Copper-doped lithium triborate (LiB$_3$O$_5$) crystals: A photoluminescence, thermoluminescence, and electron paramagnetic resonance study

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**ABSTRACT**

When doped with copper ions, lithium borate materials are candidates for use in radiation dosimeters. Copper-doped lithium tetraborate (Li$_2$B$_4$O$_7$) crystals have been widely studied, but little is known thus far about copper ions in lithium triborate (LiB$_3$O$_5$) crystals. In the present investigation, Cu$^+$ ions (3d$^{10}$) were diffused into an undoped LiB$_3$O$_5$ crystal at high temperature. These ions occupy both Li$^+$ and interstitial positions in the crystal. A photoluminescence (PL) band peaking near 387 nm and a photoluminescence excitation (PLE) band peaking near 273 nm verify that a portion of these Cu$^+$ ions are located at regular Li$^+$ sites. After an irradiation at room temperature with x rays, electron paramagnetic resonance (EPR) spectra show that Cu$^+$ ions at Li$^+$ sites have trapped a hole and converted to Cu$^{2+}$ ions (3d$^9$) while Cu$^+$ ions at interstitial sites have trapped an electron and converted to Cu$^0$ atoms (3d$^{10}$ 4$s^1$). Two distinct Cu$^{2+}$ trapped-hole spectra are formed by the x rays: one due to isolated Cu$^{2+}$ ions with no nearby defects and the other due to perturbed Cu$^{2+}$ ions. When the x-ray-irradiated crystal is heated above room temperature, a thermoluminescence (TL) peak appears at 120 °C with a maximum in the emitted light near 630 nm. EPR shows that this TL peak occurs when trapped electrons are thermally released from interstitial Cu$^0$ atoms. Thermal quenching above room temperature prevents the electron-hole recombination at Cu$^{2+}$ ions from contributing to the TL emission.

1. Introduction

Lithium triborate (LiB$_3$O$_5$) is a well-established nonlinear optical material widely used in frequency conversion applications ranging from the mid-infrared to the deep ultraviolet [1–3]. In recent years, this material has also been proposed as a possible candidate for radiation dosimeters [4–10]. Further investigation, however, is needed to determine if LiB$_3$O$_5$ can serve as a practical thermoluminescence (TL) dosimeter. A related borate compound, lithium tetraborate (Li$_2$B$_4$O$_7$), is known to be an excellent TL dosimeter material when doped with copper [11–16]. Because of the similarities of the two materials (LiB$_3$O$_5$ and Li$_2$B$_4$O$_7$), we have initiated a study of copper in LiB$_3$O$_5$. Interest in both materials also arises because the $^6$Li and $^{10}$B nuclei have large cross-sections for thermal neutron absorption. Enrichment with either or both isotopes may allow these materials to be used as neutron detectors.

Our focus on copper is a result of the unique role played by Cu$^+$ ions in the TL response of doped Li$_2$B$_4$O$_7$. These monovalent ions serve as both hole traps and electron traps during an exposure to ionizing radiation [17]. This diametrically opposite behavior occurs because the Cu$^+$ ions are located at two quite different sites within the Li$_2$B$_4$O$_7$ crystals. When substituting for Li$^+$ ions, the Cu$^+$ ions trap holes and become Cu$^{2+}$ ions. The Cu$^+$ ions also occupy interstitial sites where they trap electrons and become Cu$^0$ atoms. During a subsequent heating after an irradiation, electrons are thermally released from Cu$^0$ centers and recombine with holes at the Cu$^{2+}$ ions. This produces an intense TL signal in Li$_2$B$_4$O$_7$ because electron-hole recombination at the Cu$^{2+}$ sites is primarily radiative. Similar behavior has been reported for Ag$^+$ ions in Li$_2$B$_4$O$_7$ crystals [18,19].

In the present paper, we identify the Cu-related electron and hole trapping sites in LiB$_3$O$_5$ that are active during an exposure to ionizing radiation, and we also explore the recombination process when charge is thermally released by heating above room temperature. Diffusion at 650 °C is used to introduce Cu$^+$ ions (3d$^{10}$) into a previously grown undoped crystal. The Cu$^+$ ions occupy both substitutional Li$^+$ sites and interstitial sites in the LiB$_3$O$_5$ crystal. Complementary optical and magnetic resonance characterization techniques are then applied. These are optical absorption, photoluminescence (PL), photoluminescence excitation (PLE), thermoluminescence (TL), and electron paramagnetic resonance (EPR). The PL and PLE results verify that Cu$^+$ ions are...
present at Li+ sites in the diffused crystal. After irradiating at room temperature with x rays, EPR spectra show that Cu+ ions at Li+ sites have trapped a hole (Cu2+ ions are formed) and Cu+ ions at interstitial sites have trapped an electron (Cu0 atoms are formed). A TL peak near 120 °C corresponds to the release of electrons from the Cu0 traps. Surprisingly, the spectral dependence of the TL signal peaks near 630 nm, thus showing that this TL-related radiative recombination is not occurring at the Cu2+ ions.

