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Investigation of thermoluminescence properties of metal oxide doped lithium triborate

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Abstract In this study, lithium triborate (LiB_3O_5) doped with different metal oxides were investigated to explore its thermoluminescence properties. Solid-state reaction method was employed for the synthesis of the desired materials. The formation of the produced phases was confirmed by Powder X-Ray Diffraction (XRD), Infrared (IR), Differential Thermal Analysis (DTA) and Scanning Electron Microscopy (SEM) examinations. It was found that, CuO and Al_2O_3 doped lithium triborate samples exhibit very significant thermoluminescence glow curves to be promising dosimetric material.

Introduction

Borates are attractive candidates in thermoluminescence dosimetry (TLD) for the quantitative measurement of radiation dose. Due to high cost of the most popular thermoluminescence dosimeters and also due to some complications attending its reuse such as permanent radiation damage effects and the sensitivity to the temperature of heat treatment, the attention was directed toward new thermoluminescence materials. Borates are relatively stable chemical compounds and respond without serious problems to attempts to dope them with TL sensitizers such as the rare earths, copper and manganese ions. The resultant materials show high sensitivity, linearity, and good storage properties. Also they avoid many of the earlier problems such as fading, light sensitivity and humidity sensitivity [1].

Lithium borate based TL dosimeters, has recently attracted much attention as radiation proof materials for optical devices and tissue-equivalent material for radiation dosimetry with an effective atomic number (Zeff) of 7.3 [2]. The first TL material based on lithium borate, $Li_2B_4O_7$:Mn, was introduced in dosimetry by Schulman et al. in 1965 [3]. The material was prepared by melting Li_2CO_3 and H_3BO_3 at 950 °C, which is higher than the melting point of lithium tetraborate (917 °C), then rapidly cooled to room temperature. The resultant glassy material was then crystallized by subsequent heating at 650 °C. The dopants were added at the melt stage.

Several transition metals and rare-earth elements have been tried as alternative dopants to manganese, but initially only silver resulted in comparable thermoluminescence efficiency [4]. Rzyski and Nambi [5] confirmed these disappointing results with 14 rare-earth elements of the lanthanide series. Furthermore, all these alternative dopants, particularly the rare earths, have considerably higher atomic numbers than manganese, and therefore may adversely affect the good tissue-equivalence of lithium borate even at the low doping concentrations used in these investigations (0.1–1.6% by weight).

Lithium tetraborate is simpler to handle as it does not require annealing after reading as LiF series [1, 6–8]. In particular, single crystals are transparent to visible light,

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which makes them very effective for the collection of emitted light from the inner parts of the sample. Also the resistance to humidity due to its stochiometric composition [9] and easy handling compared with powder samples [10] make the lithium tetraborate single crystal promising thermoluminescence dosimetry (TLD) when doped with Cu, Mn, and Mg ions [2].

Most of the research studies about TL properties of lithium borates are focused on lithium tetraborate. However, luminescence properties of lithium triborate have been insufficiently studied when compared to lithium tetraborate and no publication has been met related with thermoluminescence dosimetric properties of doped lithium triborate.

Ogorodnikov et al. [11, 12] detected four TL-peaks for the lithium tetraborate glow curve (two principal peaks at 130 and 240 K). Kuznetsov et al. [13] have proposed a satisfactory model for the trapped electron center B^{2+} in the lithium tetraborate.

Ivanov et al. [14] investigated the luminescence of lithium triborate crystals under high intensity synchrotron radiation. In a similar investigation carried out in 1998 by Ogorodnikov et al. [15] the spectral, luminescent and polarization properties of the oriented LiB_3O_5 crystals under excitation with a polarized synchrotron radiation was studied.

The recombination processes and lattice defects in crystals of alkali metal borate—LiB_3O_5 were studied by means of TL and electron spin resonance (ESR) techniques in 2001 by Ogorodnikov et al. [16]. Two TL peaks were observed at 130 and 240 K.

In this research our aim is the investigation of the TL properties of lithium triborate by doping it with different metal oxide dopants. This is the first time that the TLD properties of LiB_3O_5 doped with CuO, MnO_2, MgO, Fe_2O_3, $CoCO_3$ and Al are indicated in the literature [17, 18].

