THERMOLUMINESCENCE MECHANISM IN Li₂B₄O₇:Cu

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Abstract — Samples of Li₂O.2B₂O₃ doped with CuO have been produced by melting appropriate mixtures of Li₂CO₃ and H₃BO₃ at 980°C and then quenching to room temperature. Glasses thus obtained were devitrified. The absorption spectra of non-irradiated and irradiated samples indicate that γ radiation changes Cu²⁺ into Cu⁺. ESR spectra of Cu-doped lithium borate exhibits the typical BOHC centres 'five-line-plus-a-shoulder' between the ±½Mₙ-lines. It is proposed that by heating the Cu-doped lithium borate, BOHC has an important role in the TL emission process.

INTRODUCTION

Some characteristics of manganese-doped lithium borate as a low Z thermoluminescent phosphor were first reported by Schulman et al[1]. This TL material is characterised by TL peaks at 55°C and 220°C, a supralinearity above about 1.5 Gy, a small (20%) energy dependence below 100 keV, a sensitivity 3 to 10 times lower than that of TLD-100 (LiF:Mg, Ti), and a fading of about 8% in the first month. Takenaga et al[2,3] showed that copper-doped lithium borate is 4 times more sensitive than the manganese-doped one. While they found only two TL peaks at 120°C and 205°C, Kutomi et al[4] encountered five: at 90, 160, 200, 260 and 320°C. These authors also found a TL emission spectrum with absorption bands at about 370 nm and 560 nm. Based on this result, they proposed two reactions which will be discussed.

EXPERIMENTAL

Lithium borate glasses were produced by firing at 980°C an appropriate mixture of reagent grade Li₂CO₃ and H₃BO₃ and then cooling rapidly to room temperature. Copper as 0.01, 0.02, 0.04, 0.08, 0.16, 0.22, 0.30, 0.40 and 0.50 wt% was added to produce samples designated C1, C2, C4, C8, C16, C22, C30, C40 and C50.

TL glow curves and other TL measurements were carried out on a Harshaw 2000A reader, and for ESR measurements a JEOL JES-ME3X spectrometer was used.

Absorption spectra for irradiated and non-irradiated C1, C2, C4, C8, C16, C22 and C50 samples in the range of 5000 to 30,000 cm⁻¹ were obtained. For irradiation, γ rays from a ⁶⁰Co source at IPEN were used.

For TL measurements, doped and undoped glasses, devitrified or not, were pulverised and sieved to retain, as usual, grain sizes between 80 and 180 μm.

ESR measurements were performed with C22 and C40 samples irradiated to 10⁴ Gy γ rays. A C16 sample

γ irradiated to 10⁵ Gy was used for isothermal decay measurements at 120°C and 180°C.

Correspondingly, isothermal TL decay measurements were carried out for comparison sake.

RESULTS AND DISCUSSION

The absorption band at 12,500 cm⁻¹ (800 nm), shown in Figure 1, is due to Cu²⁺. It increases with the concentration of copper. After irradiation, however, the 12,500 cm⁻¹ band is clearly visible only in C16, C22 and C50 samples, as shown in Figures 2 and 3. The band height is smaller compared to that in corresponding non-irradiated samples. On the other hand, a new absorption band at 18,000 cm⁻¹ (555 nm) can be seen in C1, C2, C4 and C8, but not in C16 and C50. This is due to a Cu⁺ centre from the reaction Cu²⁺ + irrad. = Cu⁺.

Kutomi et al[4] found in devitrified Li₂B₄O₇:Cu (0.03 wt%) TL peaks at 90, 160, 200, 260 and 320°C while in a single crystal Li₂B₄O₇:Cu only 90, 165 and 230°C peaks appeared. Takenaga et al[2,3] on the other hand, found in a sintered Li₂B₄O₇:Cu only two peaks, one at 120°C and the second one at 205°C.
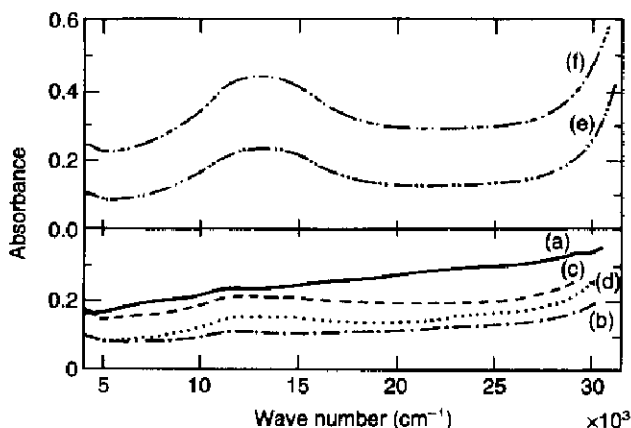

Figure 1. Absorption spectra for wave numbers in the region between 5000 and 30,000 cm⁻¹ (2000 nm to 333 nm) of non-irradiated Li₂O.2B₂O₃ glass doped with (a) 0.01; (b) 0.02; (c) 0.04; (d) 0.08; (e) 0.16 and (f) 0.22 wt% Cu.