2. Experimental

Lithium triborate (LiB3O5) crystals have an orthorhombic structure (space group Pna21) for all temperatures below their 834 °C melting point. At room temperature, lattice constants are a = 8.447 Å, b = 7.3789 Å, and c = 5.1408 Å [20–22]. There are three inequivalent boron sites and five inequivalent oxygen sites in LiB3O5. All the lithium sites are equivalent. The 36 atoms in a unit cell separate into four sets of nine atoms that transform into each other according to the symmetry elements of the crystal [23]. More generally, the LiB3O5 crystals are best described as helices of fully connected (B3O7)5− anionic groups separated by Li+ cations [3]. Each (B3O7)5− anionic group has two boron ions that are part of BO3 units and one boron ion that is part of a BO4 unit. A “ball-and-stick” representation of this basic building block is shown in Fig. 1.

The sample used in our optical and EPR experiments was rectangular in shape and had nominal dimensions of 2.5 × 3 × 3.5 mm3 along the a, b, and c axes, respectively. The following process was used to diffuse copper into an undoped LiB3O5 crystal. After wrapping a single layer of copper foil (0.0125 mm thick) around a sample, it was placed in a one-zone tube furnace and heated to 650 °C in a static air atmosphere. The sample, surrounded by copper, was held at this temperature for 11 h, and then was quickly cooled to room temperature. At the high temperature, copper enters the crystal as close-shelled Cu+ ions and occupies Li+ sites and interstitial spaces. A mismatch in both size and charge prevents Cu+ ions from occupying B3+ sites. It is not known if the copper was uniformly distributed within our diffused crystal.

A Horiba Fluorolog-3 spectrometer was used to take the PL and PLE spectra (slits for the excitation and emission monochromators were set at 10 nm resolution). The PL spectra were not corrected for system response. A Bruker EMX spectrometer operating near 9.40 GHz was used to convert the Cu+ ions to Cu2+ ions and Cu0 atoms. The duration of each x-ray irradiation was three minutes.

3. Optical and magnetic resonance results

3.1. Photoluminescence (PL and PLE)

After diffusing Cu+ ions into the LiB3O5 crystal, an intense PL emission band is observed at room temperature. This PL band peaks near 387 nm (3.20 eV) when the excitation light is 275 nm. Its full width at half maximum (FWHM) is 0.40 eV. The corresponding room-temperature PLE band, obtained by monitoring the emission at 385 nm, has a peak at 273 nm (4.54 eV) and a FWHM of approximately 0.43 eV. These PL and PLE bands are shown in Fig. 2. Their Stokes shift is approximately 1.34 eV. The bands in Fig. 2 were not present before the LiB3O5 crystal was diffused with copper. We assign the PLE band to the 3d10 to 3d4s1 intracenter transition of Cu+ ions substituting for Li+ ions and the PL band to the Stokes-shifted 3d4s4p1 to 3d10 emission. A two-level configurational coordinate diagram describes this localized excitation and emission. PL and PLE bands similar to those shown in Fig. 2 have been previously attributed to Cu+ ions substituting for Li+ ions in Li2B4O7 and LiAlO2 crystals [11,12,14,24,25].

The intensity of the PL emission band at 387 nm in the copper-diffused LiB3O5 crystal was monitored as the temperature was raised above room temperature. These results are shown in Fig. 3. The data suggest that the PL signal from the Cu+ ions is thermally quenched even at 75 °C. The intensity of this PL emission is expected to be much larger for temperatures below room temperature. The Cu+ emission in LiB3O5 is nearly 100% quenched at 100 °C. For comparison, data taken...
under identical conditions from a Cu-doped Li$_2$B$_4$O$_7$ crystal are also shown in Fig. 3. For this latter crystal, the intensity of the emission at 370 nm from Cu$^+$ ions [24] was recorded as the temperature was steadily increased. As seen in Fig. 3, the Cu$^+$ emission in Li$_2$B$_4$O$_7$ does not begin to significantly quench until the temperature is above 200 °C.