Experimental procedure

Solid-state reaction method was employed for the synthesis of lithium triborate and metal doped lithium triborate. Li_2CO_3 and H_3BO_3 were used as the starting materials and stochiometric quantities of these materials were mixed according to the estimated reaction given below and they were finely powdered by agate mortar. The mixture was first pre-heated in a porcelain crucible at 300 °C for 4 h. Then it was heated slowly starting from room temperature to 750 °C for 14 h with intermittent grinding at the end of each 7 h.

$$Li_2CO_3 + 6H_3BO_3 \rightarrow 2LiB_3O_5 + CO_2 + 9H_2O$$

During doping studies, different dopants like CuO, MnO_2, Fe_2O_3, $CoCO_3$, MgO, and Al_2O_3 were weighed separately in different fractions ranging from 0.1 to 1% wt. of constant amount of LiB_3O_5. The mixtures were ground by agate mortar for homogenization and then transferred into a porcelain crucible and heated slowly starting from room temperature to 750 °C for 7 h. All the samples were kept in desiccators against moisture [17, 19].

Powder X-Ray Diffraction (XRD) investigations were carried out by Rigaku MiniFlex X-Ray Diffractometer/PW 3710 equipped with $CuK\alpha_1$ radiation and the patterns were recorded from $10° < 2\theta < 80$ °C.

Nicolet FTIR Infrared Spectrometer was employed for the measurement of IR spectra in the wave number range 400–4,000 cm^{-1}. The IR pellets were prepared by using spectroscopic grade KBr (KBr: Sample ratio = 100 mg:3 mg).

In order to establish the solidification and thermal behavior of the materials prepared by solid-state reactions, Setaram Labsys TGA/DTA Simultaneous Thermogravimetric Analyzer and Differential Thermal Analyzer was used. The measurements were performed in a nitrogen flux atmosphere with a uniform heating rate of 10 °C/min.

For the surface characterization of the lithium triborate samples, the Scanning Electron Microscopy (SEM) technique was applied. The measurements were carried out by using JSM-6400 Electron Microscope (JEOL), equipped with NORAN System 6 X-ray Microanalysis System & Semafore Digitizer.

In determination of thermoluminescence dosimetric characteristics of lithium triborate and doped lithium triborate compounds, Harshaw 3500 Manual Model TLD Reader at Physics Engineering Department of Gaziantep University, Türkiye, was applied. The measurements were carried out on 20 mg samples. All the samples were annealed at 400 °C for 1 h prior to irradiation and then irradiated 5 min by ^{90}Sr–^{90}Y beta (β) source at room temperature. All glow curves were read out at 1 °C/s ramp after the samples were exposed to the same dose level (nearly 4.5 Gy) at room temperature. In order to establish the degree of fading of the stored dose information, the TL response of the samples were recorded 24 h after irradiation.

Results and discussions

During doping studies, to determine the suitable dopant type yielding in good thermoluminescence property for dosimetric use, different dopants: CuO, MnO_2, Fe_2O_3, $CoCO_3$, MgO and Al_2O_3 were examined. The metals were selected based on the previous studies reported on

thermoluminescence properties of lithium tetraborate [2, 20–24].

According to TLD studies carried out on lithium triborate samples doped separately with 1% wt. of CuO, MnO_2, Fe_2O_3, $CoCO_3$, MgO, and Al_2O_3; except for the $CoCO_3$ doped sample, all the metals doped lithium triborate samples gave a response to irradiation process with changing peak temperatures and intensities. Between these samples, LiB_3O_5:Cu and LiB_3O_5:Al yielded the most significant TLD properties and therefore the results of CuO and Al_2O_3 doping studies are given here.

Figure 1 reveals the diffractograms of undoped and CuO doped (wt. concentration between 0.1 and 1%) lithium triborate phases. As can be seen, the obtained pattern for lithium triborate, is in good agreement with the XRD pattern given in the literature [25–28] and JCDPS Card No: 32–549 [29] with very small amount of impurities [30]. Moreover, the XRD patterns obtained for LiB_3O_5:Cu sample does not contain any reflections associated with CuO which means that crystal structure did not change significantly with the addition of CuO.