In the present work, the addition of Cu plus devitrification produced peaks at 110, 165, 230 and 320°C. The peak height increases with Cu concentration. The glow curves (Figure 4) for higher Cu concentrations (C8, C16 and C22) show a very fast growth of the 165°C peak compared to other peaks. Furthermore, it shifts to higher temperatures up to 185°C with increasing Cu concentration.

Non-irradiated pure samples presented no ESR signal. Those doped with Cu and without irradiation showed the typical Cu^{2+} spectrum composed of four lines in the region of 2600–3200 Gauss magnetic field.
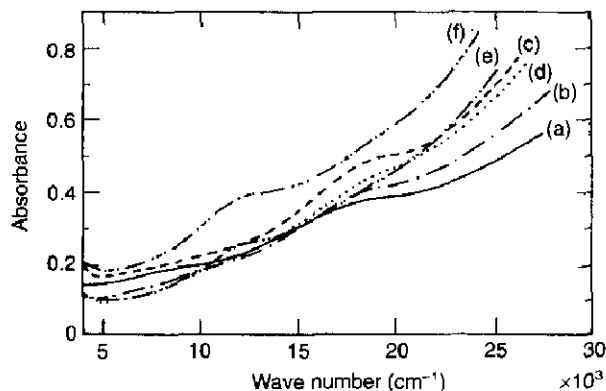
Figure 5 shows a typical 'five-lines-plus-a-shoulder' of irradiated Cu-doped $Li_2B_4O_7$ between the m = ±1/2 lines of Mn^{2+}. Griscom et al[5] demonstrated that the paramagnetic state responsible for the 'five-lines-plus-a-shoulder' is basically a boron–oxygen orbital. Further-

Figure 2. Absorption spectra for wave numbers in the region between 5000 and 30,000 cm⁻¹ (2000 nm to 333 nm) of irradiated $Li_2O.2B_2O_3$ glass doped with (a) 0.01; (b) 0.02; (c) 0.04; (d) 0.08; (e) 0.16 and (f) 0.22 wt% Cu.

Figure 4. TL glow curves of $Li_2B_4O_7$: (······) 0.08 wt% Cu-doped and devitrified sample; (---) 0.16 wt% Cu-doped and devitrified; (——) 0.22 wt% Cu-doped and devitrified.
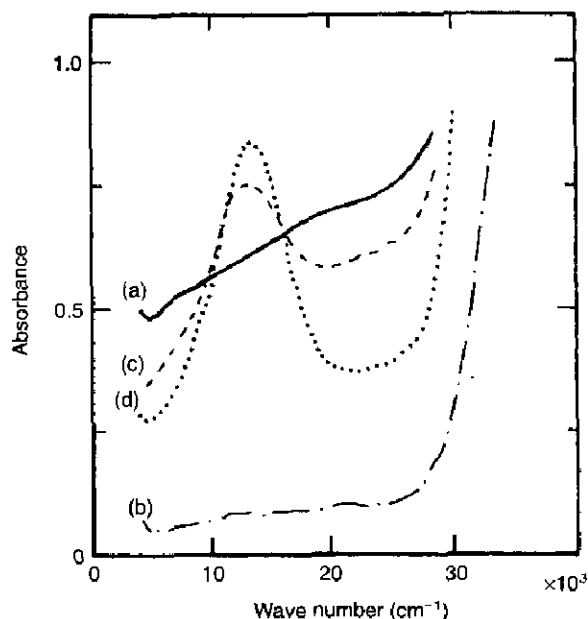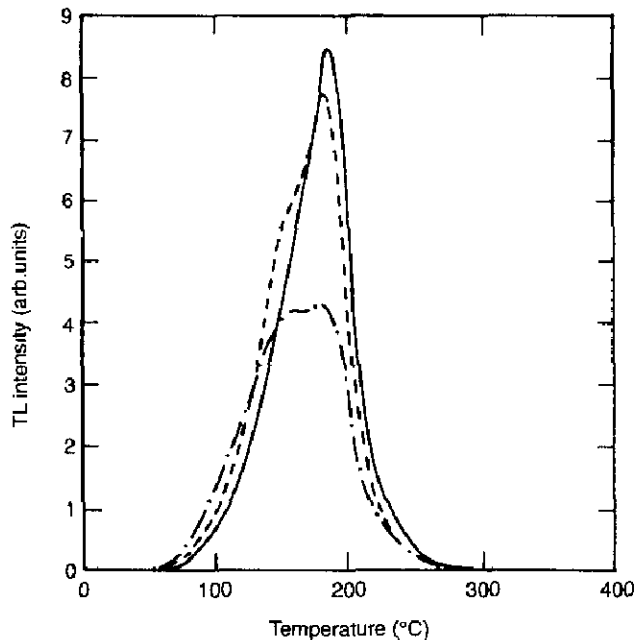

