Study of Thermal Treatment and Kinetic Parameters of Prepared $Li_2B_4O_7$: Cu Thermoluminescence Dosimeter

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Different concentrations from copper were added to lithium borate, as a doping material to get a good dosimeter compatible with the commercial one. It was found that the gradual addition of Cu to $Li_2B_4O_7$ causes gradual enhancement in the TL intensity up to a concentration value of 0.023 wt%, above that a draw back on the TL intensity occurs. It was also found that for preparation of this dosimeter the optimum sintering temperature was 850°C for 1 hour followed by quenching in liquid nitrogen. The use of liquid nitrogen as a cooling agent after the sintering treatment increases the phosphor sensitivity with about 4 times. Moreover, the kinetic parameters of the main peak of $Li_2B_4O_7$:Cu phosphor was calculated and it stood in good agreement with the previous work. So, $Li_2B_4O_7$:Cu phosphor can be prepared in the laboratory with high quality and can be used for radiation protection dosimetry applications.

Introduction

Danieles and his research group suggested the Thermoluminescence (TL) as a technique in radiation dosimetry more than forty years ago [1]. They had appreciated that irradiated material contains stored energy, which could be thermally released. From this date, the scientists began to research about the various materials, which have this property. It started by Flourides [2] and then followed by Oxides [3], Sulphates [4] and Borates [5]. There are many reasons make the borates are of great interest as a thermoluminescence dosimetry (TLD). One of them is that the materials such as $Li_2B_4O_7$ or MgB_4O_7 have a close tissue-equivalence and are thus worth considering for their TL properties. Indeed the lithium borate dosimeters are superior to LiF in terms of tissue-equivalence. As well as the borates are relatively stable chemical compounds and respond without serious problems for attempts to dope them with TL sensitizers such as the rare earths, copper or manganese ions. The resultant materials show some desirable features for TL in terms of high sensitivity, linearity and storage and many of the earlier problems of fading, light sensitivity and poor humidity behavior have been avoided.

In the present work the authors try to complete their studies about the evaluation of the kinetic parameters of the traps of the prepared dosimeters of which dosimetric properties were previously studied [6].

Experimental

In the present work, Cu element is doped into $Li_2B_4O_7$ as activator using the sintering method of Takenaga [7] in the following procedure: 1 gm of $Li_2B_4O_7$ of purity 99.9% from "Aldrich" company is added to several weights of $Cu(NO_3)_2$ of purity 99.90% ranging from 0.08 to 0.365 wt%. These materials then heated in silica crucibles for 1 hour at 850°C. The TL-signals were evaluated on TL reader one day after irradiation. The sources used for irradiation of the samples during this study were: ^{137}Cs (type γ-cell-40, Canada) with dose rate of 13.6 mGy/s, ^{60}Co (type γ-cell-4000A, India) with dose rate of 0.3 Gy/s, and ^{90}Sr/^{90}Y (type Harshaw model 2000, USA) with dose rate of 0.74 mGy/s.

The Harshaw-4000 (USA) TL reader is used throughout this work and it is a precision, microprocessor-based, manually operated, TLD system. It is used to evaluate TL materials in chip, powder, rod or card form. It has rapid, accurate, linearly ramped heating to a maximum of 400°C. It also has a stable reference light source, consisting of carbon-14 activated CaF_2(Eu), to be used for troubleshooting and verifying instrument gain and stability.

Results and Discussion

1. Thermal Treatments:

1.1. Sintering Temperature and Copper Concentration:

$Li_2B_4O_7$: Cu samples of different copper concentrations were thermally heated in silica crucibles for one hour at temperatures 800, 850 and 910°C. These samples were then subjected to fast cooling in liquid nitrogen and then irradiated with a test γ-dose of 1 Gy from ^{137}Cs source. Table (1) shows the TL-response as a function of sintering temperatures and it can be seen that the TL-response increases gradually with increasing sintering temperature and copper concentration within the range from 800 to 850°C and from 0.08 to 0.23% wt respectively.

Table (1): TL-response of $Li_2B_4O_7$: Cu phosphor as a function of sintering temperature.