The XRD patterns of LiB_3O_5 and LiB_3O_5 doped with 0.1–1% wt. of Al_2O_3 was illustrated in Fig. 2. For all concentrations of Al_2O_3, the patterns are the same as the XRD pattern of pure lithium triborate proving occurrence of no structural changes as in CuO doping. No reflections demonstrating the existence of Al_2O_3 were observed in the structure.

The IR spectra obtained for LiB_3O_5 and LiB_3O_5 doped with CuO and Al_2O_3 are given in Figs. 3 and 4. It can be stated from both figures that, the bands are in good agreement with the bands of lithium triborate given in the literature [31–37]. For the trigonal coordination the characteristic bands are the stretching bands of the highest intensity, occurring above 1,200 cm^{-1} and the weaker bands in the region 700–800 cm^{-1} attributed to scissor vibrations of B–O–B bridges in the boron oxygen network.

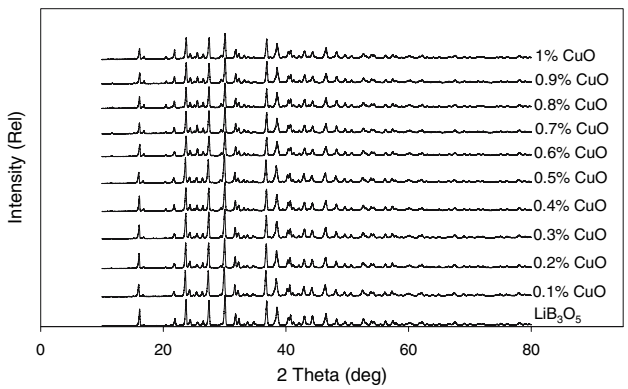

Fig. 1 Powder X-Ray Diffraction patterns of LiB_3O_5 and LiB_3O_5 doped with CuO at 750 °C for 7 h

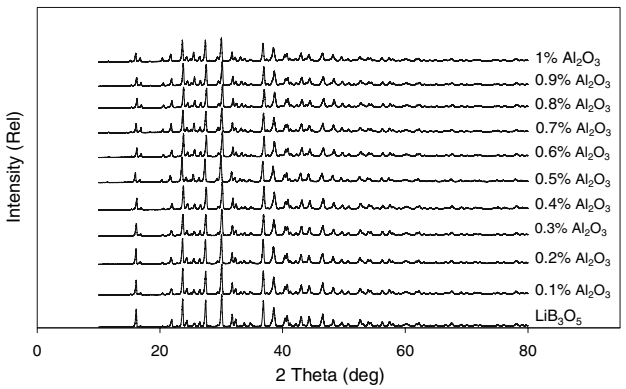

Fig. 2 Powder X-Ray Diffraction patterns of LiB_3O_5 and LiB_3O_5 doped with Al_2O_3 at 750 °C for 7 h

