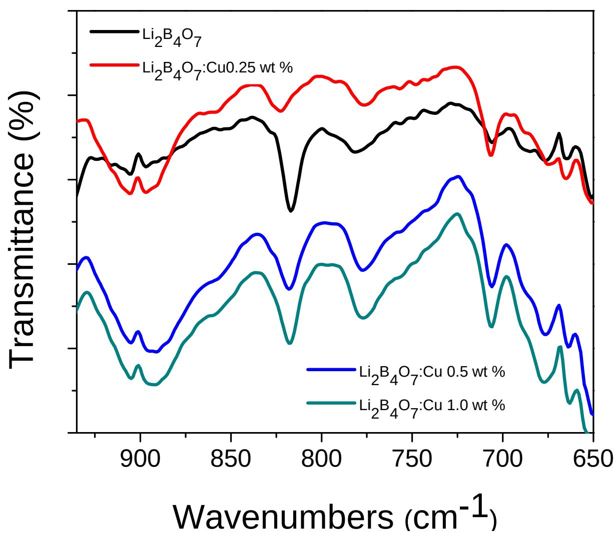

Figure 3. The FT-IR-ATR spectra of $Li_2B_4O_7$ and $Li_2B_4O_7$:Cu doped with 0.25, 0.5, and 1.0 wt %.

Figure 4 shows TL glow curve of $Li_2B_4O_7$ doped with different concentration of copper. It can be seen from the figure that among the Cu doped lithium tetraborate, the concentration of 0.5 wt % has the highest TL response to beta radiation.

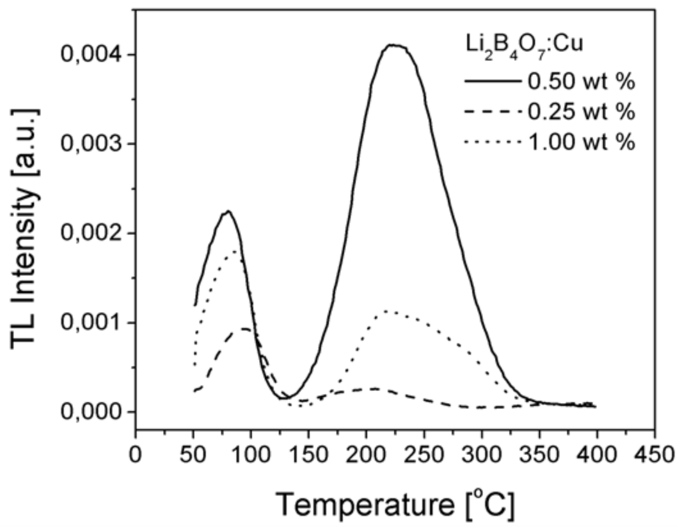

Figure 4. TL glow curves of $Li_2B_4O_7$ doped with different concentration of copper.

The glow curve of the most efficient copper doped borate shows a main stable peak centered at 225°C and a second low temperature peak centered at 80°C. The low temperature peak disappears completely after 16 hours of storage in darkness and at room temperature or after an annealing at 120°C for 10 seconds (Figure 5). On the other hand, the main peak of the $Li_2B_4O_7$:Cu remains constant.

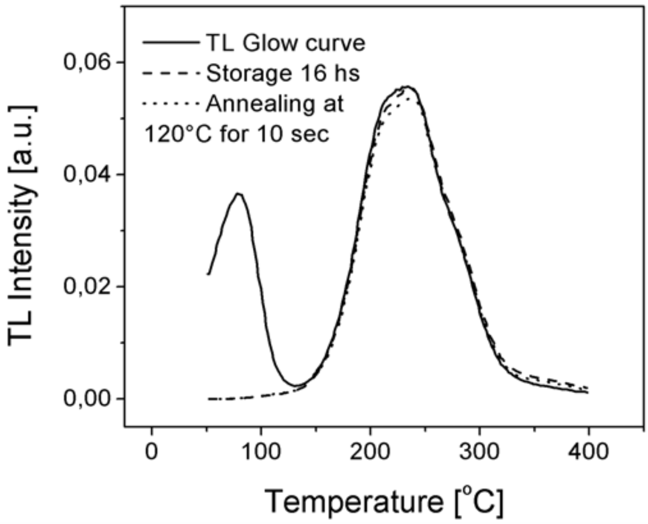

Figure 5. TL glow curve of $Li_2B_4O_7$:Cu (0.5 wt %) measured inmediately after irradiation (solid), after 16 hours of storage in darkness and at RT (dash) and after an annealing at 120°C for 10 seconds (dot), respectively.

The dose response of $Li_2B_4O_7$:Cu (0.5 wt %) after an annealing at 120°C for 10 seconds was investigated and the results are shown in Figure 6. As can been seen from Figure 7 the 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 gives a very acceptable linear TL response.