Concentration of activator (wt%)	Sintering temp. (°C)	TL-response (Arb. Unit)	Concentration of activator (wt%)	Sintering temp. (°C)	TL-response (Arb. Unit)
0.08	800 850 910	1208 ± 17 1342 ± 23 1300 ± 80	0.189	800 850 910	1611 ± 83 1941 ± 69 1816 ± 79
0.1	800 850 910	1246 ± 62 1451 ± 74 1397 ± 49	0.230	800 850 910	1727 ± 51 2139 ± 99 1941 ± 39
0.135	800 850 910	1371 ± 35 1573 ± 61 1435 ± 91	0.257	800 850 910	1654 ± 64 2041 ± 31 1893 ± 59
0.1456	800 850 910	1451 ± 83 1701 ± 91 1512 ± 79	0.284	800 850 910	1654 ± 39 2041 ± 82 melted
0.169	800 850 910	1539 ± 59 1831 ± 46 1618 ± 68	0.314	800 850 910	1421 ± 93 1761 ± 59 melted
			0.365	800 850 910	1248 ± 85 1949 ± 43 melted

Above these temperatures the samples undergo a complete melting and can not be collected again. At the temperature 910°C, samples were melted completely for concentrations more than 0.284 %. Therefore, the optimum sintering thermal treatment is 850°C for copper concentration of 0.23% wt. yield the optimum TL-response [Fig. (1)].

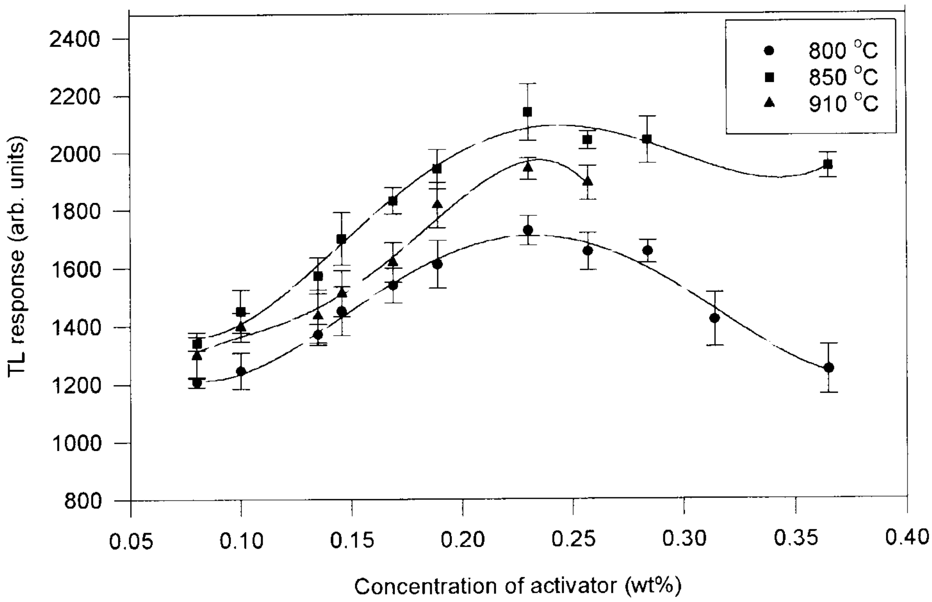

Fig. (1) : Effect of sintering temperature on TL-response of $Li_2B_4O_7$: Cu.

1.2. Sintering Cooling Method:

The effect of sintering cooling method on the TL-response of $Li_2B_4O_7$:Cu samples has been studied. Four groups of the samples were thermally treated at 850°C for 1 hour. One group of these samples was allowed to be quenched in liquid nitrogen, the second group was allowed to be quenched on ice, the third was allowed to be cooled in cooled air down to room temperature, and the fourth was allowed to be cooled slowly in the off-furnace. The samples were irradiated with the test γ-dose of 1Gy and its TL was evaluated. Table (2) shows the effect of type of cooling on the TL-response, whereas Table (3) represents the relative TL sensitivity of $Li_2B_4O_7$:Cu phosphor as a function of sintering cooling method (normalized to that of cooled air as unity). From these tables, it is clear that the TL sensitivity in case of quenching in liquid nitrogen has the greatest value and greater than that of cooled air with ~ 4%, while the slow cooling in the off-furnace produces the poorest sensitivity. This may be explained as follows: the rapid cooling may freeze the equilibrium distribution of the impurities and vacancies exist at the higher temperature [850^{o}C, Fig. (2)], while the slow cooling allows the formation of aggregates of the impurities [8].

Table (2): Effect of the type of cooling on the TL-response

Concentration of activator (wt%)	Type of Cooling	TL-response (Arb. Unit)	Concentration of activator (wt%)	Type of Cooling	TL-response (Arb. Unit)
	C	1350 ± 35		C	1981 ± 49
0.08	O	1210 ± 28	0.189	O	1731 ± 52
	C	1473 ± 31		C	2180 ± 52
0.1	O	1390 ± 17	0.230	O	1790 ± 32
	C	1583 ± 22		C	2093 ± 39
0.135	O	1496 ± 28	0.257	O	1678 ± 25
	C	1766 ± 31		C	1810 ± 28
0.1456	O	1582 ± 39	0.284	O	1603 ± 17
	C	1802 ± 61		C	1769 ± 31
0.169	O	1663 ± 41	0.314	O	1574 ± 49
				C	1692 ± 41
			0.365	O	1492 ± 13

Table (3): Relative TL-response of $Li_2B_4O_7$: Cu phosphor as a function of sintering cooling method.

