Optically stimulated luminescence (OSL) from Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystals

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Abstract

Optically stimulated luminescence (CW-OSL) is observed from Ag-doped lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) crystals. Photoluminescence, optical absorption, and electron paramagnetic resonance (EPR) are used to identify the defects participating in the OSL process. As-grown crystals have Ag^+ ions substituting for Li^+ ions. They also have Ag^+ ions occupying interstitial sites. During a room-temperature exposure to ionizing radiation, holes are trapped at the Ag^+ ions that replace Li^+ ions and electrons are trapped at the interstitial Ag^+ ions, i.e., the radiation forms Ag^{2+} ($4d^9$) ions and Ag^0 ($4d^{10}5s^1$) atoms. These Ag^{2+} and Ag^0 centers have characteristic EPR spectra. The Ag^0 centers also have a broad optical absorption band peaking near 370 nm. An OSL response is observed when the stimulation wavelength overlaps this absorption band. Specifically, stimulation with 400 nm light produces an intense OSL response when emission is monitored near 270 nm. Electrons optically released from the Ag^0 centers recombine with holes trapped at Ag^{2+} ions to produce the ultraviolet emission. The OSL response is progressively smaller as the stimulation light is moved to longer wavelengths (i.e., away from the 370 nm peak of the absorption band of the Ag^0 electron traps). Oxygen vacancies are also present in the Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystals, and their role in the OSL process as a secondary relatively short-lived electron trap is described.

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1. Introduction

Lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$), known simply as LTB, has emerged in recent years as an important and versatile radiation-detector material. The primary focus thus far has been on the thermoluminescence (TL) properties of $\text{Li}_2\text{B}_4\text{O}_7$ [1-15]. Only recently has optically stimulated luminescence (OSL) been reported from this material [16-19]. These TL and OSL investigations have shown that light emission is greatly enhanced when $\text{Li}_2\text{B}_4\text{O}_7$ is doped with either Cu^+ or Ag^+ ions. These monovalent dopants are unique in $\text{Li}_2\text{B}_4\text{O}_7$, as they serve as both a hole trap and an electron trap during exposures to ionizing radiation [6,11]. When substituting for Li^+ ions, the Cu^+ and Ag^+ ions trap holes and become Cu^{2+} and Ag^{2+} ions. The Cu^+ and Ag^+ ions also occupy interstitial sites in this material where they trap electrons and become Cu^0 and Ag^0 atoms. After being thermally or optically released, these electrons recombine with holes at Cu^{2+} and Ag^{2+} ions and produce large TL and OSL signals. There is also interest in $\text{Li}_2\text{B}_4\text{O}_7$ because the ^6Li and ^{10}B nuclei have large cross-sections for thermal neutron absorption. Enrichment with either or both of these isotopes may allow $\text{Li}_2\text{B}_4\text{O}_7$ to be used as a neutron detector.

In the present paper, we investigate the fundamental mechanisms responsible for OSL in Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystals. One of the primary goals of our study is to establish the properties of the optical absorption band that allows OSL stimulation light to release electrons at room temperature. Photoluminescence (PL), photoluminescence excitation (PLE), electron paramagnetic resonance (EPR), and optical absorption are used to identify the electron and hole traps that are participating in the OSL process. The dependence of the OSL intensity on the wavelength of the stimulation light is determined and the specific recombination site for the OSL is identified. In addition to the primary interstitial Ag^0 electron trap, unintentionally present oxygen vacancies are identified as a second active electron trap in the Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystals. These oxygen vacancies decrease the rate at which OSL light is emitted during stimulation, and thus reduce the OSL sensitivity of the material. Taken together, our results suggest that Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ will be a highly sensitive OSL-based radiation detector with commercial promise.

