Green luminescence from Cu-diffused LiGaO₂ crystals

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Abstract

An intense green luminescence is observed from single crystals of LiGaO₂ doped with copper. Czocharalski-grown undoped crystals are wrapped in thin copper foil and then held at 900 °C for 1 h in a flowing nitrogen atmosphere. Large concentrations of Cu⁺ ions enter the crystals during this process and occupy Li⁺ sites. These copper-diffused crystals are characterized with optical absorption, photoluminescence (PL), photoluminescence excitation (PLE), thermoluminescence (TL), and electron paramagnetic resonance (EPR). An optical absorption band peaking near 350 nm is assigned to the Cu⁺ ions at Li⁺ sites and represents an excitation from a 3d¹⁰ ground state to a 3d⁹4s¹ excited state. A broad PL emission from these excited Cu⁺ ions has a peak near 523 nm and the related PLE band has a peak near 356 nm (this PLE band links the emission to the optical absorption band). Illuminating a Cu-diffused crystal at room temperature with 325 nm laser light converts a portion of the Cu⁺ ions to Cu²⁺ ions. EPR spectra from these 3d⁹ ions are easily seen at low temperatures and their angular dependence is used to determine the g matrix and the ⁶³Cu hyperfine matrix. Subsequent heating produces a TL peak near 122 °C with a maximum in its spectral dependence near 535 nm. Correlated EPR measurements show that this TL peak occurs when trapped electrons are thermally released from unintentionally present transition-metal ions (most likely Fe) and recombine with holes at the Cu²⁺ ions.

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1. Introduction

Lithium gallate (LiGaO_2) is a wide-band-gap semiconductor with an optical absorption edge near 236 nm (5.26 eV) and a wurtzite-like crystal structure. This material is analogous to ZnO (an ordered replacement of half the Zn^{2+} ions with Li^+ ions and half with Ga^{3+} ions results in LiGaO_2). As expected, band-gap engineering is readily accomplished by alloying LiGaO_2 with ZnO [1-4]. If suitable shallow donors and/or acceptors are identified, the LiGaO_2 -ZnO materials system may be used to fabricate photodetectors and laser diodes operating across much of the ultraviolet region. Thus far, however, as it awaits the development of its electronic and light-emitting properties, LiGaO_2 has been used principally as a lattice-matching substrate for growth of thin films of GaN and ZnO [5-7].

A potential immediate application of LiGaO_2 , and a primary reason for the present study, is radiation detectors and phosphors. In particular, LiGaO_2 is a candidate for optically stimulated luminescence (OSL) and thermoluminescence (TL) dosimetry. The successful development of solid-state dosimeters requires identifying appropriate dopants to serve as deep electron and hole traps. This can be readily accomplished in LiGaO_2 because large single crystals are easily grown [5] and the existence of monovalent (Li^+) and trivalent (Ga^{3+}) cation sites allows efficient doping with a variety of impurities (e.g., transition-metal and rare-earth ions) [8-11]. The presence of ^6Li nuclei with their large cross-section for thermal neutron absorption provides an added reason for interest in LiGaO_2 . When enriched with ^6Li , this material may be used to detect neutrons.

The present paper describes the results of an investigation of copper impurities in single crystals of LiGaO_2 . Copper is a hole trap in this lithium-containing material and also serves as an efficient radiative recombination center. Diffusion at 900 °C is used to introduce copper ions into previously grown undoped crystals. Complementary optical and magnetic resonance characterization techniques are then applied. These include optical absorption, photoluminescence (PL), photoluminescence excitation (PLE), thermoluminescence (TL), and electron paramagnetic resonance (EPR). The copper enters the material as Cu^+ ($3d^{10}$) ions substituting for Li^+ ions. An ultraviolet absorption band (peaking near 350 nm) and PL and PLE bands (peaking near 523 and

356 nm, respectively) are assigned to these Cu^+ ions. The charge state of the copper ions can be changed from Cu^+ to Cu^{2+} ($3d^9$) by illuminating at room temperature with wavelengths of light falling within the absorption band of the Cu^+ ions (a 325 nm laser is used). These photoinduced Cu^{2+} ions have $S = 1/2$ and are monitored at low temperature with EPR. For electrons to leave the Cu^+ ions during an exposure to ultraviolet light and move to temporary trapping sites (e.g., other transition-metal ions with a partially filled d shell), the material's conduction band must be thermally accessible from one or more of the excited states of the Cu^+ ions. A TL peak near 122 °C is observed during heating when the electrons are thermally released from their trapping sites and recombine with holes trapped at the Cu^{2+} ions.

