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Thermally stimulated luminescence studies of undoped, Cu and Mn doped lithium borate compounds

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Abstract Thermally stimulated luminescence (TSL) studies of undoped, Cu and Mn doped $Li_2B_4O_7$ are reported in this paper. The polycrystalline samples of undoped and doped $Li_2B_4O_7$ were prepared by melting method. The formation of the undoped compound was checked by X-ray diffraction and Fourier transform infrared (FTIR) studies. The compound has orthorhombic structure at room temperature. In TSL studies undoped sample exhibits two glow peaks at the temperatures 190 and 280°C. The Cu-doped lithium tetraborate sample exhibits three glow peaks at the temperatures185, 290 and 350°C whereas the Mn doped sample exhibits glow peaks at 190 and 300°C. Our results show that Cu-doped Lithium tetraborate is more sensitive and the TSL intensities of 185 and 290°C glow peaks in Cu doped $Li_2B_4O_7$ are enhanced by about 25 and 10 times respectively when compared with the corresponding glow peak intensities in undoped $Li_2B_4O_7$.

Keywords Thermally stimulated luminescence, XRD, FTIR.

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1. Introduction

Borate compounds containing impurities such as Cu and Mn find application as phosphors because they have tissue like characteristics and high sensitivity and hence they are worth studying for personal dosimetry [1]. These compounds find application not only as high sensitive phosphors used in thermoluminescence dosimetry of ionizing radiation but also as a non-linear optical material used for laser harmonic generation for example, barium borate [2]. Attempts have been made by many researchers to study the properties of lithium borate employing different preparation methods. The preparation of these samples is very tricky and these phosphors can be prepared only by doping impurity at temperatures very close to the melting [3-6]. The synthesis of the pure lithium borate and lithium borate doped with Cu and Mn are carried out in the laboratory. The thermally stimulated luminescence (TSL) studies of pure, Cu and Mn doped $Li_2B_4O_7$ are reported.

2. Experimental details

The samples of pure and doped lithium borate compounds were prepared by melting method [7]. The preparation of lithium borate samples has been made by mixing lithium carbonate (99%, Loba Chemie, Bombay) and boric acid (99.5%, S. d. fine-Chem Ltd., Boisar) in stoichiometric ratio and the mixture is melted at 950°C in a silica crucible and then rapidly cooled to room temperature. The resultant glassy mass is heated at 650°C for 0.5 hr. Then it is ground and sieved to obtain 100 to 200 mesh powder. Doped $Li_2B_4O_7$ samples are prepared in a similar manner by taking the starting materials in stoichiometric ratio and adding 0.5 wt% of $CuCl_2$ (98%, Loba Chemie, Bombay) or $MnCl_2$ (99.5%, S. d. fine-Chem Ltd., Boisar) in the mixture.

The characterization of $Li_2B_4O_7$ is carried out by X-ray diffraction and FTIR studies. X-ray diffractogram of the compound was taken in Central Research Facility, IIT Kharagpur at room temp. in a wide range of Bragg angle $2\theta(20^0 \le 2\theta \le 80^0)$ using a Rigaku (Miniflex, Japan) X-ray diffractometer with CuKa radiation (λ = 1.5418Å) at a scanning rate of 2°/min. The FTIR spectrum (KBr pellet) in the region 400 to 4000 cm^{-1} was recorded in the Chemistry Department, Indian School of Mines on FTIR-2000, (Perkin Elmer, Switzerland spectrometer).

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All samples were heated to 400^{0}C for 5 mins and then quenched to RT before X-irradiating them. The powder samples were irradiated by X-rays obtained from Cu target of Machlett tube operated at 20 KV and 15 mA. The TSL studies were made by using Personal Computer Based Thermoluminescence Analyzer System (Type 1007) supplied by Nucleonix Systems Private Limited, Hyderabad, India. The glow curves were recorded by heating the samples at a uniform rate of 4^{0}K/s with the help of a temperature controller (type 574) and the luminescence emission was detected by a photo-multiplier tube (type 9924 B). The photo-current from PM tube is amplified by a DC amplifier which is interfaced to a personal computer. The TSL out put is finally recorded by a printer connected to the personal computer.