3.2. Electron paramagnetic resonance (EPR)

Irradiating the copper-diffused LiB$_3$O$_5$ crystal at room temperature with x rays produces EPR signals from Cu$^{2+}$ (3d$^9$) ions and Cu$^0$ (3d$^{10}$4s$^1$) atoms. Although the majority of the “free” electrons and holes created by the x rays quickly recombine in otherwise perfect regions of the crystal, a small portion become trapped at existing defects and create the EPR signals. The Cu$^{2+}$ ions are at Li$^+$ sites in the crystal and are formed when a radiation-induced hole is trapped at a Cu$^+$ ion [26]. At the same time, the Cu$^0$ atoms are formed when a radiation-induced electron is trapped at an interstitial Cu$^+$ ion. The spectra assigned to Cu$^{2+}$ ions have strong angular dependence, $g$ values greater than 2.00, and small hyperfine splittings. In contrast, the spectrum assigned to Cu$^0$ atoms has very little angular dependence, a $g$ value of 2.00, and large hyperfine splittings.

The EPR spectra of two distinct x-ray-induced Cu$^{2+}$ ions are shown in Fig. 4. These data were obtained at 25 K after irradiating the crystal at room temperature with x rays. The magnetic field is along the $b$ axis and the microwave frequency is 9.398 GHz. Upper (red) stick diagrams are lines from the isolated Cu$^{2+}$ ions and lower (blue) stick diagrams are lines from the perturbed Cu$^{2+}$ ions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Hyperfine interactions with the two stable isotopes of copper allow these spectra in Fig. 4 to be unambiguously assigned to Cu$^{2+}$ ions. The $^{63}$Cu nuclei are 69.2% abundant with $I = 3/2$ and the $^{65}$Cu nuclei are 30.8% abundant with $I = 3/2$. Two sets of hyperfine lines, with four lines in each set, are observed for each Cu$^{2+}$ spectrum as a result of these $I = 3/2$ nuclear spins (the number of EPR lines in a set is given by $2I + 1$). For a specific spectrum, the separations between the four $^{65}$Cu lines are greater (by a small amount) than the separations between the four $^{63}$Cu lines. This is a result of the magnetic moment of the $^{65}$Cu nucleus being slightly larger than the moment of the $^{63}$Cu nucleus. The different natural abundances of the two copper isotopes explain why $^{63}$Cu lines are more intense than $^{65}$Cu lines in Fig. 4.

The EPR spectrum from the x-ray-induced Cu$^0$ atoms is shown in Fig. 5. This spectrum was taken at room temperature with the magnetic...
field along the crystal’s c axis. There are four widely separated groups of EPR lines in Fig. 5, centered approximately at 185, 240, 335, and 450 mT. As indicated by the stick diagrams above the spectrum, these four groups are due to hyperfine interactions with $^{63}$Cu and $^{65}$Cu nuclei. The large Cu hyperfine parameters and their isotopic nature establish that the responsible defect is, to first order, a copper atom. Also present in Fig. 5 are a set of Cu$^{2+}$ lines near 285 mT. A comparison of the Cu$^{0}$ and Cu$^{2+}$ spectra shows that the magnitude of the hyperfine interaction, as expected, is much larger for a Cu$^{0}$ atom. This is because the unpaired spin is in a 4$s$ orbital for the Cu$^{0}$ atom and is in a 3$d$ orbital for the Cu$^{2+}$ ion. The larger interaction for the Cu$^{0}$ atoms causes the separation between adjacent sets of lines to increase from low to high field in Fig. 5.

Fig. 6 is an expanded view of the lowest-field set of Cu$^{0}$ EPR lines in Fig. 5. Each Cu hyperfine line is split into additional superhyperfine lines by an interaction with a boron neighbor. Lines from both $^{10}$B and $^{11}$B are identified in Fig. 6. As shown by stick diagrams above the spectrum in Fig. 6, the $^{60}$Cu line and the $^{62}$Cu line are separately split into a set of four lines due to an interaction with a $^{11}$B nucleus (80.2% abundant, $I = 3/2$) at one nearby boron site and a set of seven lines due to the interaction with a $^{10}$B nuclei (19.8% abundant, $I = 3$) at the same nearby boron site. This pattern of seven lines of smaller intensity and four lines of larger intensity is consistent with a boron interaction. The large Cu hyperfine interaction with a10B nuclei (19.8% abundant, $I = 3/2$) at one nearby boron site and a set of seven lines due to the nuclear magnetic moment of $^{10}$B is nearly three times smaller than the nuclear magnetic moment of $^{11}$B, thus explaining why the $^{10}$B lines appear between the $^{11}$B lines. A detailed analysis of the EPR spectra from these Cu$^{2+}$ and Cu$^{0}$ centers in LiB$_{3}$O$_{5}$, including the determination of their spin-Hamiltonian parameters, will be reported in a later publication.

