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Thermoluminescent Characteristics of $Li_2B_4O_7$ Doped with Mn^{2+} and Eu^{3+} Ions

P. TREJO-GARCÍA [1], E. CRUZ-ZARAGOZA[3], R. ACEVES[2], J. E. ESPINOSA[1], R. PALOMINO MERINO[1*]

[1]Facultad de Ciencias Físico-Matemáticas, B. Universidad Autónoma de Puebla., Pue., Ciudad Universitaria, Puebla, Pue., México. P.O. Box 1067, C.P. 72001 México.

[2]Departamento de Investigación en Física, Universidad de Sonora, Apdo. Postal 5-088, 83190 Hermosillo Sonora, México.

[3]Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, A.P. 70-543, 04510 Ciudad de México, México

[1*]**Email: palomino@fcfm.buap.mx**

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Abstract Analysis of thermoluminescent properties were made for two samples; $Li_2B_4O_7$, $Li_2B_4O_7$:Mn^{2+}:Eu^{3+}. These samples were prepared by melt quenching method. The glow curves of the samples show two broad peaks at 160º C and 245 ºC, and a high peak at 130ºC for $Li_2B_4O_7$ doped. The response of the materials were analyzed according to the doses (0.2-80 Gy), fading (0-72 hours) and reproducibility of the experiment (10 times). To determine how the glow curve is formed, thermal bleaching for a dose of 5 Gy were made from room temperature to 300º C. Besides, X-ray diffraction patterns were recorded to identify the structure and grain size of the samples.

Keywords: Lithium tetraborate, rare earths, thermoluminiscence.

1. INTRODUCTION

Lithium tetraborate ($Li_2B_4O_7$) has attracted the attention of many researchers because it has many applications, for example in surface acoustic wave (SAW), bulk acoustic wave (BAW) devices, and dosimeter radiotherapy [1, 2]. Related to radiotherapy, the similarity in atomic composition between the dosimeters and the biological tissue is an important property for thermoluminescent dosimeters for estimation of absorbed dose in tissues exposed to ionizing radiation [3]. In the table (1) the effective atomic numbers for different tissues

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and dosimeters based on lithium tetraborate are calculated from the equation (1) of Spiers.

Where f_i is related to the fraction of the total number of electrons, z_i is the atomic number of each element and 2.94 is related to the energy range used. Also, introducing a small quantity of dopant ions into the lithium tetraborate we can enable the sensitivity to ionizing radiation. It has been founded that cooper and manganese are promising dopants for applications as a radiation proof materials and for optical devices [5].

Moreover, in this work the use of europium 3+ like a dopant *of -manganese doped Lithium tetraborate* ($Li_2B_4O_7$*:*Mn^{2+}*)-* is used to overcome the drawback of TL sensitivity and TL emission spectra at around 218ºC for LiBO:Mn^{2+} to an emission spectrum of europium activator, at about someone of the bands with maxima around of 130 ºC.

2. EXPERIMENTAL PROCEDURE

The samples for this study ($Li_2B_4O_7$ and $Li_2B_4O_7$:Mn^{2+}:Eu^{3+}) were synthetized by the melt quenching method [5]. To synthesize the $Li_2B_4O_7$, a stoichiometric mixture of Li_2CO_3, H_3BO_3 and H_2O were gotten. After that, the mixture get dried and posteriorly it was heated until 930º C during 4 hour. The product gotten get cooled until reach the room temperature (RT), once this temperature was reached, the sample were heated until 600º C for two hours, finally the sample get cooled. The material gotten was a transparent crystal that, once it was cooled, it was grind in an Agate mortar.

The doped sample was gotten by the mixture of $Li_2B_4O_7$, $MnCL_2$ and $Eu(NO_3)_3$ (0.5 wt.%, 0.025wt%) in alcohol. The sample were dried and after that, it was heated until 830º C in an air muffle furnace during 1 hour. This doped sample was under thermal treatment at 600º C for two hours and cooled at room temperature. In this case the sample gotten is reddish.