Sintering cooling method	Relative TL-response
Liquid nitrogen	1.04 ± 0.019
Ice	1.02 ± 0.021
Cooled air	1.00 ± 0.024
Off-furnace	0.82 ± 0.018

2. Kinetic parameters:

To obtain the kinetic parameters of the prepared dosimeter, its glow curve was studied carefully. The obtained glow curve [6] showed that $Li_2B_4O_7$: Cu has two peaks, the first at about 133°C and the second one at 178°C.

2.1. Kinetic order:

The kinetic order for the main glow peak of $Li_2B_4O_7$:Cu phosphor can be determined by means of Chen [9] based on the value of the symmetry factor, μ_g. Chen found that the value of μ_g is not sensitive to changes in the activation energy (E) and the frequency factor (s), but it changes with the kinetic order. Azorin [10] concluded that the value of μ_g indicates whether the peak is of first or second order kinetics as follows:

$\boldsymbol{\mu_g < (1+\Delta)/e}$ for first order kinetics

$\boldsymbol{\mu_g \geq (1+\Delta)/e}$ for second order kinetics

where $\mu_g=\delta/\omega=(T_2-T_m)/(T_2-T_1)$, $\Delta=2kT_m/E$, e=2.718, k is the Boltzmann's constant in J/K, E is the activation energy of the peak in J. It was found that the symmetry factor (μ_g) of the mean peak of $Li_2B_4O_7$: Cu phosphor equals 0.44, i.e., $<(1+\Delta)/e$. It is obvious that this gave us an indication that this peak is of first order.

2.2. Evaluation Methods:

The methods currently used for determining the trap parameter are based on a simple model for TL, which assumes that the irradiation produces free electrons, which originate energy levels within the forbidden band. The most important parameters are the activation energy (E), namely the thermal energy needed to free the trapped electrons, and the frequency factor (s).

2.2.1. Initial rise method:

It is based on the analysis of the temperature side of the TL-glow curve where the amount of trapped electrons can be assumed constant, so that with some reasonable approximations the temperature depend of the TL-signal is given by:

$$I(t) \propto \exp(-E/kt) \tag{1}$$

where E is the activation energy (eV), k Boltzmann's constant (eV/K), and T is the temperature (K). Figure (3) shows the linear relation obtained by plotting lnI against 1/T for the raising part of the main peak of $Li_2B_4O_7$: Cu. The slope of this plot equals (-E/k). Hence, it is possible to evaluate "E" without any knowledge of the frequency factor (s) as follows:

$$E = -k\, d(\ln I) / d(1/T) \tag{2}$$

The frequency factor (s) is given by Chen and Winter [11]

$$s = BE/2kT_m \; \exp(E/kT_m) \tag{3}$$

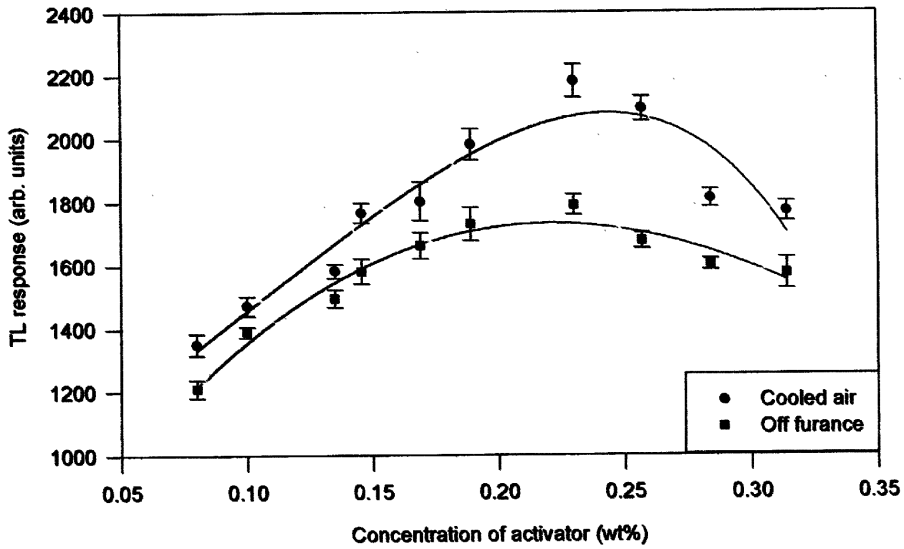

Fig. (2) : Effect of anneaaling cooling type on TL response.