Figure 3. Absorption spectra for wave numbers in the region between 5000 and 30,000 cm⁻¹ (2000 nm to 333 nm) of (a) irradiated pure sample; (b) non-irradiated pure sample, (c) irradiated 0.5 wt% Cu-doped sample; (d) non-irradiated 0.5 wt% Cu-doped sample.
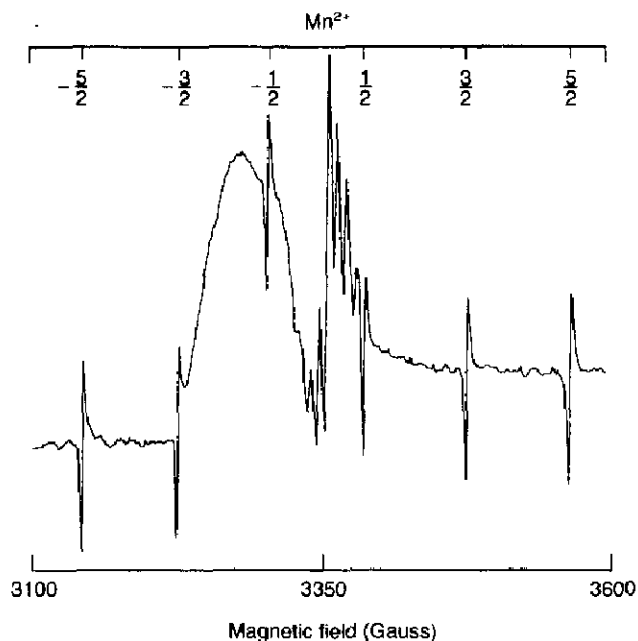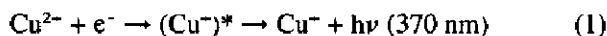

Figure 5. ESR spectra of irradiated C16 sample exhibiting 'five-line-plus-a-shoulder' due to BOHC created by irradiation; the 'five-line-plus-a-shoulder' appear between the ±1/2 Mn^{2+} lines.

more, they stated that the oxygen which shares the unpaired spin must be in a bridging position, since a non-bridging oxygen would surely trap the hole in the non-bonding p_x orbital in the plane of the BO_3 triangle, rather than in the π_z bonding level.

The centres are, therefore, holes trapped in the π_z levels of oxygens which bridge between three and four-coordinated borons in the glass structure. Such borons are found in diborate structure. Taylor and Bray[6] have shown that in alkaline borate with 33% alkaline oxide composition diborate structure predominates. It is suggested that the mechanism responsible for binding the hole to this locale is the proximity of the charged four-coordinated boron unit. This is the so-called BOHC: boron-oxygen hole centre.

Kutomi et al[4] found a TL emission band at 370 nm; which has been assigned to an inner transition of Cu^+ ions from $3d^94s$ to $3d^{10}$ states. They propose then, either

$$Cu^{2-} + e^- \rightarrow (Cu^-)^* \rightarrow Cu^- + h\nu \ (370 \ nm) \qquad (1)$$

or

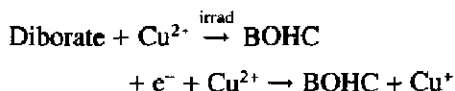$$Cu^0 + hole \rightarrow (Cu^+)^* \rightarrow Cu^- + h\nu \ (370 \ nm) \qquad (2)$$
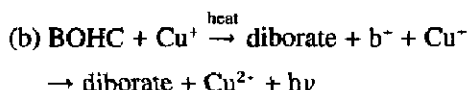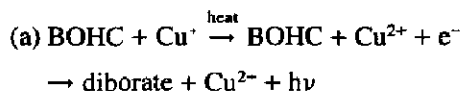
takes place under heating of the sample. Where the electrons or holes come from is not mentioned.