2. Experimental

A single crystal of $\text{Li}_2\text{B}_4\text{O}_7$ doped with Ag was grown by the Czochralski method at the Institute of Physical Optics (L'viv, Ukraine). A congruent melt, exposed to air, was contained in a Pt crucible. The growth axis was [001] and the pulling and rotation velocities did not exceed 0.3 mm/h and 10 revolutions/min, respectively. This method produces $\text{Li}_2\text{B}_4\text{O}_7$ crystals of high optical quality with sizes up to 25 mm in diameter and 40 mm in length. All of the OSL, PL, optical absorption, and EPR data reported in this paper were taken from one sample cut from the larger as-grown boule. The concentration of Ag in this sample is estimated, from the starting materials, to be 0.02 at.%. Its dimensions are approximately $0.83 \times 3 \times 6.5 \text{ mm}^3$, with the [001] direction normal to the broad faces.

The symmetry of $\text{Li}_2\text{B}_4\text{O}_7$ crystals is tetragonal (space group $I4_1cd$ and point group $4mm$) with lattice constants $a = 9.475 \text{ \AA}$ and $c = 10.283 \text{ \AA}$ at room temperature [20-23]. There are 104 atoms (eight formula units) in a unit cell. A $(\text{B}_4\text{O}_9)^{6-}$ anionic group, consisting of two BO_3 and two BO_4 units, serves as the repeating structural building block. In general, $\text{Li}_2\text{B}_4\text{O}_7$ crystals have two inequivalent boron sites and four inequivalent oxygen sites. All the lithium sites are crystallographically equivalent. Each oxygen ion has two boron neighbors, whereas each lithium ion has four close oxygen neighbors (arranged asymmetrically around it) and two additional slightly more distant oxygen neighbors. Fig. 1 shows a $(\text{B}_4\text{O}_9)^{6-}$ group along with one nearby Li^+ ion and its additional neighboring oxygen ions.

An Horiba Fluorolog-3 spectrometer was used to obtain the PL, PLE, and OSL data. This spectrometer has a xenon lamp as the excitation source, a Hamamatsu R928 photomultiplier as a detector, and two double-grating monochromators to measure emission and excitation spectra. The spectrometer was operated in a kinetics mode when acquiring OSL data (i.e., emission data were collected as a function of time while using fixed excitation and monitoring wavelengths). In all experiments, the slit widths were set at 10 nm resolution for the excitation monochromator and 5 nm resolution for the emission monochromator.

Optical absorption data were obtained with a Cary 5000 dual-beam spectrophotometer from Varian. The absorption spectra were taken at room temperature with corrections made for surface reflective losses. A Bruker EMX spectrometer operating near 9.38 GHz was used to take the EPR data. The crystal was irradiated at room temperature using an x-ray tube (Varian OEG-76H) operating at 60 kV and 30 mA. Irradiation times were 2 min. Before each exposure to the x rays, the crystal was held at 400 °C for 3 min to remove any effects of previous irradiations.

3. Results

A comprehensive set of experiments was performed on a Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal. The goals were to identify the defects participating in the OSL response, determine the site where the OSL radiative recombination occurs, and find the optimum stimulation wavelengths that produce OSL. The following subsections describe the results obtained from these PL, PLE, OSL, optical absorption, and EPR experiments.

3.1. Photoluminescence (PL and PLE)

Fig. 2 shows the PL and PLE spectra obtained at room temperature from our Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal. Prior to taking these data, the sample was reset to its as-grown state by heating to 400 °C. The PL band has a peak at 270 nm and a full width at half maximum (FWHM) of 0.54 eV, whereas the corresponding PLE band has a peak near 210 nm and a FWHM of 0.41 eV. Earlier studies [7,9,16] have assigned these PL and PLE bands to Ag^+ ions occupying Li^+ sites in the $\text{Li}_2\text{B}_4\text{O}_7$ crystals. The excitation band corresponds to a $4d^{10}$ to $4d^95s^1$ intracenter transition of the Ag^+ ion while the emission band is a Stokes-shifted $4d^95s^1$ to $4d^{10}$ transition back to the ground state (excitations and emissions of this type are usually described by a two-level configurational coordinate diagram). The observation of this 270 nm emission peak and 210 nm excitation peak in our crystal before an x-ray irradiation verifies that Ag^+ ions are present.

