Growth and luminescent properties of Li$_2$B$_4$O$_7$ single crystal doped with Cu

Bui The Huy$^1$, Bui Minh Ly$^1$, Vu Xuan Quang$^1$, Huynh Ky Hanh$^1$, Doan Phan Thao Tien$^1$, Vinh Hao$^1$ and Tran Ngoc$^2$

$^1$Nha Trang Institute of Technology Research and Application, 2 Hung Vuong Street, Nha Trang, Vietnam
$^2$Quang Binh University, Quang Binh, Vietnam

E-mail: buithehuy.nt@gmail.com

Abstract. The authors have primarily succeeded in the study of the technology for growing single crystal Li$_2$B$_4$O$_7$ doped with Cu ions by Bridgman technique. The TL-3D spectra show peaks at around 375 nm (3d$^9$4s $\rightarrow$ 3d$^{10}$ radiative excitation transition). This success opened up an opportunity in the radiotherapy to manufacture scintillators for neutron detection. The kinetic parameters of thermal stimulation luminescence were investigated by the three point method.

Keywords: Single crystal, kinetic parameter, three points, TL spectra.

1. Introduction
Lithium Tetraborate, Li$_2$B$_4$O$_7$ (LBO) single crystals have attracted much attention of researchers for use in surface acoustic wave (SAW), bulk acoustic wave (BAW) devices and dosimeter in radiotherapy. LBO is considered to be a promising material for piezoelectric materials due to its high electromechanical coupling coefficient ($k^2$=1) and very low temperature coefficient of delay (TCD, 0 ppm/°C) [1]. LBO materials have found application in neutron detection and nonlinear harmonic generation [2]. Initially, Lithium Tetraborate single crystals were grown by the Czochralski method and subsequently both vertical and horizontal Bridgman methods were applied [3, 4]. The LBO single crystals of larger size were grown by Bridgman [5].

Thermoluminescence (TL) phenomenon is a result of the stimulated radiative recombination of released electrons, initially trapped by some centers and defects in the material lattice after being exposed to a source of ionizing radiation. The studies of TL have revealed useful information on the properties of the various types of defects within insulator or semiconductors. Many TL glow curve have been determined and a variety of methods for analyzing TL glow curve have been developed. Several methods are applied to obtain the trap parameters of the glow peaks [6-9].

LBO single crystals Cu-doped were grown in a graphite crucible by the Bridgman method at our laboratory. The three point method of M.S. Rasheedy [10] has been applied for the investigation of the kinetic parameters of thermal stimulated luminescence as the order kinetics, energy of trap, etc.
2. Theoretical basis of TL kinetics
The calculations will be given here in outline form taken from the original paper by M.S. Rasheedy [10]. For general-order, the behavior of TL intensity of a phosphor is governed by the following equation:

$$I = -\frac{dn}{dt} = \frac{n^n}{N^{b-1}}S \exp\left(-\frac{E}{kT}\right),$$  \hspace{1cm} (1)

where $I$ (in arbitrary unit) is the TL intensity, $n$ (cm$^{-3}$) the electron concentration trapped at time $t$ (s), $N$ (cm$^{-3}$) the trap concentration and $k$ (eV/K) is the Boltzmann’s constant. Equation (1) is more general than the two equations describing the first and second-order kinetics. The solution of equation (1) for $b \neq 1$ is given as

$$I = \frac{n_0 S'' \exp(-E/kT)}{\left(1 + [((b-1)S'')/\beta]\int_{T_0}^{T} \exp(-E/kT')dT'ight)^{b/(b-1)}},$$  \hspace{1cm} (2)

where $\beta$ (Ks$^{-1}$) is the linear heating rate and $n_0$ (cm$^{-3}$) is the concentration of traps populated at the starting heating temperature $T_0$ (K). The pre-exponential factor $S'' = S(n_0/N)^{b-1}$ is constant for a given dose.

These expressions assuming the concentration of populated traps at a temperature $T_i$ during the TL run is proportional to the area $A_i$, where $A_i$ is the area under the glow peak between the $T_i$ and $T_f$ ($T_f$ is the final temperature of the glow peak).

The kinetic parameters $E$, $b$, $S''$ and $n_0$ was given from the below equations:

$$E = \left[\ln(z) - b \ln\left(\frac{A_x}{A_y}\right)\right]\frac{kT_y}{T_x - T_y},$$  \hspace{1cm} (3)

$$b = \frac{T_y}{T_x - T_z}\ln(y) - T_z\left(T_x - T_y\right)\ln(z),$$  \hspace{1cm} (4)

$$S'' = \frac{\beta E \exp(E/kT_m)}{\left(\frac{1}{bkT^2_m}\right) - (b-1)E\Phi \exp(E/kT_m)},$$  \hspace{1cm} (5)

with $T_m$(K) is the temperature corresponding to the maximum intensity $I_m$ of the glow peak, $y = I_x/I_y$, $z = I_x/I_z$ and

$$\Phi = \int_{T_0}^{T_m} \exp\left(-\frac{E}{kT'}\right)dT',$$  \hspace{1cm} (6)

$$n_0 = \frac{I_m \exp(E/kT_m)}{S''} \left[\frac{bkT^2_m S''}{\beta E \exp(E/kT_m)}\right]^{-b/(b-1)}.$$  \hspace{1cm} (7)
3. Experimental