3.3. Optical absorption

Optical absorption spectra from the LiB$_{3}$O$_{5}$ crystal diffused with copper are shown in Fig. 7. These spectra were taken at room temperature using unpolarized light propagating along the c direction. The lower (blue) spectrum was taken from the as-diffused crystal and the upper (red) spectrum was taken after an irradiation at room temperature with x rays. Before the irradiation, the crystal had broad absorption bands peaking near 292 nm (4.25 eV), 254 nm (4.88 eV), and 226 nm (5.49 eV), with the 292 nm band being weakest and the 226 nm band being most intense. The defects responsible for these absorption bands are not unambiguously identified in our study. These bands are tentatively assigned to transitions from the ground state to different excited states of the Cu$^{+}$ ions. After the x-ray irradiation (red curve), additional absorption bands are present near 355 nm (3.49 eV) and 312 nm (3.97 eV). These latter two bands are most likely associated with the radiation-induced Cu$^{2+}$ and Cu$^{0}$ defects seen with EPR (see Section 3.2). Singly ionized oxygen vacancies ($V'_O$) have an optical absorption band near 300 nm (4.13 eV) in LiB$_{3}$O$_{5}$ [27], and they may also be contributing to the after-irradiation absorption spectrum (red curve) in Fig. 7. Future in-depth studies will help determine final assignments for these optical absorption bands appearing in the copper-diffused LiB$_{3}$O$_{5}$ crystal.

3.4. Thermoluminescence (TL)

Recently, investigators [4,7] reported that a thermoluminescence (TL) glow curve occurs near 120 °C when a LiB$_{3}$O$_{5}$ crystal containing copper is exposed at room temperature to ionizing radiation. As seen in Fig. 8, our copper-diffused LiB$_{3}$O$_{5}$ crystal also shows this 120 °C TL peak (green curve). The TL data in Fig. 8 were obtained with a heating rate of 1 °C/s after an irradiation at room temperature with x rays. To help identify the defects participating in this TL glow curve, a series of EPR measurements that reproduced the TL heating rate were made on the same copper-diffused LiB$_{3}$O$_{5}$ crystal. After an irradiation at room temperature with x rays, the EPR spectra of the isolated and perturbed Cu$^{2+}$ trapped-hole centers and the Cu$^{3+}$ trapped-electron centers were monitored during an isochronal...
Thermal anneal. The irradiated copper-diffused LiB₃O₅ crystal was placed in the microwave cavity and the three EPR spectra were taken at 25 K. Next, the sample was moved to a small furnace (preheated to 60 °C) and held at this temperature for 23 s before being returned to the microwave cavity where the EPR spectra were again recorded at 25 K. This incremental process was repeated at 85 °C and again in 25 °C steps above 85 °C with 23 s holding times at each of the elevated temperatures. The equivalent constant heating rate was approximately 1.09 °C/s. Following each heating step, the three EPR spectra were recorded at 25 K. Next, the sample was moved to a small furnace (preheated to 85 °C) and held at this temperature for 23 s before being returned to the microwave cavity where the EPR spectra were again recorded at 25 K. This incremental process was repeated at 85 °C and again in 25 °C steps above 85 °C with 23 s holding times at each of the elevated temperatures. The equivalent constant heating rate was approximately 1.09 °C/s. Following each heating step, the three EPR spectra were recorded at 25 K monitoring temperature. Results from these thermal anneals are included in Fig. 8. The TL peak intensity and the initial intensities of the isolated Cu²⁺ and the Cu⁰ spectra are normalized. The intensity of the perturbed Cu²⁺ spectrum is not normalized; instead, its initial value is set to approximately 60% of the initial intensity of the isolated Cu²⁺ spectrum, thus indicating that the x-ray irradiation initially created more isolated Cu²⁺ ions than perturbed Cu²⁺ ions.

In Fig. 8, the intensity of the Cu¹ trapped-electron spectrum increases slightly in the 30–85 °C region and then decreases rapidly in the 85–160 °C region and is completely gone at 160 °C. At 120 °C, the intensity of the Cu⁰ EPR spectrum has decreased by half. This thermal decay of the Cu¹ centers correlates very well with the width and peak position of the TL glow curve. In contrast, the intensity of the isolated Cu²⁺ trapped-hole spectrum decreases gradually over the 30–160 °C region. Approximately 23% of these trapped-hole centers remain after the 160 °C anneal step and there is no further decay when the anneal temperature reaches 185 °C. The intensity of the perturbed Cu²⁺ EPR spectrum does not decrease over the 60–185 °C region in Fig. 8.