The green photoluminescence band that is described in the present paper was previously observed in nominally undoped LiGaO_2 crystals [5]. Its origin, however, was not identified in that study. We now show that this PL band is associated with Cu^+ ions. The earlier observance, when combined with our present results, suggests that Cu^+ ions may be present at trace levels in many LiGaO_2 crystals and substrates, even though the material has not been deliberately doped. This means that a green emission will often be seen when this material is exposed to ultraviolet light in the 325-375 nm wavelength range. If a wide-band-gap semiconductor (e.g., ZnO or GaN) is grown on a LiGaO_2 substrate, the observation of a broad green PL emission may be incorrectly attributed to the semiconducting film instead of the underlying substrate.

2. Experimental

Undoped single crystals of LiGaO_2 , polished on both sides, were purchased from the MTI Corporation (Richmond, CA). These crystals have a melting point of 1585 °C and are grown by the Czochralski technique. Samples with dimensions $3 \times 5 \times 0.5 \text{ mm}^3$ were cut from a larger [001] plate and used in both the optical and EPR experiments. Copper was diffused into several of these smaller crystals. 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 900 °C in flowing nitrogen gas. The wrapped sample was held at this high temperature for 1 h, and was then quickly cooled to

room temperature within 2 min. Copper enters the crystal as Cu^+ ions and replaces Li^+ ions. The Cu^+ ions prefer the Li^+ sites because of the similar charge and size. In fourfold coordination [12], the ionic radii of Li^+ and Cu^+ are 0.59 and 0.60 Å, respectively, whereas the ionic radius of Ga^{3+} is 0.47 Å. In the most likely diffusion process, interstitial Cu^+ ions enter the crystal, move along open channels, and exchange positions with regular Li^+ ions. The newly formed interstitial Li^+ ions then diffuse out of the crystal. From EPR, the concentration of Cu^{2+} ions produced by a 325 nm illumination is estimated to be approximately $5 \times 10^{17} \text{ cm}^{-3}$. This number of Cu^{2+} ions produced by the light, however, is limited by the number of available electron traps. Thus, the total amount of copper in the crystals (i.e., the sum of Cu^+ and Cu^{2+}) may be 10 to 100 times greater than the Cu^{2+} EPR estimate alone. Our study did not verify that copper is uniformly distributed within the diffused crystals, although we expect that it is because these crystals are thin c plates.

The LiGaO_2 crystals are orthorhombic (space group $Pna2_1$) and the lattice constants are $a = 5.402$ Å, $b = 6.372$ Å, and $c = 5.007$ Å at room temperature [13]. A schematic representation of this crystal structure is shown in Fig. 1. Table I gives the x,y,z positions for the ions in Fig. 1. The LiGaO_2 structure resembles the GaN wurtzite structure, where each anion has four cation neighbors (three in the basal plane and one along the c axis). In LiGaO_2 , each oxygen ion has two lithium neighbors and two gallium neighbors, each lithium ion has four oxygen neighbors, and each gallium ion has four oxygen neighbors. All the Li^+ sites are equivalent and all the Ga^{3+} sites are equivalent. The oxygen ions occupy two crystallographically inequivalent sites (labeled O_I and O_II in Fig. 1). These oxygen sites are distinguished by which ion, a Li^+ or a Ga^{3+} , is the nearest neighbor along the c axis (i.e., the $[001]$ direction). The O_I ions have an adjacent lithium ion in the c direction and the O_II ions have an adjacent gallium ion in the c direction.

Optical absorption spectra were recorded using a Cary 5000 spectrophotometer. A Horiba Fluorolog-3 spectrometer was used to take the PL and PLE spectra (slits for the excitation and emission monochromators were set at 5 nm resolution). The PL spectrum was not corrected for system response. A Harshaw TLD-3500 reader provided the TL “glow” curve and the spectral dependence of the TL emission was determined using a USB2000+ CCD detector from Ocean

Optics. A Bruker EMX spectrometer operating near 9.40 GHz was used to take the EPR spectra. An Oxford helium-gas flow system controlled the sample temperature and magnetic fields were measured using a Bruker teslameter. At room temperature, the 325 nm beam from a He-Cd laser was used to convert Cu^+ ions to Cu^{2+} ions. The 442 nm light from this laser reversed the effect.