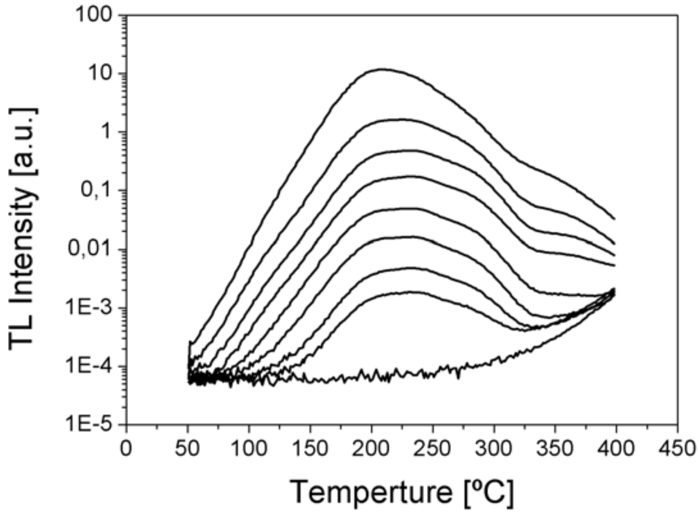

Figure 6. Glow curves of $Li_2B_4O_7$:Cu (0.5 wt %) from 100 up to 0.01 Gy from top to bottom, respectively. The bottom curve has been recorded for an unirradiated sample.

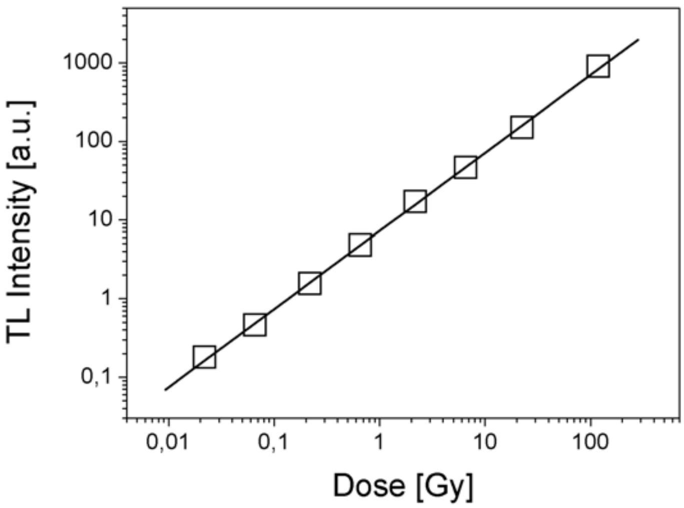

Figure 7. Dose response of $Li_2B_4O_7$:Cu (0.5 wt %) between 0.01 and 100 Gy. The solid line is a linear fit included for the eye guide.

Figure 8 shows the RL response of $Li_2B_4O_7$ doped with the three concentration of copper. It is evident from the figure that the higher light emission is obtained for 0.5 wt %. Besides, no changes in RL sensitivity during irradiation and no afterglow with long decay time is 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 [Damkjaer *et al.*, 2008].

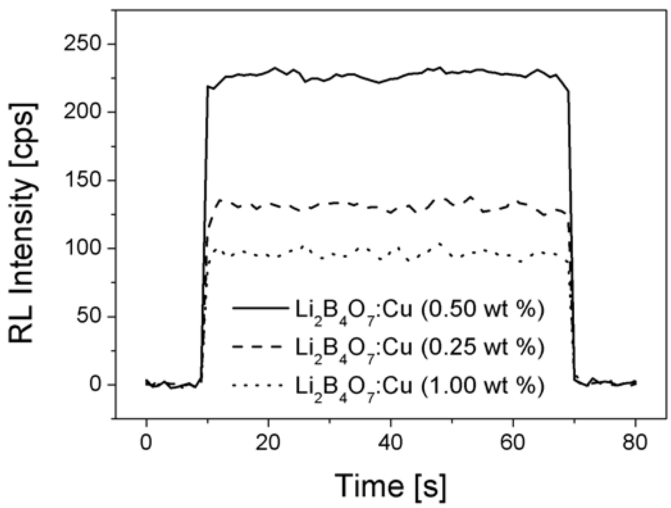

Figure 8. RL response of $Li_2B_4O_7$ doped with three different concentration of copper.

In Figure 9 is observed the RL intensity and TL integrated intensity normalized to the highest response in each case. The integrated TL intensity for $Li_2B_4O_7$: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.