Fig. 9 shows the wavelength dependence of the emitted light associated with the 120 °C TL peak. These data were obtained using a spectrograph and a CCD camera as the sample was heated in a TL experiment. The spectral curve in Fig. 9 was collected during a 1.1 s interval of time while the temperature of the sample was near 120 °C (i.e., corresponding to the peak of the TL glow curve). The maximum in this emission spectrum occurs at 630 nm (1.97 eV) and the FWHM of the band is 0.31 eV. Light near 380 nm was not detected when the crystal was at 120 °C.

4. Discussion of the TL mechanism

The early studies [4,7] of the TL response of copper-doped LiB₃O₅ did not identify the participating electron and hole traps and did not specify a recombination site. Now, however, by combining the results from our EPR, thermal quenching, and spectral-dependence experiments, we have sufficient information to establish the primary physical mechanisms responsible for the TL glow curve peaking at 120 °C in a copper-diffused LiB₃O₅ crystal.

The EPR results in Figs. 4, 5, and 8 show that isolated Cu²⁺ ions at Li⁺ sites are the active hole traps and that Cu⁰ atoms at interstitial sites are the active electron traps. In Fig. 8, a portion of the isolated Cu²⁺ ions and all of the perturbed Cu²⁺ ions survive after the temperature reaches 185 °C, whereas all of the Cu⁰ atoms disappear by 160 °C. These annealing results, with their 100% change in the Cu⁰ spectrum, demonstrate conclusively that the 120 °C TL peak is caused by the thermal release of electrons from Cu⁰ centers. If the TL peak were caused by holes being thermally released from isolated Cu²⁺ ions, then the intensity of their EPR signal would be 100% gone after the anneal step at 160 °C. There is a second, and smaller effect, also present in Fig. 8. Increases in the intensity of the Cu⁰ trapped-electron spectrum and decreases in the intensity of the isolated Cu²⁺ trapped-hole spectrum appear at 60 and 85 °C. We attribute these changes in the Cu⁰ and Cu²⁺ spectra in the 60–85 °C range to the thermal release of electrons from singly ionized oxygen vacancies [26]. The released electrons are trapped at interstitial Cu¹ ions to form additional Cu⁰ atoms and they recombine with holes at isolated Cu²⁺ ions to restore Cu⁺ ions at Li⁺ sites.

Thermal quenching results in Fig. 3 strongly suggest that the electron-hole recombination site in the TL process is not the isolated Cu²⁺ ions. The 3d⁴⁴s¹ to 3d⁴⁰ emission of a Cu⁺ ion in LiB₃O₅ is completely quenched (i.e., is non-radiative) at 120 °C, and thus they do not contribute to the TL emission. Additional evidence that the electron-hole recombination responsible for the observed emission does not occur at Cu²⁺ ions comes from the 630 nm maximum in the spectral dependence of the TL emitted light (see Fig. 9). Annalakshmi et al. [10] recently studied the TL properties of Mn-doped LiB₃O₅ and reported an
emission peak near 600 nm. They suggest that Mn\(^{2+}\) ions trap holes and convert to Mn\(^{3+}\) during an irradiation. Trapped electrons are released during heating and recombine radiatively with the holes at the Mn\(^{3+}\) ions, thus forming Mn\(^{2+}\) ions in an excited state, which then relax to the ground state while emitting 600 nm photons. Similarly, TL investigations of Mn-doped Li\(_2\)B\(_4\)O\(_7\) [28–32] have reported light emission near 580–615 nm. Thus, for our present study, we conclude that the most likely radiative recombination site in the copper-diffused LiB\(_3\)O\(_5\) crystal are Mn\(^{2+}\) ions at Li\(^+\) sites. In support of this assignment, our EPR spectra show that trace amounts of Mn\(^{2+}\) are present in the copper-diffused crystal. These Mn\(^{2+}\) EPR signals are very weak in our sample.

Although difficult to observe, we were able to establish their similarity to the EPR spectra from Mn\(^{2+}\) ions in Li\(_2\)B\(_4\)O\(_7\) crystals. As part of the study, comparisons were made with Cu-doped Li\(_2\)B\(_4\)O\(_7\) crystals. For these devices to be useful, radiative recombination at Cu\(^{2+}\) ions in LiB\(_3\)O\(_5\) crystals is needed to produce an intense TL peak above room temperature.

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References