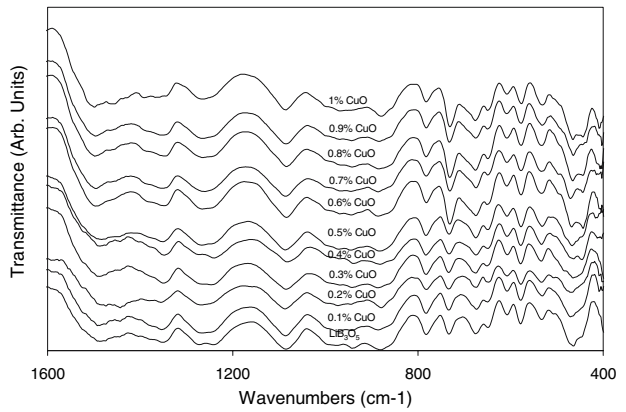

Fig. 3 IR spectra of LiB_3O_5 and LiB_3O_5 doped with CuO

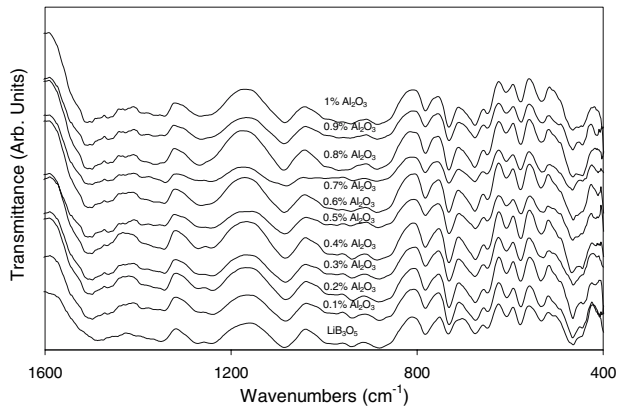

Fig. 4 IR spectra of LiB_3O_5 and LiB_3O_5 doped with Al_2O_3

For the tetrahedral coordination, the typical bands are situated in the 850–1,100 cm^{-1} range ascribed to the stretching vibration as B–O. The addition of metal dopants in the weight concentration range from 0.1 to 1% did not make significant change in the shape and the number of

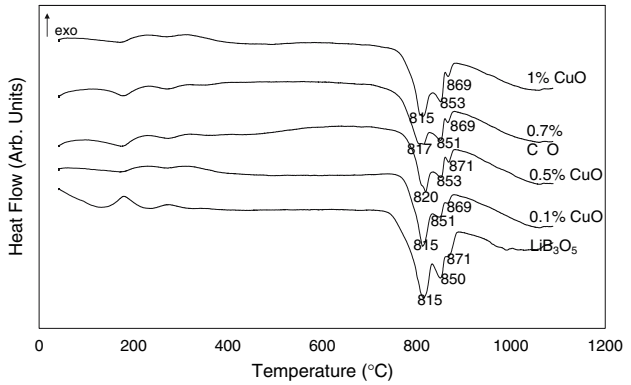

Fig. 5 DTA curves of LiB_3O_5 and LiB_3O_5 doped with 0.7% CuO

bands observed in IR spectra as indicated by Thomazini et al. [37]. No infrared bands associated with CuO and Al_2O_3 dopants were detected in the spectra.

In order to examine the possible changes in thermal behavior of lithium triborate samples doped with CuO and Al_2O_3, the samples were subjected to differential thermal analysis. The DTA curves recorded for the lithium triborate and lithium triborate compound doped with 0.1, 0.5, 0.7 and 1% wt. CuO are postulated in Fig. 5. When the DTA curves for the doped samples were compared with the undoped lithium triborate, it was seen that, no appreciable change was recorded in thermal behavior of the lithium triborate samples when doped with CuO.

Figure 6 illustrates the DTA curves of lithium triborate and lithium triborate doped with Al_2O_3. As in the case of CuO dopant, the addition of Al_2O_3 did not alter significantly the DTA curve of lithium triborate.

Figure 7 shows the SEM photographs taken from different parts of the sample obtained by heating precursor mixture at 750 °C for 14 h LiB_3O_5 sample. According to these photographs, rod-like particles with size ranging between 40 and 55 μm are dominant. Moreover, irregularly shaped particles were also detected.