The PL spectrum in Fig. 2 was acquired by operating the emission monochromator of the Fluorolog-3 spectrometer in second order (i.e., this monochromator was scanned from 470 to 630

nm while detecting the actual emission in the 235 to 315 nm region). Also, the PLE spectrum in Fig. 2 has not been corrected either for the rapidly decreasing intensity of the xenon lamp in the 220 to 200 nm region or for the wavelength dependence of the excitation monochromator. These corrections (that account for changes in incident photon flux) will shift the PLE peak closer to the 205 nm value that has been reported by earlier investigators [7,9,16]. We do not attempt to make these corrections in our PLE data because a calibrated power meter was not available for use in determining the wavelength dependence of the combined output of our xenon lamp and excitation monochromator in this short-wavelength region. The lack of a correction is not a significant deficiency since the optical absorption data presented in Section 3.3.2 verifies that the excitation band producing the PL has a peak at 205 nm.

3.2. *Optically stimulated luminescence (OSL)*

A large OSL response was observed from our Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal after exposing it to ionizing radiation (i.e., x rays) at room temperature. Three OSL decay curves are shown in Fig. 3. These OSL data were taken with our Fluorolog-3 spectrometer operating in the kinetics mode. The excitation monochromator was set for 10 nm resolution and centered at either 400, 450, or 500 nm, while the emission monochromator was set at 5 nm resolution and used to monitor (in second order) the emission at 270 nm. As seen in Fig. 3, the 400 nm stimulation light is more efficient than the 450 or 500 nm light at generating an OSL signal. Although not shown, the OSL response is even larger when 350 nm stimulation light is used. Our optical absorption curves in Section 3.3.2 provide an explanation for this dependence on stimulation wavelength. The OSL decay curves in Fig. 3 are nonexponential and a cursory examination suggests that fast and slow components may be present. As described in Section 3.4, oxygen vacancies serving as electron traps may be partly responsible for the slow component.

The series of spectra in Fig. 4 illustrate the wavelength dependence of the OSL emission. As the OSL signal was decaying as a function of time during stimulation with 400 nm light, the emission monochromator in the Fluorolog-3 spectrometer was set to scan repeatedly from 470 to

630 nm, thus allowing detection of the 270 nm emission band in second order. Each scan took 12 s with 4 s required to reset the monochromator (this resulted in a large number of scans being acquired during one OSL decay). The five spectra shown in Fig. 4 were taken 6, 38, 86, 278, and 630 s after turning on the 400 nm stimulation light. These five scans show no significant change in the wavelength dependence of the emission during the OSL decay which, in turn, suggests that the recombination site remains the same during the decay. The most intense (i.e., first) emission curve in Fig. 4 has a peak near 270 nm and a FWHM of 0.53 eV. This and the other OSL emission curves in Fig. 4 strongly resemble the PL curve in Fig. 2. The same peak position and shape suggests that these two emissions have a common origin (i.e., the recombination that gives rise to the PL and OSL emissions in our $\text{Li}_2\text{B}_4\text{O}_7$ crystal occurs at a Ag ion that occupies a Li^+ site).

As expected, the OSL signal from our Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal was much larger when a 65 mW diode laser emitting 405 nm light was used as a stimulation source. The intensity of this laser light was significantly greater than the intensity of the 400 nm light from the coupled xenon lamp and excitation monochromator in the Fluorolog-3 spectrometer. With the stronger stimulation light from the laser, the OSL decay occurred in a shorter time and the signal-to-noise ratio of the OSL signal was much greater than in Fig. 3. A second factor affecting the OSL signal is our use of a monochromator on the detection side of the Fluorolog-3 spectrometer (when recording the OSL response in second order, the resolution of this emission monochromator was set at 5 nm). The signal-to-noise ratio of the OSL light will be larger if this monochromator is removed and all the emitted light is incident on the photomultiplier tube (with perhaps one or more filters to eliminate unwanted light).