Single crystal of LBO:Cu was grown by the modified vertical Bridgman method. The electric furnace has two independent heating zones. The raw material was a polycrystalline disc of 99.99% purity. The raw material was charged into the graphite crucible after being doped Cu₂O 0.03 wt.%. The inside diameter of the crucible is 20 mm and the length is 110 mm. The charge was melted in a nitrogen atmosphere. A seed crystal oriented to <110> direction with a dimension of 5 mm in diameter and 50 mm in length was placed at the bottom of the crucible.

An important parameter of the growth process is temperature gradient of the furnace system. It requires that the gradient should be from 15 to 20°C/cm. The furnace was heated to 930°C in both zones, the temperature gradient was reached at 17°C/cm.

The raw materials were melted for 10 hours and then the crucible was moving down with the rate of movement of 0.4 mm/hour in 100 hours. The furnace was cooled with rate of 20°C/hour to room temperature. After the growth, the crucible was peeled off to get the crystal out.

4. Results and discussion

The crystal sample has the cylinder shape with about 35 mm in length. The crystal is transparent but there are some bubbles on the outside surface of sample. The reason is the difference between heat transfer coefficients of graphite and the crystal. The block crystal is shown in figure 1.

![Figure 1. Block crystal Li₂B₄O₇ doped Cu.](image1)

The block crystal was cut perpendicularly to the growth direction and polished to mirror finish. The crystal sample was measured by slice surface measurement method at Shonan Institute of Technology-Japan. The measurements were carried out with the four sites 0, 90, 180, and 270 degree of cylinder slice-sample. At the each site there were 3 measurements with the positions 0, +7, and -7. The figure 2 shows X-ray diffraction pattern of crystal at site 0. It proves that the quality of the single crystal is good. At the others sites, the results are similar.

![Figure 2. X-ray diffraction pattern of LBO:Cu crystal.](image2)

The TL glow curves were received from Harshaw Reader 3500 with the heating rate 1°C/sec as shown in figure 3. There are three individual peaks P1, P2 and P3 at 209, 254 and 345°C, respectively.
The crystal samples were measured the TL- 3D and shown in figure 4. The spectra show that there is a peak at around 375 nm (3d⁹4s→3d¹⁰ radiative ed-excitation transition) and 200°C.

In order to determine the kinetic parameters it was at first started with obtaining the kinetic parameters of the highest temperature peak 345°C - P3 by (3), (4), (5) and (7). Secondly, these values are used in equation (2) in order to fit the experimental glow curve into the theoretical glow curve. Five runs of the three points method were performed with random selections on the glow curve. The average values of the parameters in this peak are found equal to b = 1.80 ± 0.03, E = 1.42 ± 0.02 eV, S" = 2.011E ± 10.s⁻¹ and n₀ = 4.089E ± 6. The results of two glow curves are illustrated in figure 5. The theoretical curve of peak 3 fits well with the experimental one.

The experimental curve after subtraction of the peak P3 will be used for the determination of parameters P1, P2. The procedures are similarly repeated for P2 and P1. The results of all calculations are listed in table 1.
Table 1. The results of kinetic parameters of the P1, P2 and P3.

|        | P1 (209°C) | P2 (254°C) | P3 (345°C) |
|--------|------------|------------|------------|
| b      | 1.88 ± 0.02| 1.43 ± 0.05| 1.80 ± 0.03|
| E (eV) | 1.73 ± 0.05| 1.96 ± 0.08| 1.42 ± 0.02|
| S\(^{\prime}\) (s\(^{-1}\)) | 0.9631E+17 | 6.7682E+17 | 2.011E+10 |
| n\(_0\) | 3.4719E+07 | 2.2726E+06 | 4.089E+6  |

The glow curve of P1, P2, P3 and experimental data are shown in the figure 6. The theoretical curves of the peaks are a good fitting to the experimental ones.

Figure 6. Experimental curve (circle), theoretical curve of peaks P1-P3 (line).

5. Conclusion
Single crystals of Li\(_2\)B\(_4\)O\(_7\) have been grown to a size of 20 mm in diameter and 35 mm in length by the Bridgman method. These results open an opportunity in the radiotherapy to manufacture single crystal scintillators for neutron detection. The kinetic parameters were determined by the three point method. The results presented in table 1 show that each peak has individual values which agree with the experimental data. Therefore this method is reliable and accurate in evaluation of kinetic parameters of thermoluminescence curves.

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Acknowledgments
The authors wish to thank Prof. M. Ishii, Shonan Institute of Technology- Japan for his assistance in providing our laboratory with the Bridgman furnace as a gift. This work is supported in part by the Vietnam Academy of Science and Technology.