3. Results and discussion

The X-ray diffraction of $Li_2B_4O_7$ is taken at room temperature as shown in Figure 1. The sharp and single diffraction peaks of the XRD pattern suggested the formation of single-phase new compound. From the 2θ values of the diffraction lines, interplanar spacing (d) of the peaks was calculated. The diffraction lines were indexed and unit cell configuration was identified using a computer program package 'Powdmult' [8,9]. Out of those a suitable orthorhombic unit cell was selected for which $\sum \Delta d$ ($= d_{obs} - d_{cal}$) was found to be minimum. The lattice parameters of the unit cell were refined using least-squares method and were found to be : a = 14.1085 Å, b = 10.0754 Å, c = 13.4154 Å. A good agreement between the observed and calculated d-values (Table 1.) suggests the suitability of the crystal structure and unit cell parameters. The FTIR spectrum of $Li_2B_4O_7$ is taken at room temperature as shown in Figure 2. The FTIR study [10,11] of undoped sample shows the presence of bands corresponding to borate anions at 1387.5 cm^{-1} and 779.8 cm^{-1} which also confirms the formation of $Li_2B_4O_7$ compound

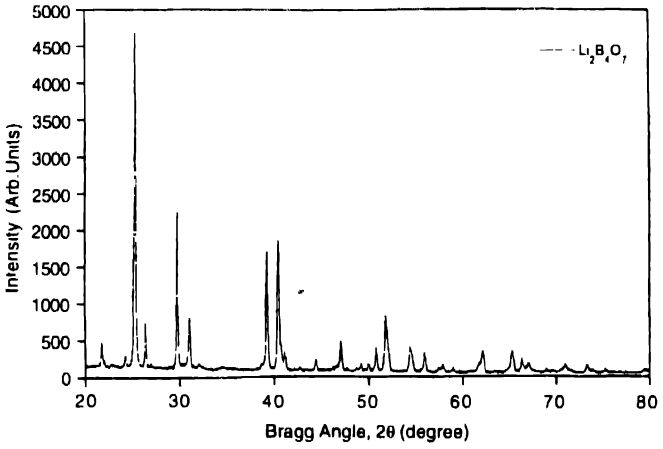

Figure 1. XRD pattern of $Li_2B_4O_7$ sample at room temperature

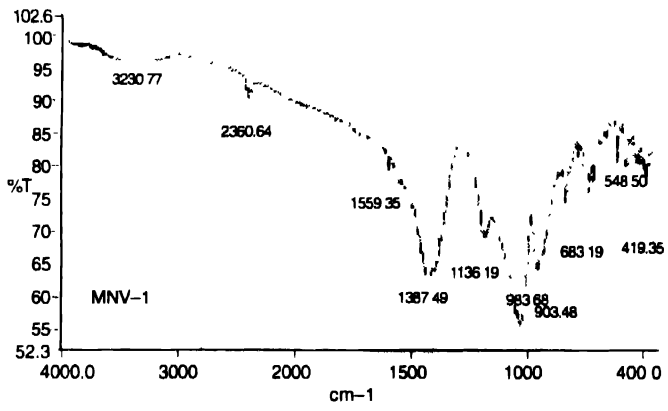

Figure 2. FTIR spectra of $Li_2B_4O_7$ sample at room temperature.

Table 1. Comparison of observed and calculated d-values (Å) of some reflections of $Li_2B_4O_7$ sample at room temperature.

h	k	l	d_{obs}	d_{cal}	I/Io*100
1	2	0	4.7443	4.7443	10
3	1	0	4.2615	4.2615	6
0	1	3	4.0873	4.0873	100
2	2	1	3.9198	3.9207	16
2	2	2	3.4868	3.4980	48
0	2	3	3.3442	3.3443	17
4	1	3	2.6683	2.6703	76
0	1	5	2.5923	2.5927	83
2	2	5	2.2448	2.2450	10
4	1	5	2.0887	2.0890	8
4	4	0	2.0511	2.0498	37
4	4	2	1.9616	1.9603	18
5	1	5	1.9097	1.9092	13
8	1	0	1.7367	1.7371	15
4	1	7	1.6614	1.6609	15

The TSL glow curves of $Li_2B_4O_7$ powder samples were recorded by X-irradiating at RT for 5,10,15,20 and 30 min as shown in the Figure 3. The samples of X-irradiated $Li_2B_4O_7$