3.3. Primary defects involved in OSL

3.3.1. Electron paramagnetic resonance (EPR)

Two trapped-hole centers and one trapped-electron center, each with an unpaired spin, are formed when our Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal is irradiated at room temperature with x rays [6,13].

Fig. 5(a) shows the EPR signals from each of these $S = 1/2$ centers. This spectrum was taken at 32 K with the magnetic field along the [001] direction. The two distinct hole centers (which we have labeled isolated Ag^{2+} and perturbed Ag^{2+}) are observed in the low-field region of Fig. 5(a). These labels, respectively, refer to a Ag^{2+} ion with no other defect nearby and a Ag^{2+} ion with an adjacent defect. These trapped hole centers are formed when Ag^+ ($4d^{10}$) ions at Li^+ sites trap the radiation-induced holes and become Ag^{2+} ($4d^9$) ions. Direct evidence that the two EPR spectra represent Ag^{2+} ions comes from their large positive g shifts, their small hyperfine splittings, and the unambiguous electron-nuclear double resonance (ENDOR) identification of ^{107}Ag and ^{109}Ag as the nuclei responsible for the hyperfine splittings [6]. In previous papers [6,13], these trapped-hole centers were simply labeled Center A and Center B, respectively. Our new labels are more informative. The perturbing entity associated with Center B was suggested, in the past, to be a Na^+ or Ag^+ ion at an adjacent regular lithium site [13]. Our observations of how OSL stimulation light affects the two EPR signals (these results are described in Section 3.3.3) now suggest that an adjacent lithium vacancy is a third, and very likely, possibility for the perturbation. Analogous defects, i.e., isolated Cu^{2+} ions and $\text{Cu}^{2+}\text{-V}_{\text{Li}}$ centers, have been previously observed in $\text{Li}_2\text{B}_4\text{O}_7$ and LiAlO_2 crystals [11,24].

The electron center in Fig. 5(a) has a 16-line EPR spectrum centered at 335.4 mT. This defect is formed during the x-ray irradiation when an interstitial Ag^+ ($4d^{10}$) ion traps an electron and becomes a Ag^0 ($4d^{10}5s^1$) center. As described previously [6], the trapped-electron spectrum in Fig. 5(a) has 16 lines because of resolved hyperfine interactions with ^{107}Ag and ^{109}Ag nuclei and one additional $I = 3/2$ nucleus. A comparison of our spectrum with the analogous spectrum from radiation-induced Cu^0 centers in Cu-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystals [11] strongly suggests that the $I = 3/2$ nucleus in our Ag^0 spectrum is a ^{11}B neighbor. In the Cu^0 centers, the participating $I = 3/2$ nucleus must be ^{11}B because resolved less intense hyperfine lines from ^{10}B nuclei are also seen (^{11}B nuclei are 80.1% abundant with $I = 3/2$ while the ^{10}B nuclei are 19.9% abundant with $I = 3$).

The large hyperfine interaction of approximately 3.9 mT with the neighboring ^{11}B nucleus in the Ag^0 trapped-electron center provides supporting evidence that this Ag^0 center is located at

an interstitial position in the Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystals. Such a large hyperfine interaction is not expected if the Ag^0 atom occupies a regular Li^+ site in the crystal (this is because of the relatively large separation distance of 2.7 Å between a Li^+ site and the nearest B^{3+} site). Having the Ag^0 center at an interstitial position is, however, consistent with one large ^{11}B hyperfine interaction. In as-grown or reset crystals (i.e., before an x-ray irradiation), Ag^+ ions will occupy interstitial positions that are preferentially located near a $(\text{BO}_3)^{3-}$ or $(\text{BO}_4)^{5-}$ unit, since the positive charge of the Ag^+ ion is attracted to the negative charge of the borate unit. After an irradiation, the 5s electron in the interstitial Ag^0 atom will have significant overlap with this one nearest-neighbor boron (a result in agreement with the EPR hyperfine data). In addition to this boron hyperfine result, the relative sizes of the Li^+ and Ag^+ ions also support having Ag^+ ions occupy interstitial positions during growth. The ionic radius of Ag^+ (1.15 Å) is greater than the ionic radius of Li^+ (0.76 Å) in sixfold coordination, and thus replacement of regular Li^+ ions with Ag^+ ions requires significant distortion in the surrounding lattice.