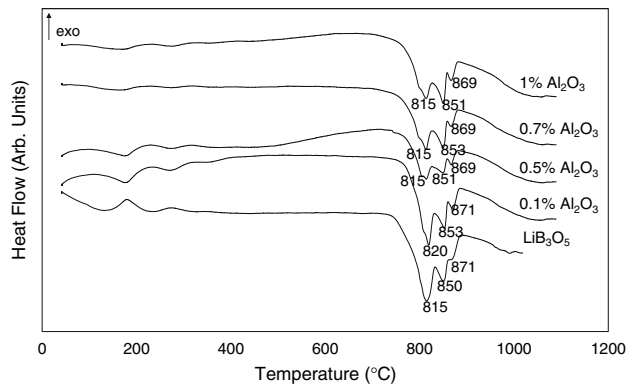

Fig. 6 DTA curves of LiB_3O_5 and LiB_3O_5 doped with Al_2O_3

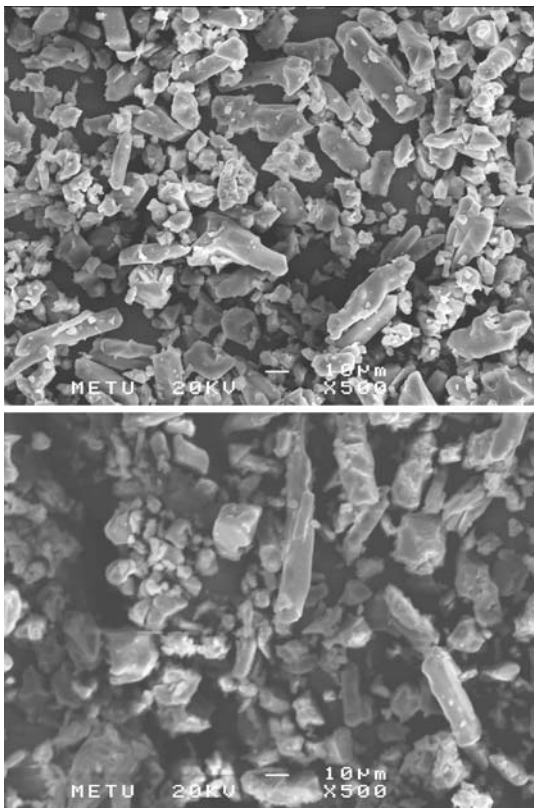

Fig. 7 SEM images of LiB_3O_5 produced from the solid-state reaction of Li_2CO_3 and H_3BO_3

Figure 8a and b represent the SEM photographs of LiB_3O_5 doped with 0.7 and 1% CuO, respectively. When these figures were analyzed carefully by comparing them with the SEM photograph of LiB_3O_5, it can be seen that, no phase indicating the precipitation of dopant dispersed in the matrix was recorded even with the addition of 1% CuO as approved by the XRD and IR investigations.

SEM images of LiB_3O_5, doped with 0.7 and 1% Al_2O_3 are given in Fig. 9a and b, respectively. According to these figures, no phase demonstrating the existence of Al_2O_3 was observed as confirmed by the XRD and IR studies carried out on the same samples.

The only change between the SEM photographs of undoped lithium triborate and lithium triborate samples doped separately with CuO and Al_2O_3 was recorded in the shape of particles. The rod-shaped particles seen in undoped lithium triborate was replaced by smooth rounded surfaces in doped lithium triborate samples.

Results of TLD measurements

Figure 10 illustrates the TL glow curve structure of undoped lithium triborate. According to this figure, two glow peaks around 137 and 200 °C were observed when

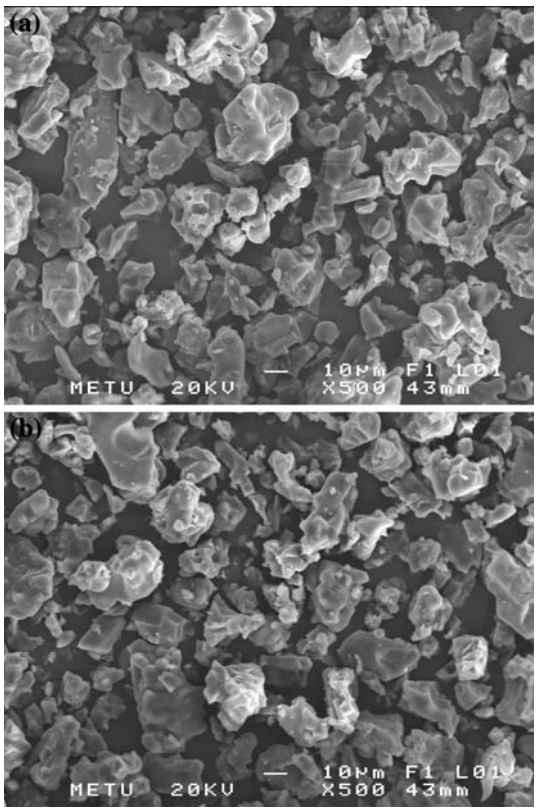

Fig. 8 (**a**) SEM images of LiB_3O_5 doped with 0.7% wt. CuO, (**b**) SEM images of LiB_3O_5 doped with 1% wt. CuO