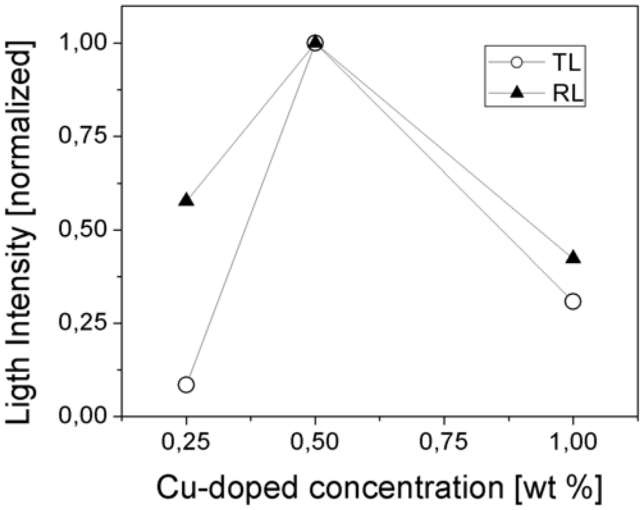

Figure 9. RL and TL response normalized to the highest intensity in each case.

RL spectrum of $Li_2B_4O_7$:Cu (0.5 wt %) under beta irradiation is shown in Figure 10. This borate has a broad emission band between 300 and 500 nm with a maximum at 370 nm. This emission is attributed to the Cu^+ emission due to the transition $3d^{10}$ <–> $3d^9$-$4s^1$ [Shahare *et al.*, 1994].

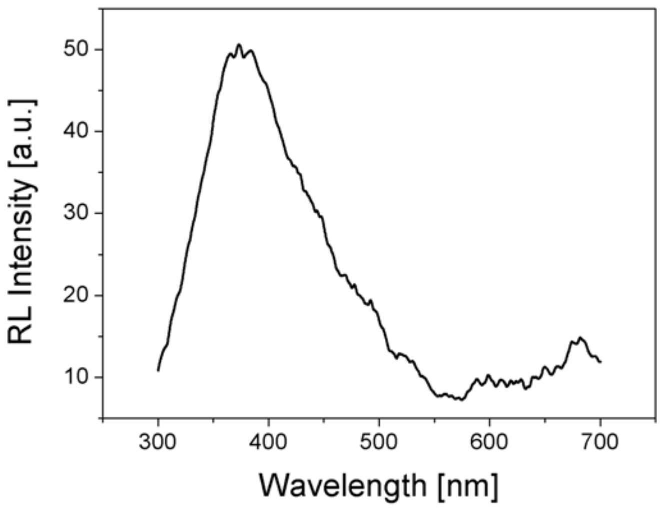

Figure 10. RL spectrum of $Li_2B_4O_7$:Cu (0.5 wt %).

4.- DISCUSSION

The crystal structure of un-doped and doped with copper lithium tetraborate was determined using X-ray diffraction patterns. The crystal structure is body-centered tetragonal with space group $I4_1cd$ (C_{4v}^{12}) and point group $4mm$. Fourier transform infrared attenuated total reflectance spectroscopy was used as an auxiliary characterization method. Figure 2 and 3 shows the spectral similarity between samples produced by solid state reaction at high temperature of undoped lithium tetraborate and Cu doped lithium tetraborate with different weight percent of the impurity. The presence of characteristic B–O trigonals and tetragonals bindings in the spectrum confirmed the structure spected for this phosphors. The infrared bands between 600 and 800 cm^{-1} observed are mainly due to B–O bending [N. D. Zhigadlo *et al.*, 2001].

The TL intensity of the glow curve of $Li_2B_4O_7$ doped with copper at 0.5wt % was the most intense, probable that the Cu impurity produce aggregate at the other higher concentration (0.25, 1 wt %). The first glow peak at 80 °C was ascribed to the presence of the Cu impurity in the lattice. This low temperature peak disappears after 16 h of storage in darkness or after an annealing at 120°C for 10 s because this peak is related to the shallowest traps in the band gap, and the other hand, the main peak of the $Li_2B_4O_7$:Cu remains constant due to the deep traps. The clean effect of the low peak at 80 °C makes a good linear TL response of this phosphor under beta radiation, and also the RL response at the different concentration of copper impurity. The RL spectrum shown a broad emission band with a maximum at 370 nm, that is attributed to the Cu^+ due to the transition $3d^{10}$ <–> $3d^9$-$4s^1$.

5.- 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 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.

The glow curve of the Cu doped $Li_2B_4O_7$ at 0.5 wt % has the highest TL response to beta radiation. All samples at different concentration exhibit a good radioluminescence (RL) response. The RL response of Cu doped [0.5 wt %] is almost twice higher than the other concentration of copper. 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 last emission is attributed to the Cu^+ due to the transition $3d^{10}$ <–> $3d^9$-$4s^1$.

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