Table 1: Effective atomic number calculated from the Spiers equation for different tissues and for synthesized samples.

Material	$Li_2B_4O_7$	$Li_2B_4O_7$:Mn^{2+}	$Li_2B_4O_7$:Mn^{2+}:Eu^{3+}	Tissue: $C_{21}H_{140}O_{57}N_3$	Tissue: $C_{22}H_{170}O68N_3$
Effective atomic number	7.24	8.42	20.9	7.1	7.12

3. RESULTS AND DISCUSSION

3.1 XRD pattern

The X-ray diffraction (XRD) patterns were recorded using Cu-Kα (1.5406 Å) radiation in an X-ray Bruker Discover D8 diffractometer, operated at 40kV and 40 mA, to corroborate the phase of the samples synthesized. The slow scan was performed in the 2θ range from 15-80°. The results obtained were matched with the standard data available (Card No. =04-010-0882), this patterns belong to the crystalline structure best known as Diomignite with a tetragonal lattice and lattice parameters a=b=9.47900, c=10.29000 Å respectively. The Figure 1 shows the X-ray diffraction pattern of the synthesized samples with (hkl) values, moreover, in the table (2) are shown the lattice parameters and volume for each sample. It should be pointed that the patterns shown small slides in the 2θ axe probably due to the change of lattice volume.

From the Scherer formula λ/ (βcosθ), where is the geometric factor (0.9 using spheres model), λ is the Wavelength (1.54060 Å), β is the full width at half maximum (FWHM) and θ the Bragg angle; the grain size was calculated. We got 29.7631 nm for $Li_2B_4O_7$ and 42.2860 nm for $Li_2B_4O_7$:Mn^{2+}:Eu^{3+}.

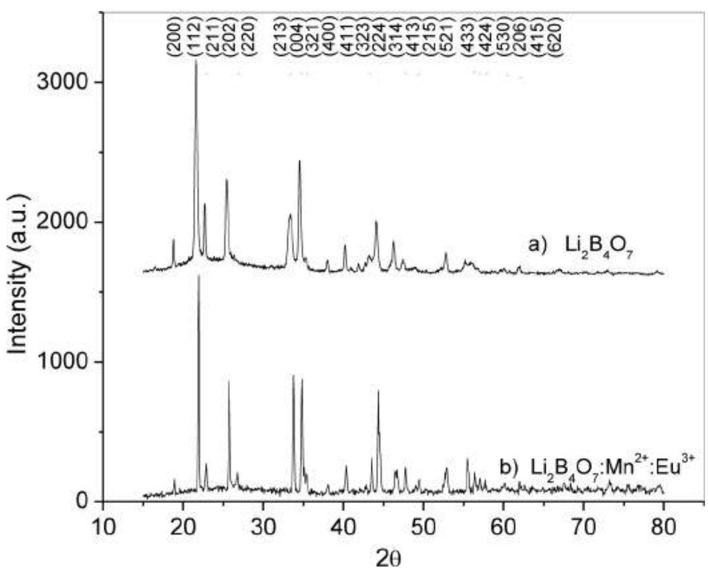

Figure 1: X-ray diffraction spectra of $Li_2B_4O_7$ and $Li_2B_4O_7$:Mn2+:Eu^{3+}. Both samples show the crystalline structures known as Diomignite.

Table 2: Experimental lattice parameters of the samples.

	Lattice parameters (Å)		Volume (Å^3)	Grain size
Sample	**a = b**	**c**		
$Li_2B_4O_7$	9.4786	10.4505	938.9132	29.7631
$Li_2B_4O_7$:Mn^{2+}:Eu^{3+}	9.4729	10.2701	921.5959	42.2860

3.2 Thermoluminiscence measurements

To study thermoluminiscence (TL) properties, the dose-response, fading, reproducibility and thermal bleaching measurements were made. The samples were irradiated by different doses in the range of 0.2- 80 Gy from ^{60}Co (Gammacell 200) with a dose rate of 0.153065 Gy/min. TL glow curves were recorded using a Harshaw TLD 3500 reader with linear heating rate of 2° C/s.