Interestingly, the EPR spectra from the trapped-hole and trapped-electron centers can be observed at room temperature after an x-ray irradiation (see Fig. 5(b)). Comparing the spectra in Figs. 5(a) and 5(b) shows that the EPR signals from the two trapped-hole centers broaden significantly, but are still easily recognizable, at the higher temperature. As the temperature increases, lines from the isolated Ag^{2+} centers broaden at a slightly greater rate than lines from the perturbed Ag^{2+} centers. In contrast, the signals from the trapped-electron centers broaden only slightly as the temperature increases. The option of observing these EPR spectra at room temperature allows easier monitoring of the trapped holes and trapped electrons when searching for correlations with OSL and TL emissions (i.e., there is no need to have access to low-temperature EPR capabilities).

3.3.2. Optical absorption

Fig. 6 shows the optical absorption spectrum of the Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal before and after an irradiation at room temperature with x rays, and also after exposures to OSL stimulation light. These data were taken at room temperature using unpolarized light propagating along the

[001] direction in the crystal. The sample thickness was 0.83 mm and the two broad faces of the crystal were polished. Known values of the refractive indices of crystalline $\text{Li}_2\text{B}_4\text{O}_7$ in the 800 to 195 nm region [25] were used to correct the spectra for surface reflective losses. Before the irradiation with x rays (trace a), the only absorption feature present is a band peaking near 205 nm (6.05 eV). This band has been widely reported and is assigned to Ag^+ ions at Li^+ sites [7,9,16].

After the x-ray irradiation, the optical absorption spectrum is very different (see trace b in Fig. 6). The x-rays have introduced four additional absorption bands that extend across the visible and well into the ultraviolet region [26-28]. The primary radiation-induced band peaks near 370 nm (3.35 eV), while the others peak near 250 nm (4.95 eV), 296 nm (4.19 eV), and 650 nm (1.91 eV). Attempts to deconvolute the after-irradiation spectrum (trace b) in Fig. 6 into a set of Gaussian bands suggest that two overlapping bands with peaks in the 340-400 nm region are needed to replicate the large 370 nm absorption feature. The band in the longer wavelength portion of this 370 nm feature is assigned to the electric-dipole-allowed $4d^{10}5s^1$ to $4d^{10}5p^1$ transition of the Ag^0 center [26]. This $4d^{10}5p^1$ excited state has a delocalized character and is near, or possibly in, the conduction band [29,30]. Thus, stimulation wavelengths within this band easily release trapped electrons from the Ag^0 centers. These released electrons then recombine with trapped holes at Ag^{2+} ions and produce OSL emission. The second band, on the short wavelength side of the 370 nm feature, is possibly due to a charge-transfer process associated with the isolated Ag^{2+} center (i.e., an electron is transferred from a neighboring oxygen ion to the Ag^{2+} ion) [31]. Stimulation light in this second band will create an excited state that can decay in either of two ways. The excited-state complex (consisting of a Ag^+ ion with an adjacent O^- ion) may decay radiatively to restore the initial Ag^{2+} and O^{2-} ions [26] or the hole on the oxygen ion may migrate away from the Ag^+ ion (i.e., by hopping from oxygen to oxygen). This latter decay mechanism may provide a possible, although less likely, alternative path to generate an OSL response wherein the holes optically released from Ag^{2+} ions move to Ag^0 centers and recombine with the trapped electrons to produce the characteristic 270 nm emission light.