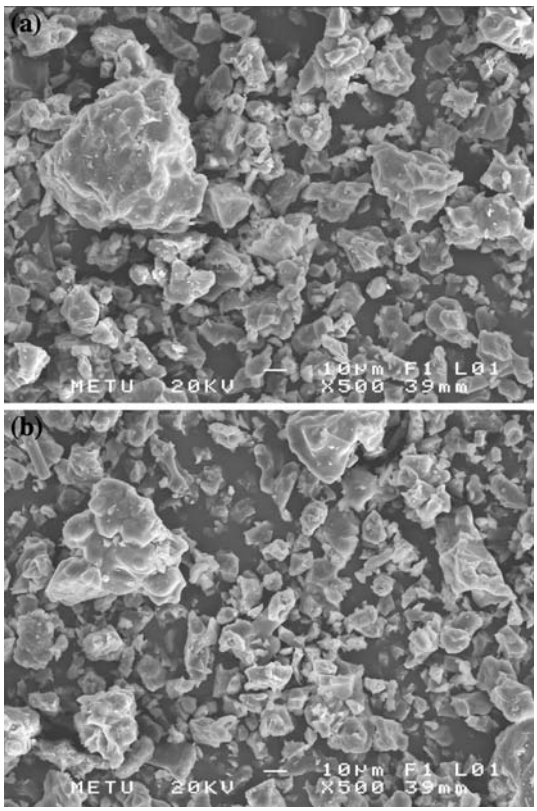

Fig. 9 (**a**) SEM images of LiB_3O_5 doped with 0.7% wt. Al_2O_3, (**b**) SEM images of LiB_3O_5 doped with 1% wt. Al_2O_3

the lithium triborate sample was irradiated 5 min by Beta, ^{90}Sr–^{90}Y source. The second curve which indicates fading information on the same figure implies that the stored radiation was not lost after 24 h from irradiation operation.

According to TLD studies, between the doped lithium triborate samples, CuO doped lithium triborate, with a well resolved single TL peak at about 120 °C gave the most appreciable TL response with the highest intensity but with high amount of fading measured 24 h after irradiation.

The second good glow curve structure was resulted by the lithium triborate sample doped with 1% Al_2O_3. Here, two well-resolved peaks are apparent in this figure. The maximum TL responses of the two peaks are produced at about 137 and 200 °C. No fading of the stored TL signal was recorded this time for both glow peaks as a result of measurement 24 h after irradiation process.

Therefore, with the two promising results come out with LiB_3O_5:Cu and LiB_3O_5:Al, these two samples were investigated in details with dopant concentration of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1% wt.

Figures 11–14 postulate the TL glow curve structures of lithium triborate doped with 0.1, 0.5, 0.7 and 1% wt. CuO. In all the figures, single, well-resolved, high intensity but low temperature peak was observed around 120 °C. When the TL response of the sample was measured 24 h after irradiation process, it was recorded that, almost 40% of the stored TL information was lost which may due to the low temperature

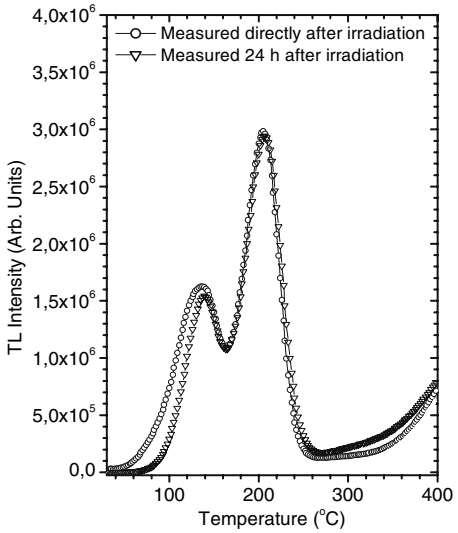

Fig. 10 The glow curve of LiB_3O_5 produced from the solid-state reaction of Li_2CO_3 and H_3BO_3