3.2.1 Dose-response

The samples $Li_2B_4O_7$ and $Li_2B_4O_7$:Mn^{2+}:Eu^{3+}were irradiated from 0.2 80 Gy with gamma photons. TL glow curves for $Li_2B_4O_7$ (Figure 2) are composed by two broad bands overlapping with maxima at 160 and 245ºC, moreover, it can be observed that the unique change is the height of the intensity TL depending of the dose, however, the ratio between response and dose is not linear such as can be observed in the Figure 4.

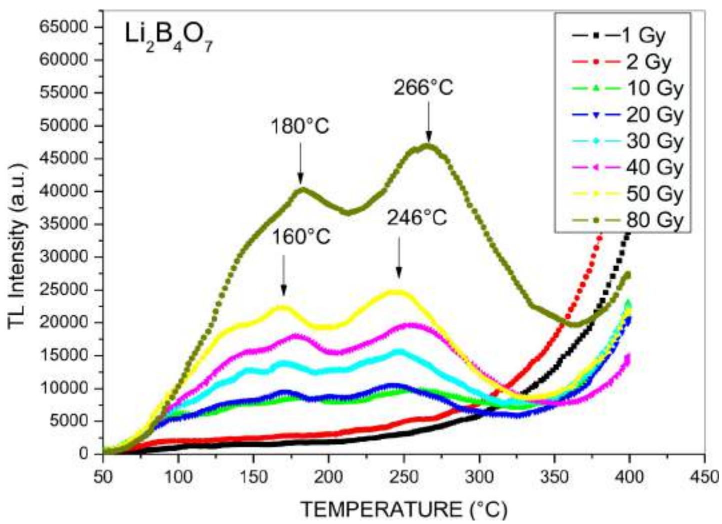

Figure 2: TL glow curves of $Li_2B_4O_7$ at low doses with gamma radiation using a ^{60}Co source.

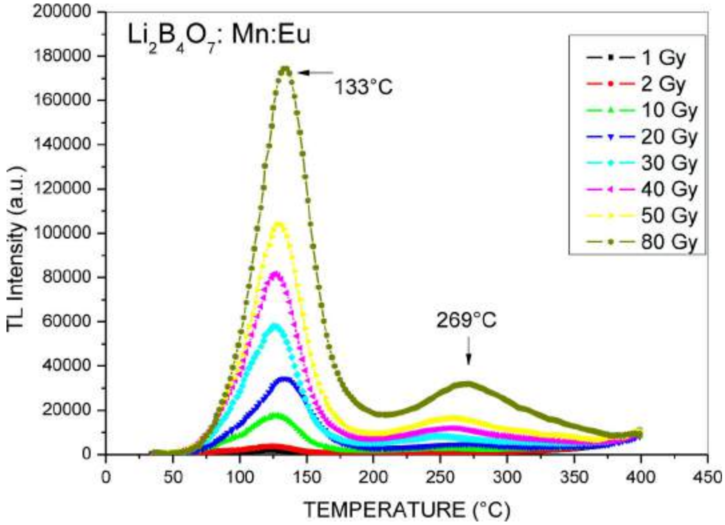

Figure 3: TL glow curves of $Li_2B_4O_7$:Mn^{2+}:Eu^{3+} at low doses with gamma radiation using a ^{60}Co source.