We present following alternative mechanisms. During the γ irradiation, the following reaction can take place:

$$Diborate + Cu^{2-} \xrightarrow{irrad} BOHC$$

$$+ e^- + Cu^{2+} \rightarrow BOHC + Cu^+$$

At the heating stage, one of the following reactions or both can occur:

(a) $BOHC + Cu^+ \xrightarrow{heat} BOHC + Cu^{2+} + e^-$

$\rightarrow diborate + Cu^{2-} + h\nu$

(b) $BOHC + Cu^+ \xrightarrow{heat} diborate + b^+ + Cu^-$

$\rightarrow diborate + Cu^{2-} + h\nu$

Which one occurs first, depends upon whether the liberation of e^- from Cu^+ requires more or less energy than freeing b^+ from BOHC. At present no data is available to decide which takes place first.

A third possibility relies on the possible existence of Cu^0 atoms in the lithium borate, as claimed by Kutomi et al[4].

$BOHC + Cu^0 \rightarrow BOHC + e^- + (Cu^+)^*$
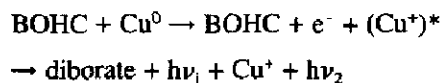
$\rightarrow diborate + h\nu_1 + Cu^+ + h\nu_2$

Figure 4 of Ref. 4, shows two TL emission peaks, one at 370 nm and the other one at 580 nm. Kutomi et al[4] identify $h\nu_2$ with 370 nm photons. It is possible that $h\nu_1 = 580$ nm photons.

Additional measurements are required to decide the actual TL mechanism in Li₂B₄O₇:Cu.

Figure 6 shows thermal decay of both ESR signals and 165°C TL peak at 120°C. It shows that BOHC is responsible for this TL peak.
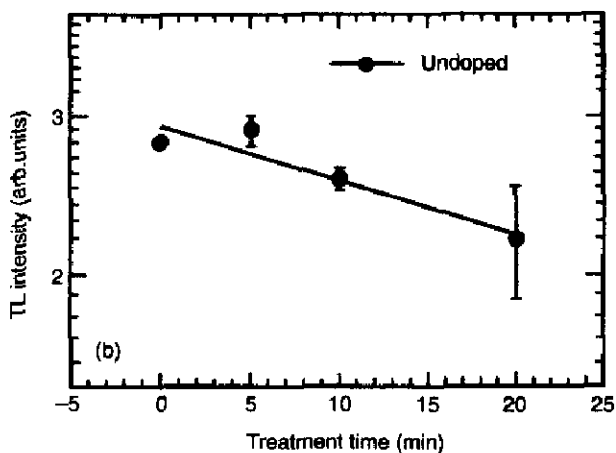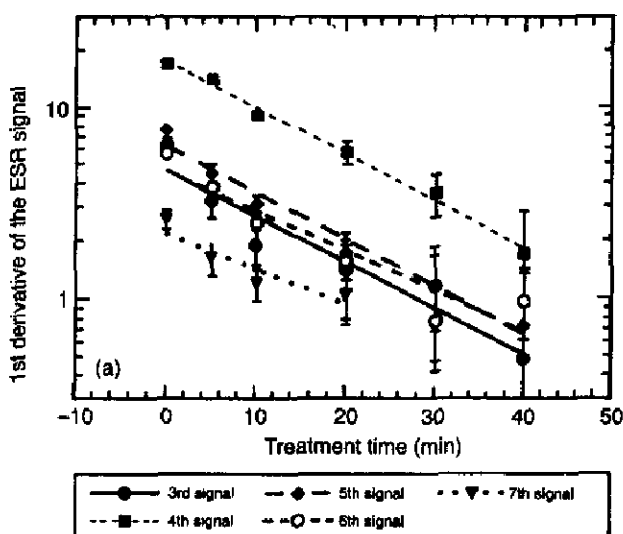
ACKNOWLEDGEMENTS

Figure 6. Thermal decay at 120°C for 0, 5, 10, 20, 30 and 40 min: (a) first derivative of ESR signal of C16 sample, irradiated to 10^5 Gy γ rays; (b) TL intensity of same samples.

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