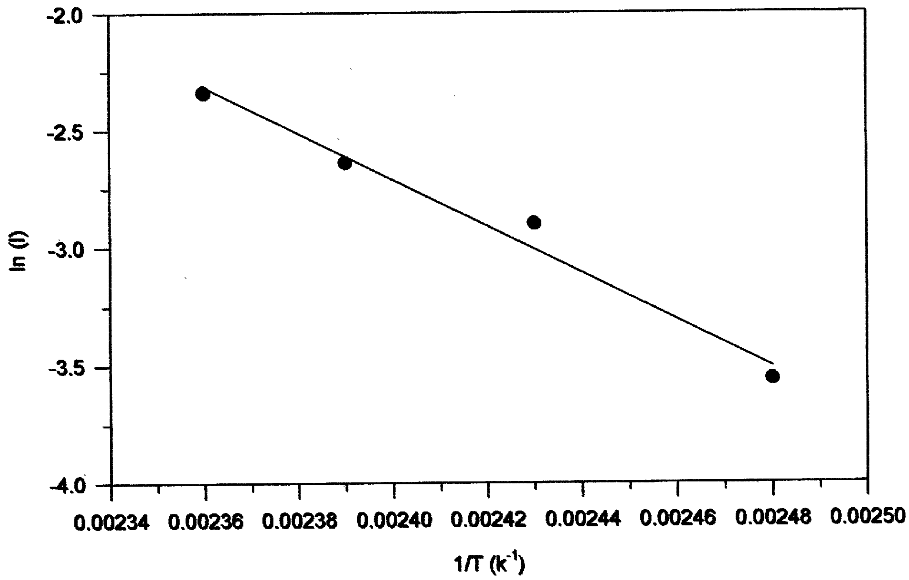

Fig. (3) : Relation between (1/T) versus ln(I).

2.2.2. Peak shape Method:

The peak shape methods used in this study were those of Lushchik [12], Halperin and Brener [13] and Chen [9]. The activation energy (E) for the main glow peak of $Li_2B_4O_7$: Cu phosphor was calculated as follows:

Lushchik's method:

$$\mathbf{E = 0.976\ kT^2_m/\delta} \qquad \text{(first order kinetic)}$$

Halperin -braner equation:

$$\mathbf{1.51(kT^2_m/\tau) = 3.16\ kT_m} \qquad \text{(first order kinetic)}$$

Chen's method:

$$\mathbf{E = C_\alpha\,(kT^2_m/\alpha) - b_\alpha\,(2kT_m)}$$

with $\alpha=\tau$, δ or ω, where $\tau=T_m-T_1$, $\delta=T_2-T_m$, $\omega=T_2-T_1$ and the values of C_α and b_α for the three methods are $C_\tau=1.51+3(\mu_g-0.42)$, $C_\delta=0.976+7.3(\mu_g-0.42)$, $C_\omega=2.52+10.2(\mu_g-0.42)$, $b_\tau=1.58+4.2(\mu_g-0.42)$, $b_\delta=0$ and $b_\omega=1$.

Table (4) summarizes the result obtained applying the various methods discussed in this work to determine E & s. The best agreement for the values of E and s was obtained by means of Chen (τ), Chen (δ), Chen (ω) and Helperin-Braner methods. There are some discrepancies in the values of E given in table (4) which need to be accounted for the value of E from the initial rise method is nearly 30% lower than those calculated by other methods. This discrepancy may arise from the luminescence efficiency decreases with temperature (thermal quenching).

Table (4): E and s values obtained for $Li_2B_4O_7$: Cu using different methods.

Method	E (eV)	S (s^{-1})
Initial rise	1.03	1.63×10^{14}
Lushchic	1.44	1.42×10^{14}
Helperin-Braner	1.64	9.07×10^{15}
Chen (δ)	1.65	8.34×10^{15}
Chen (τ)	1.72	5.21×10^{16}
Chen (ω)	1.60	4.05×10^{15}

Conclusion

From the previous work it can be concluded that the gradual addition of Cu to $Li_2B_4O_7$ causes gradual enhancement in the TL intensity up to optimum concentration value of 0.023 wt% above which a draw back on the TL intensity occurs. This enhancement accompanied by the gradual addition of copper is not accompanied by any shift in the peak position of the main band. This indicated that the addition of copper increases the probability of defect formation in the structure of $Li_2B_4O_7$. For the preparation of this dosimeter the optimum sintering temperature was 850°C for 1 hour followed by quenching in liquid nitrogen after which the phosphor was completely melted and could not be collected again. It is obvious that the use of liquid nitrogen as a cooling agent after the sintering treatment increases the phosphor sensitivity with about 4 times. From the other side, the calculated kinetic parameters of the main peak of $Li_2B_4O_7$: Cu phosphor exhibits a good agreement with the previous work. So, $Li_2B_4O_7$: Cu phosphor can be prepared in the laboratory with better quality and can be used for radiation protection dosimetry applications.

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