In the case of the sample $Li_2B_4O_7$:Mn^{2+}:Eu^{3+} the glow curve (figure 3) is formed by the bands previously mentioned and other band with maxima at 130ºC (dominant dosimetric peak). This curve is formed at least for two bands with maxima at 100 and 142ºC. In the same way that the undoped sample, the TL

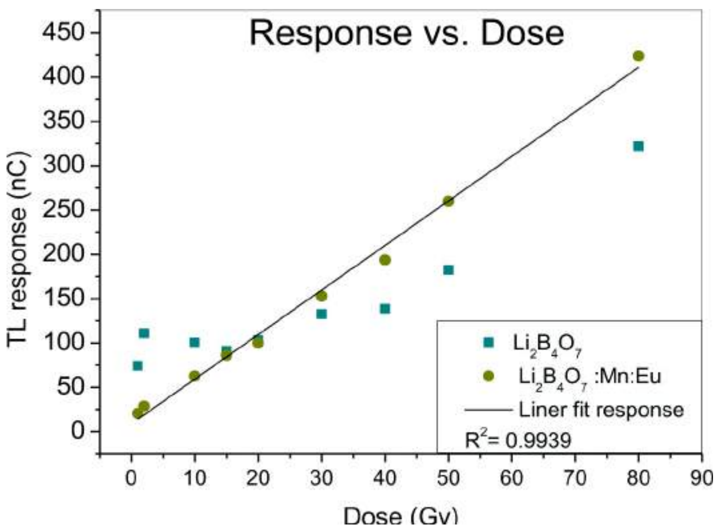

Figure 4: TL response vs dose of the samples $Li_2B_4O_7$ and $Li_2B_4O_7$:Mn^{2+}:Eu^{3+}.

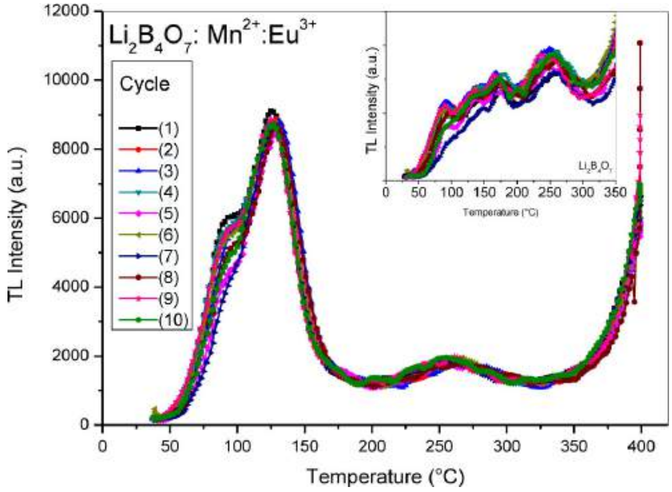

Figure 5: TL glow curves of $Li_2B_4O_7$:Mn^{2+}:Eu^{3+} in an experiment of reproducibility, the inset shows the glow curve for $Li_2B_4O_7$

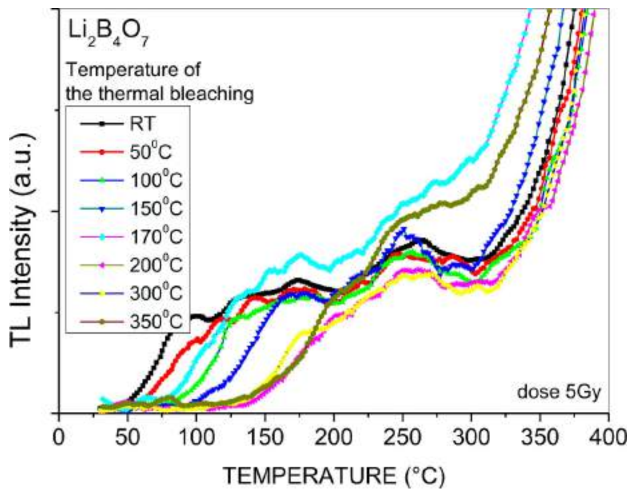

Figure 6: Glow curves for a thermal bleaching in $L_{i2}B_4O_7$ using a dose of 5 Gy.

intensity response grows as grow the dose, but in this case, the ratio between dose and response is linear (Figure 3)

3.2.2 *Reproducibility*

To evaluate the reproducibility for dose measurements of the synthesized samples, were carried out experiments ten times using a dose of 5 Gy. The glow