As illustrated in Fig. 6, the radiation-induced optical absorption decreases when 400 nm

OSL stimulation light (from the Fluorolog-3 spectrometer) is incident at room temperature on the Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal. Spectra taken after 100 s (trace c), 300 s (trace d), and 700 s (trace e) of 400 nm exposure are shown in Fig. 6. All of the absorption features decrease except for the band peaking near 296 nm (4.19 eV). The EPR results described in Section 3.3.3 show that the perturbed Ag^{2+} centers are the only defects not affected by the OSL excitation light. This, in turn, suggests that the perturbed Ag^{2+} centers (via a charge-transfer transition) are responsible for the 296 nm optical absorption band. At the present time, the absorption band peaking near 250 nm (4.95 eV) in Fig. 6 is not assigned to a specific defect. The band peaking near 650 nm (1.91 eV) is most likely due to a crystal-field (i.e., d -to- d) transition of the isolated Ag^{2+} ions [31].

3.3.3. Correlation of EPR and optical absorption with OSL

The trapped electron and trapped hole centers that participate in the OSL response of the Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal are identified by monitoring their EPR spectra during an exposure to 400 nm stimulation light. The spectrum in Fig. 7(a) was obtained immediately after an irradiation with x rays, while the spectrum in Fig. 7(b) was taken after exposing the crystal for 700 s to 400 nm stimulation light from the Fluorolog-3 spectrometer (this is the same stimulation source used to obtain the OSL data in Figs. 3 and 4). Vertical scales are kept the same for Figs 7(a) and 7(b) to allow easy comparison of signal intensities. These two EPR spectra show that the OSL stimulation light does not affect the number of perturbed Ag^{2+} centers, but significantly decreases the concentrations of isolated Ag^{2+} centers and Ag^0 centers. The results in Fig. 7 provide evidence that the recombination of electrons and holes occurring during OSL takes place only at isolated Ag^{2+} centers, and not at perturbed Ag^{2+} centers. This difference in behavior for the two trapped-hole centers is expected if the perturbed Ag^{2+} centers are electrically neutral and thus do not attract the optically released electrons at the same rate as the isolated Ag^{2+} centers with their effective positive charge. The perturbed Ag^{2+} center will be electrically neutral if a Li^+ vacancy is adjacent to the Ag^{2+} ion.

Fig. 8 shows in more detail the effects of the OSL stimulation light on the EPR and optical

absorption spectra from the participating trapped electron and trapped hole centers. Intensities of the Ag^0 EPR spectrum, the isolated Ag^{2+} EPR spectrum, and the 370 nm optical absorption band are plotted as a function of the time the crystal was exposed to 400 nm stimulation light from the Fluorlog-3 spectrometer. The observed reductions in the intensities of the three spectra in Fig. 8 (representing the concentrations of active trapped electrons and trapped holes) correlate with the emission of OSL light described in Fig. 3. In Fig. 8, the curve representing the decay of the 370 nm optical absorption band is slightly above the curves representing the two EPR centers. This suggests that there is an underlying less-intense band contributing to the optical absorption at 370 nm in Fig. 6 that is not affected by the 400 nm stimulation light. The presence of an underlying absorption band is also suggested by the small shift to shorter wavelength of the peak of the 370 nm feature during the decay sequence shown in Fig. 6.

3.4. *Role of oxygen vacancies in OSL*

Oxygen vacancies are present in our Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal [32]. These vacancies are in the doubly ionized charge state in the as-grown crystal, with no trapped electrons and thus no EPR signal. During an x-ray irradiation at room temperature, a portion of the oxygen vacancies trap an electron and form the EPR-active singly ionized charge state. These paramagnetic oxygen vacancies have a characteristic 4-line EPR spectrum due to the hyperfine interaction with one ^{11}B neighbor, thus making them easy to monitor [32]. After they are formed by the x rays, the singly ionized oxygen-vacancies slowly decay at room temperature over times on the order of 5-10 min, as the trapped electrons are thermally released from the vacancies. This means that the electrons trapped at oxygen vacancies are thermally much less stable than electrons trapped at Ag^0 centers.