3. Results

3.1. Optical absorption

Fig. 2 shows the optical absorption spectrum (red curve) from a LiGaO_2 crystal that was copper-diffused at 900 °C for 1 h. These data were taken at room temperature using unpolarized light propagating along the [001] direction. The absorption band peaking at 350 nm (along with additional absorption in the 320 to 240 nm region) is assigned to Cu^+ ions at Li^+ sites, specifically to $3d^{10} \rightarrow 3d^9 4s^1$ and $3d^{10} \rightarrow 3d^9 4p^1$ intracenter transitions of the Cu^+ ions. To verify that these absorption features are due to Cu^+ ions that enter the crystal from the copper foil during the heat treatment, a second LiGaO_2 sample was held at 900 °C for 1 h without being wrapped in copper foil. The absorption spectrum (blue curve) from this second sample is also shown in Fig. 2. The absence of a peak at 350 nm in the absorption spectrum from this second sample establishes that significant concentrations of Cu^+ ions are found in a crystal only when the copper foil was present during the heat treatment. In Fig. 2, the optical path lengths are 0.5 mm, the two broad faces of each sample are polished, and corrections are included for surface reflective losses. Values of the refractive indices are available for LiGaO_2 from 410 nm into the infrared [14]. Thus, for the absorption data in Fig. 2, the correction for reflection loss was determined at 410 nm and then applied uniformly to the 235 to 500 nm spectral range.

3.2. Photoluminescence (PL and PLE)

As shown in Fig. 3, an intense PL emission band peaking near 523 nm (2.37 eV) with a full width at half maximum (FWHM) of 0.57 eV is observed at room temperature when a copper-diffused LiGaO_2 crystal is excited with 355 nm light. The corresponding room-temperature PLE band, obtained by monitoring the emission at 525 nm, is also shown in Fig. 3 and has a peak at

356 nm (3.48 eV) with a FWHM of approximately 0.55 eV. The Stokes shift represented by the PL and PLE bands in Fig. 3 is approximately 1.11 eV. These intense PL and PLE bands were only present in LiGaO₂ samples that had been diffused with copper. In several of our undoped LiGaO₂ crystals, a weak PL peak was seen near 523 nm, presumably from trace amounts of Cu⁺ ions that were inadvertently present.

The peak of the PLE band in Fig. 3 occurs at nearly the same wavelength as the ultraviolet absorption band in Fig. 2 (356 nm vs. 350 nm). This small difference arises primarily because the PLE spectrum was not corrected for the wavelength-dependent changes in the intensity of the excitation lamp. These results suggest that the PLE and optical absorption bands in LiGaO₂ have a common origin, specifically they represent an intracenter transition of the Cu⁺ ion. The present results from LiGaO₂ are similar, yet distinctly different, from the results of an earlier study of Cu⁺ ions in LiAlO₂ [15]. The Cu⁺ absorption band shifts from 277 nm in LiAlO₂ to 350 nm in LiGaO₂ (a shift in energy of 1.13 eV) and the Cu⁺ PL band shifts from 359 nm in LiAlO₂ to 523 nm in LiGaO₂ (a similar shift in energy of 1.08 eV).

3.3. *Electron paramagnetic resonance (EPR)*

Illuminating a copper-diffused LiGaO₂ crystal at room temperature with 325 nm light from a He-Cd laser converts a portion of the Cu⁺ ions to Cu²⁺ ions. The EPR spectrum from these Cu²⁺ ions is shown in Fig. 4. This spectrum was obtained at 15 K with the magnetic field along the *a* axis. Before an exposure to 325 nm laser light, there are no significant EPR signals in this region of magnetic field. After the Cu²⁺ ions are formed with 325 nm light, they are easily destroyed by illuminating the crystal at room temperature with 442 nm light from a He-Cd laser (i.e., the Cu²⁺ ions are converted back to Cu⁺ ions by the longer wavelength light).