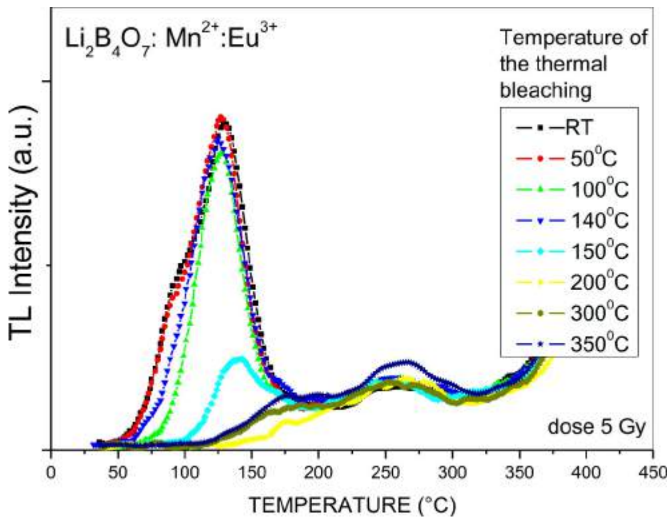

Figure 7: Glow curves for a thermal bleaching in $Li_2B_4O_7$:Mn^{2+}:Eu^{3+} using a dose of 5 Gy.

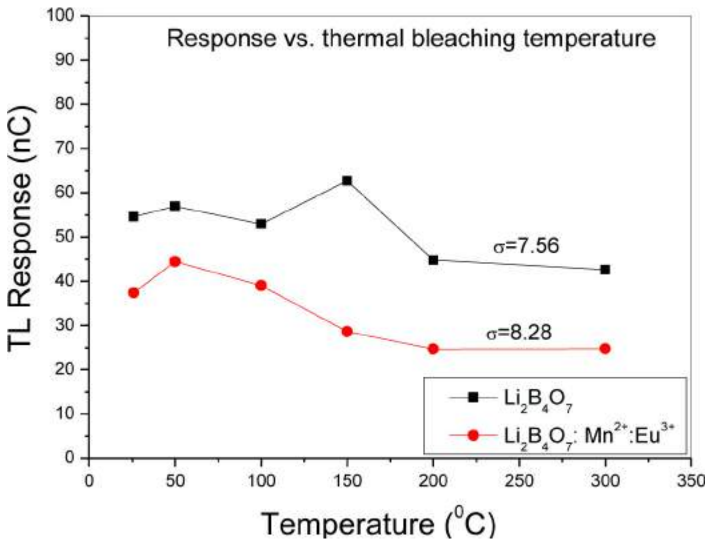

Figure 8: Glow curves related to the fading in TL response for $Li_2B_4O_7$.

curves of each experiment and both samples are shown in the figure 5. The glow curves of the undoped sample are shown in the inset of Figure 5. As it can be observed, these are too different in the range of low temperature

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(25-175ºC). In the case of the doped sample (Figure 5) the glow curve are similar in the right side of 105ºC.

3.2.3 *Thermal Bleaching*

The thermal bleaching of the sample consisted in radiate the samples at a gamma radiation of 5 Gy. For isolate the peaks that conform the glow curve. The interval temperature treatment was from room temperature to 350º C. From this experiment, it can be observed that the glow curve of the undoped sample (5) is formed by many bands with maxima at 89, 126, 157 y 200 °C. The first three peaks show low intensity, reason why these bands are not observed when the material is doped.

In the case of the doped sample (Figure 6) it was found that the main peak at 130º C can be isolated with a thermal treatment at 100ºC, which is a useful protocol of use of those materials with dosimetric properties in radiation dosimetry. It should be pointed that the main peak of $Li_2B_4O_7:Mn^{2+}$ reported in [5] for low doses is moved to 130º using the Europium like an extra dopant. In the figure 7 the TL response vs the thermal bleaching is show.