The EPR results in Fig. 9 verify that oxygen vacancies are present and active in our Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal. The spectrum in Fig. 9(a) was taken several hours after an irradiation with x rays, and is similar to the spectrum in Fig. 7(a). Then the crystal was exposed to 405 nm stimulation light from the 65 mW diode laser. After an exposure for 120 s to this laser light, the EPR spectrum in Fig. 9(b) was immediately taken. The 405 nm light releases electrons from the

Ag^0 centers, thus making the intensity of the Ag^0 EPR spectrum in Fig. 9(b) less than its intensity in Fig. 9(a). Many of the released electrons recombine with holes at the isolated Ag^{2+} ions and produce an OSL emission. Some of these optically released electrons, however, become trapped temporarily at oxygen vacancies. By acquiring the spectrum in Fig. 9(b) within 20 s of turning off the 405 nm stimulation light, the electrons trapped at oxygen vacancies did not have time to thermally decay. In Fig. 9(b), the 4-line EPR spectrum from the electrons trapped at the oxygen vacancies overlaps the 16-line spectrum from the Ag^0 centers. A difference spectrum obtained by subtracting the spectrum in Fig. 9(a) from the spectrum in Fig. 9(b) reveals the underlying EPR spectrum from the oxygen vacancies. Before the subtraction, the intensity of the 16-line Ag^0 spectrum in Fig. 9(a) was reduced to be the same as the 16-line spectrum in Fig. 9(b). The difference spectrum, shown in Fig. 9(c), represents the singly ionized oxygen vacancies. It is identical to the oxygen-vacancy EPR spectrum previously seen in undoped $\text{Li}_2\text{B}_4\text{O}_7$ crystals that had been x-ray irradiated at 77 K [32].

Our results indicate that oxygen vacancies in $\text{Li}_2\text{B}_4\text{O}_7$ serve as short-lived electron traps at room temperature and reduce the rate at which the optically released electrons recombine with holes at isolated Ag^{2+} ions. Fewer oxygen vacancies will mean larger OSL signals in Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$. Also, by showing that OSL stimulation light forms singly ionized oxygen vacancies, we verify that the optical release of electrons from Ag^0 electron traps is the primary OSL mechanism in Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$.

4. Summary

A large OSL response has been observed from a Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal. The Ag^+ ions enter the lattice and occupy two distinctly different sites (i.e., they replace Li^+ ions and they also become interstitials). During an irradiation, Ag^+ ions at Li^+ sites trap holes and become isolated Ag^{2+} ions while Ag^+ ions at interstitial sites trap electrons and become Ag^0 atoms. The Ag^0 centers have a broad optical absorption band peaking near 370 nm with a tail extending beyond 500 nm. Stimulation light with wavelengths in this Ag^0 band releases electrons, that then recombine

with holes at the isolated Ag^{2+} ions and form Ag^+ ions in a short-lived excited state, i.e., $(\text{Ag}^+)^*$ ions. The OSL emitted light with a peak near 270 nm is characteristic of the radiative decay of these $(\text{Ag}^+)^*$ ions and is the same as the photoluminescence band observed from an intracenter excitation of Ag^+ ions in $\text{Li}_2\text{B}_4\text{O}_7$. The following summarizes the primary OSL process in Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ (Ag_i represents Ag at an interstitial position and Ag_{Li} represents Ag at a Li^+ site).

(1) Irradiation step:

(2) Stimulation step:

(3) Emission step:

In conclusion, our results suggest that Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ will be a useful OSL material because of a unique combination of defect properties. (1) Doping with Ag produces both electron and hole traps since the Ag^+ ions occupy two distinctly different sites in as-grown material. (2) Electrons trapped as interstitial Ag^0 centers have an intense optical absorption band that allows the OSL stimulation light to easily release electrons. (3) Highly efficient electron-hole recombination occurs at isolated Ag^{2+} trapped-hole centers located at regular Li^+ sites. Future studies are needed to identify the optimum concentrations of interstitial Ag^+ ions (electron traps) and Ag^+ ions at lithium sites (hole traps) that must be present in the pre-irradiated $\text{Li}_2\text{B}_4\text{O}_7$ to make the most sensitive OSL dosimeters. Also, methods must be found to minimize the concentration of oxygen vacancies.