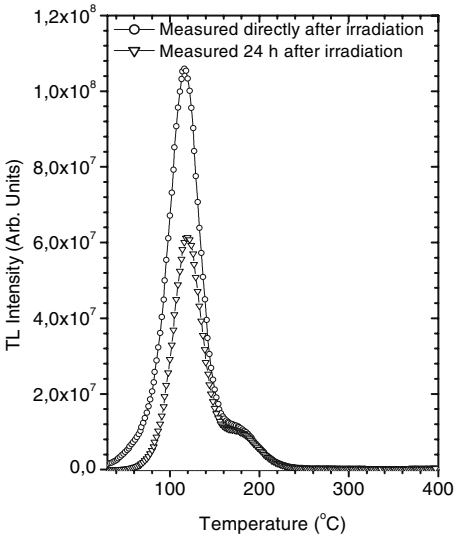

Fig. 11 The glow curve of LiB_3O_5 doped with 0.1% wt. CuO

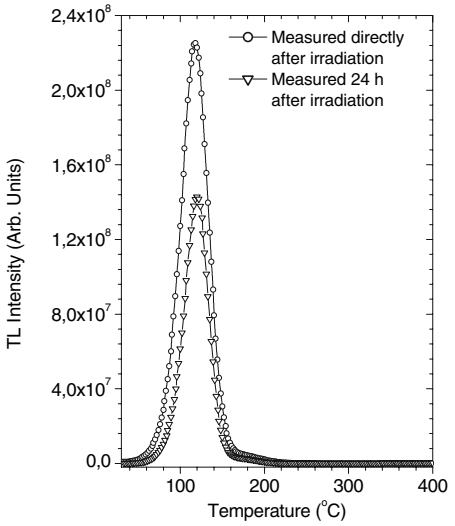

Fig. 13 The glow curve of LiB_3O_5 doped with 0.7% wt. CuO

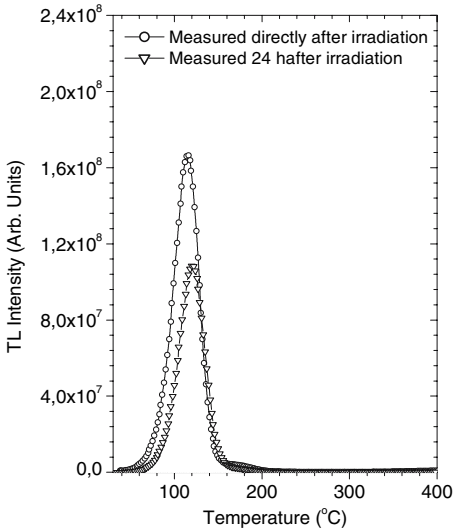

Fig. 12 The glow curve of LiB_3O_5 doped with 0.5% wt. CuO

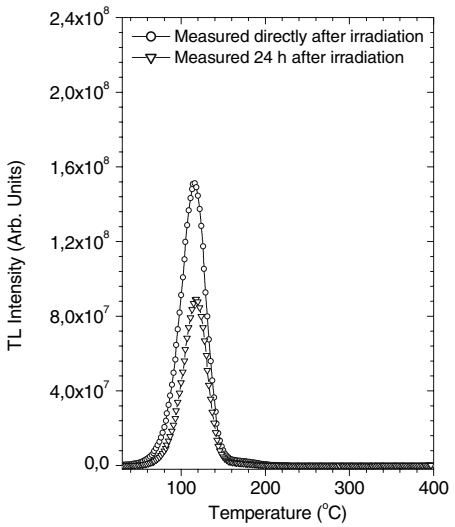

Fig. 14 The glow curve of LiB_3O_5 doped with 1% wt. CuO

of the glow peak. Changing the dopant concentration does not change the place of peak temperature and amount of fading significantly. The highest TL intensity was recorded for the lithium triborate doped with and 0.7% CuO. After 0.7% dopant addition, TL intensity started to decrease gradually.

Al_2O_3 may be another good dopant for lithium triborate showing good TL properties as mentioned above. The glow curve structures of LiB_3O_5:Al produced by 5 min irradiation and 24 h after irradiation operations were presented in Figs. 15–18. LiB_3O_5:Al samples show two characteristics TL peaks one is low-temperature peak recorded around 137 °C and the other is the high temperature peak around 200 °C which may be important for dosimetric studies.

When compared to Cu dopant, the intensity of the TL signal obtained for lithium triborate doped with Al_2O_3 is much lower. Moreover, amount of fading is lower for Al_2O_3 doped lithium triborate due to high temperature of the glow peak. As the dopant concentration increases, the increase in the TL intensity is more clear and sharper for LiB_3O_5:Al than LiB_3O_5:Cu, with the highest intensity observed at 1% Al_2O_3 addition.