3.2.4 *Fading*

In order to determine the fading characteristics of synthesized samples, these were irradiated at 5 Gy and stored in dark conditions at room temperature for different time lapses (1.5, 3, 6, 15, 24 and 72 hours). The figure 8 and figure 9 show the glow curves related to the fading of doped and undoped samples.

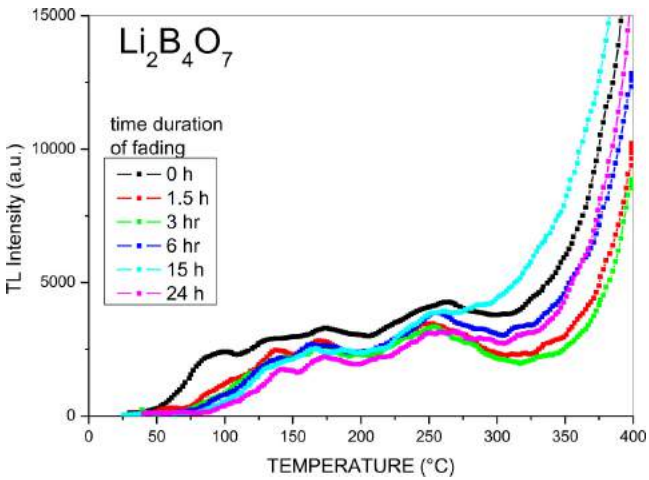

Figure 9: Fading of the TL response for $Li_2B_4O_7:Mn^{2+}: Eu^{3+}$.

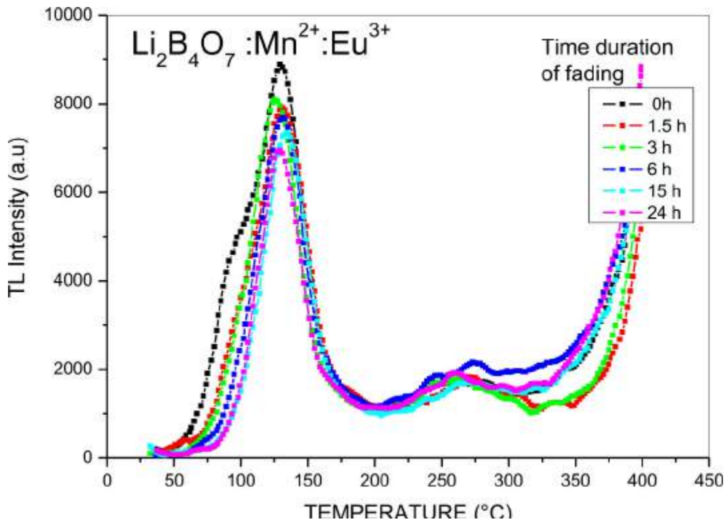

Figure 10: Fading vs time of both synthesized samples.

From this experiment it is not possible to define a behavior for the undoped sample, it is due the existence of electron traps not deep, and these traps liberate easily electrons which can implicate an entrapment at higher temperatures. This can be observed in the glow curves gotten at 1.5, 3, 6 hours.

For the doped sample, it can be observed the decreasing behavior related to the loss of information depending of the time, also the TL response it can be observed in the figure 10.

CONCLUSIONS

Dosimetric materials $Li_2B_4O_7$ and $Li_2B_4O_7$:Mn^{2+}:Eu^{3+} were obtained by melt quenching method also, is important to consider the heat treatment at 600° to ensure crystalline phases in the material. According to the XRD patterns both samples present the same crystalline phase, however, the doped sample presents a better structure than the undoped sample. The goal of overcome the drawback of TL sensitivity and TL emission spectra at around 218ºC for $Li_2B_4O_7$:Mn^{2+} to an emission spectrum of europium activator, at about someone of the bands with maxima around of 130 ºC due to Europium was achieved, also it could be possible to observe the linear relation between the doses and the response for the doped sample from 0 to 80 Gy.

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