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Figure Captions

Figure 1. Schematic representation of the $(\text{B}_4\text{O}_9)^{6-}$ basic anionic group used to construct the tetragonal $\text{Li}_2\text{B}_4\text{O}_7$ crystal. Also shown are a lithium ion and its additional surrounding oxygen ions. Lithium ions are blue, boron ions are green, and oxygen ions are red. The ions are labeled according to the scheme used in Refs. 22, 23, and 32.

Figure 2. PL and PLE spectra obtained at room temperature from Ag^+ ions in a $\text{Li}_2\text{B}_4\text{O}_7$ crystal. The PL spectrum (red curve) was taken with 210 nm excitation light and the PLE spectrum (blue curve) was obtained by monitoring (in second order) the emission at 270 nm.

Figure 3. OSL response curves taken at room temperature from an x-ray-irradiated Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal, while using 400, 450, and 500 nm stimulation light and monitoring (in second order) the emission at 270 nm. The initial OSL intensity decreases as the stimulation light moves to longer wavelengths.

Figure 4. Spectral dependence of the emitted OSL light from the Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal. The peaks in these emission scans were reached 6, 38, 86, 278, and 630 s after starting the OSL decay. All of the OSL emission curves have a maximum near 270 nm, thus demonstrating that the OSL emission has the same spectral dependence as the PL spectrum in Fig. 2.

Figure 5. EPR spectra of isolated Ag^{2+} ions, perturbed Ag^{2+} ions, and Ag^0 centers. These data were taken after the Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal was irradiated at room temperature with x rays. The magnetic field was along the [001] direction and the microwave frequency was 9.38 GHz. (a) Spectrum taken at 32 K (the intensities of the Ag^{2+} ions at low field have been reduced by a factor of 12). (b) Spectrum taken at room temperature.

Figure 6. Optical absorption from the Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal. These spectra were taken at room temperature with unpolarized light propagating along the [001] direction. (a) Before an x-ray irradiation (black curve). (b) After a room-temperature x-ray irradiation (red curve). (c) After exposure to 400 nm light for 100 s (green curve). (d) After exposure to 400 nm light for 300 s (blue curve). (e) After exposure to 400 nm light for 700 s (purple curve).

Figure 7. Effect of 400 nm stimulation light on the EPR signals from the isolated Ag^{2+} ions, the

perturbed Ag^{2+} centers, and the Ag^0 centers. These spectra were taken at room temperature with the magnetic field along the [001] direction. (a) Spectrum taken after an x-ray irradiation, but before exposure to OSL stimulation light. (b) Spectrum taken after exposure to 400 nm light for 700 s. In both spectra, the intensity of the 16-line Ag^0 center has been reduced by a factor of 3.

Figure 8. Decrease in the intensities of the 370 nm optical absorption band, the isolated Ag^{2+} center, and the Ag^0 EPR spectrum during exposure at room temperature to 400 nm OSL stimulation light. The crystal was initially irradiated with x rays. The red curve (circles) represents the 370 nm absorption band, the blue curve (triangles) represents the isolated Ag^{2+} EPR signal, and the green curve (squares) represents the Ag^0 EPR signal.

Figure 9. EPR spectra from Ag^0 centers and singly ionized oxygen vacancies in the Ag-doped $\text{Li}_2\text{B}_4\text{O}_7$ crystal. (a) Spectrum taken after an x-ray irradiation at room temperature. (b) The same spectrum taken immediately after exposing the crystal to 405 nm laser light for 120 s. (c) The difference spectrum showing the underlying four-line oxygen vacancy EPR signal. These four lines are due to the hyperfine interaction with one ^{11}B nucleus (see Ref. 32).

Figure 1

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