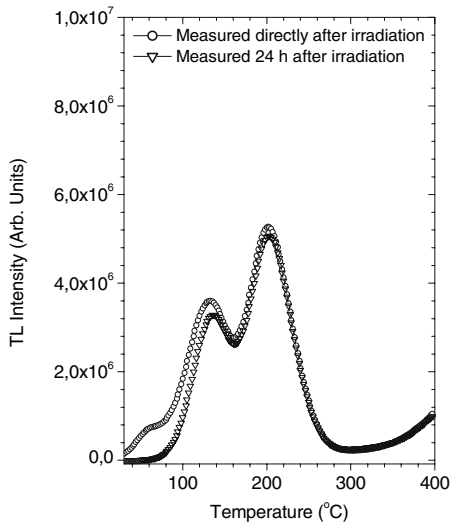

Fig. 15 The glow curve of LiB_3O_5 doped with 0.1% wt. Al_2O_3

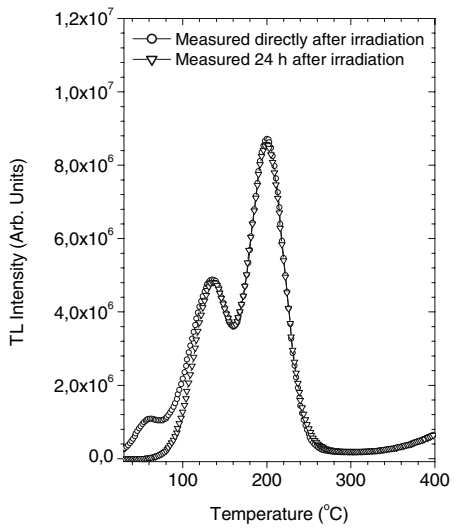

Fig. 16 The glow curve of LiB_3O_5 doped with 0.5% wt. Al_2O_3

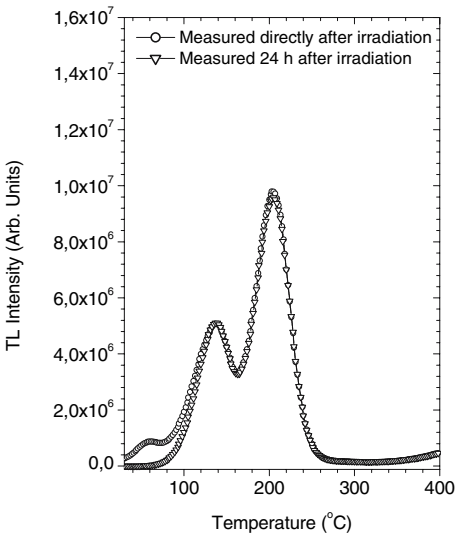

Fig. 17 The glow curve of LiB_3O_5 doped with 0.7% wt. Al_2O_3

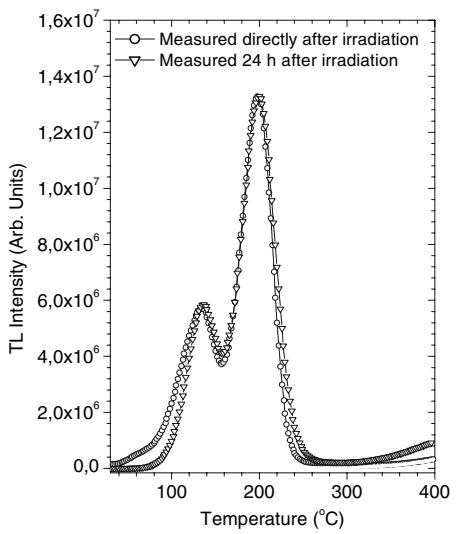

Fig. 18 The glow curve of LiB_3O_5 doped with 1% wt. Al_2O_3

Conclusions

The following results can be concluded from this study;

1. CuO and Al_2O_3 were found to be promising dopants for lithium triborate yielding significant TL response.
2. LiB_3O_5:Cu exhibits single, well resolved, high intensity but low temperature glow peak observed around 120 °C.
3. For the LiB_3O_5:Al samples, two glow peaks one of which is low temperature and the other is the high temperature were recorded around 137 and 200 °C, respectively. No fading of the TL signal was recorded this time for both glow peaks as a result of measurement 24 h after irradiation process.
4. Studies have been continuing to improve the TLD properties of LiB_3O_5:Cu and LiB_3O_5:Al for the application in personal dosimetry.

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