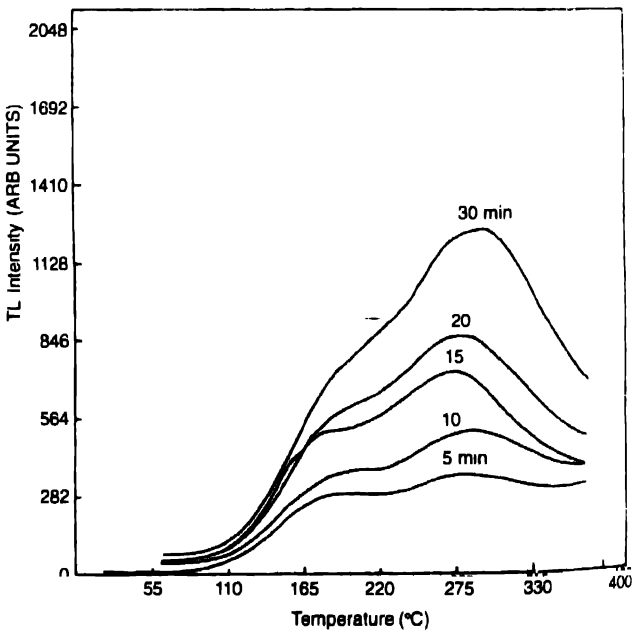

Fig 3. TSL Glow curves of $Li_2B_4O_7$ sample for different times of X-irradiation

samples exhibit two glow peaks at temperatures 190°C and 280°C of which 280°C glow peak is the strongest. Moreover the intensities of the glow peaks are found to increase with increase of the X-ray dose. The TSL glow curves of Cu-doped $Li_2B_4O_7$ powder samples were recorded by X-irradiating at RT for 10 mins. and 15 mins. as shown in Figure 4. The TSL glow curves of X-irradiated Cu-doped $Li_2B_4O_7$ exhibit three glow peaks at 185°C, 290°C and 350°C of which the intensity of 185°C glow peak is the maximum. In this case also the intensities of glow peaks are found to increase with the increase of X-ray dose. The TSL glow curves of Mn doped $Li_2B_4O_7$ powder samples were recorded by X-irradiating at room temperature for 20 mins. as shown in the Figure 5. It exhibits two glow peaks at temperature of 190°C and other at 300°C of which the glow peak at 300°C is more intense than 190°C glow peak. It is observed that in this case also, the glow peaks grow in intensities with the increase of X-ray dose.

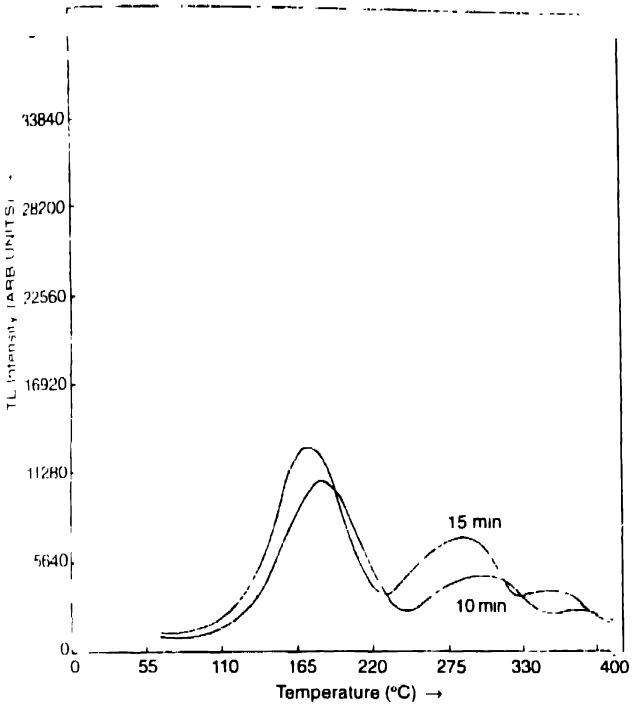

Figure 4. TSL Glow curves of Cu doped $Li_2B_4O_7$ sample for 10 & 15 mins of X-irradiation

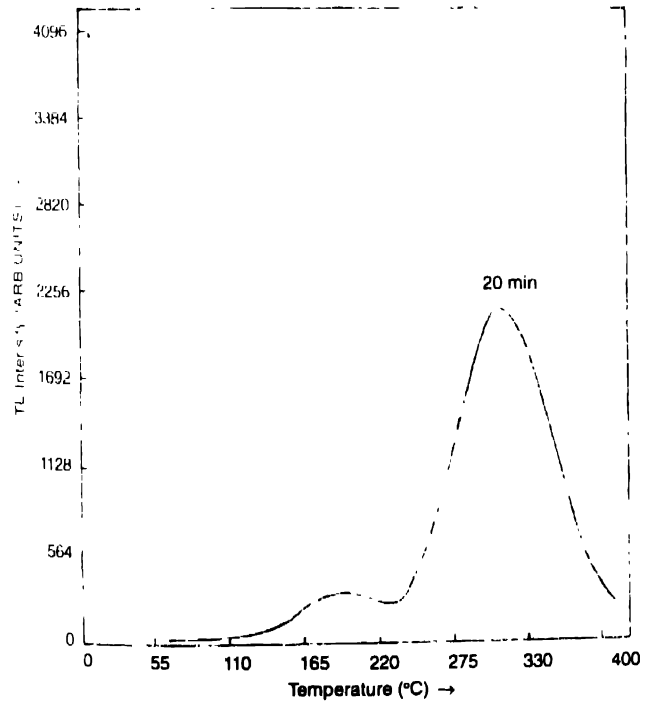

Fig 5. TSL Glow curves of Mn doped $Li_2B_4O_7$ sample for 20 mins of X irradiation

It is observed that Cu and Mn doped $Li_2B_4O_7$ and undoped $Li_2B_4O_7$ have some common features. In all these cases the first two peaks are common and occurring around 190°C and 290° C and the glow peaks are growing in intensity with the increase of X-ray dose. However, an additional peak is observed in Cu-doped Lithium tetraborate at a temperature of 350° C. Comparison of intensities of glow peaks indicates that the intensity of glow peaks of Cu doped $Li_2B_4O_7$ corresponding to 185°C and 290°C are enhanced by 25 and 10 times respectively when compared to those of undoped $Li_2B_4O_7$. However in the case of Mn doped $Li_2B_4O_7$, the intensity at 300°C glow peak is enhanced by 2.5 times when compared to that of undoped $Li_2B_4O_7$.Our results also show that the Cu doped $Li_2B_4O_7$ is more sensitive than Mn doped $Li_2B_4O_7$. Thus these results established that the sensitivity of $Li_2B_4O_7$ phosphor has been enhanced many fold with the incorporation of Cu impurity.

It has been suggested that the glow curves of Cu doped lithium tetraborate are related to the relaxation of the excited Cu^+ ions $(Cu^+)^*$.Upon irradiation, Cu^+ ions either trap an electron to become Cu^0 or they trap a hole to become Cu^{++} ions.

$$Cu^+ + \text{electron} \rightarrow Cu^0,$$

$$Cu^+ + \text{hole} \rightarrow Cu^{++}.$$

On thermal stimulation, these copper atom/ions give rise to TSL emission according to the following mechanism [12].

$$Cu^0 + \text{hole} \rightarrow (Cu^+)^* \rightarrow Cu^+ + h\nu,$$

Or $$Cu^{++} + \text{electron} \rightarrow (Cu^+)^* \rightarrow Cu^+ + h\nu.$$

The increase in the intensities of the glow curves with increase of irradiation dose can be understood by the fact that more and more traps responsible for these glow peaks were getting filled with the increase of irradiation dose and subsequently these traps release the charge carriers on thermal stimulation to finally recombine with their counterparts , thus giving rise to different glow peaks

4. Conclusions

(i) The compound $Li_2B_4O_7$ is found to have Orthorhombic structure.

(ii) The TL sensitivity of $Li_2B_4O_7$ phosphor is enhanced with the incorporation of Cu or Mn impurity.

(iii) The addition of Cu impurity to undoped $Li_2B_4O_7$

increases the sensitivity many fold as comparable to addition of Mn impurity to undoped $Li_2B_4O_7$.

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