The Cu²⁺ ions responsible for the spectrum in Fig. 4 occupy Li⁺ sites and have no nearby perturbing point defects. In contrast, two distinct Cu²⁺ EPR spectra are observed in Li₂B₄O₇ and LiAlO₂ crystals (in each case, one spectrum is from isolated Cu²⁺ ions and the other is from Cu²⁺ ions with an adjacent Li⁺ vacancy) [15,16]. The absence of a second (perturbed) Cu²⁺ spectrum

in our samples suggests that there are no (or very few) lithium vacancies present in the copper-diffused LiGaO₂ crystals. Even before the diffusion treatment, there appear to be very few (if any) isolated lithium vacancies in the as-grown LiGaO₂ crystals. In undoped LiAlO₂ crystals, an intense 11-line EPR signal is seen after an x-ray irradiation at room temperature when holes are trapped on O²⁻ ions adjacent to lithium vacancies [17]. An analogous trapped-hole EPR signal is not seen in undoped LiGaO₂ crystals after irradiating with x rays at room temperature or at 77 K.

The Cu²⁺ ions in LiGaO₂ have an easily recognized EPR spectrum as a result of hyperfine interactions with the two stable isotopes of copper (⁶³Cu is 69.2% abundant with $I = 3/2$ whereas ⁶⁵Cu is 30.8% abundant with $I = 3/2$). Two sets, each with four hyperfine lines, are observed in Fig. 4 because of these $I = 3/2$ nuclear spins (the number of EPR lines in a set is given by $2I + 1$). Stick diagrams above the spectrum identify the individual lines from each isotope. The magnetic moment of a ⁶⁵Cu nucleus is slightly larger than the magnetic moment of a ⁶³Cu nucleus, which explains why the separations between the four ⁶⁵Cu lines are greater (by a small amount) than the separations between the four ⁶³Cu lines. Similarly, the different intensities of the ⁶³Cu and ⁶⁵Cu lines in Fig. 4 are explained by the different natural abundances of the two copper isotopes.

The angular dependence of the Cu²⁺ EPR spectrum in LiGaO₂ is shown in Fig. 5. Only lines from the ⁶³Cu isotope were measured because of their greater intensity. The discrete data points in Fig. 5 represent these ⁶³Cu results. LiGaO₂ has an orthorhombic crystal structure, thus there are four crystallographically equivalent orientations (or sites) of the defect. All four sites are degenerate (i.e., magnetically equivalent) when the magnetic field is along a [100], [010], or [001] direction and they are pairwise degenerate when the field is rotated in a (100), (010), or (001) plane. All four sites can be separately resolved when the EPR spectrum is taken with an arbitrary direction of magnetic field.

The following spin Hamiltonian, with electron Zeeman, hyperfine, and nuclear Zeeman terms, describes the angular-dependence of the Cu²⁺ ions in LiGaO₂.

$$H = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} - g_n \beta_n \mathbf{I} \cdot \mathbf{B} \quad (1)$$

Twelve parameters (six for the $\mathbf{g}$ matrix and six for the hyperfine matrix) are determined from

the experimental angular dependence data in Fig. 5. The six parameters for each matrix are the three principal values and the three Euler angles that define the directions of the principal axes. There is no requirement that any of these principal axes be along the high-symmetry [100], [010], or [001] directions in the crystal. Also, there is no constraint that the principal-axis directions of the A matrix must coincide with the principal-axis directions of the g matrix.

The 8×8 matrix form of the spin Hamiltonian ($S = 1/2$, $I = 1/2$) in Eq. (1) was repeatedly diagonalized as the parameters for the g -matrix and ^{63}Cu hyperfine matrix were systematically varied during a least-squares fitting process. Input data were the magnetic-field positions and the corresponding microwave frequencies for the 120 EPR lines represented by the discrete points in Fig. 5. Final values of the parameters are given in Table 2. These best-fit parameters in Table 2 were used to generate the solid curves in Fig. 5. To further verify that this is the correct set of parameters, EPR spectra were also taken as the magnetic field was rotated from [100] to [011] in the $(1\bar{1}0)$ plane and line positions were compared to predictions made using the parameters in Table 2. The Euler angles that specify the directions of the principal axes are converted to (θ, ϕ) pairs in Table 2 (the polar angle θ is defined relative to the [001] direction and the azimuthal angle ϕ is defined relative to the [100] direction with positive rotation from [100] toward [010] in the (001) plane). In Table 2, the principal-axis directions describe one of the four distinguishable, but crystallographically equivalent, orientations of the Cu^{2+} ions in LiGaO_2 . For the remaining three orientations of the defect, the principal-axis directions can be obtained by applying rotations corresponding to the symmetry elements of the crystal.

The g matrix described in Table 2 is approximately axial. As is commonly observed for many Cu^{2+} EPR spectra [18], two of the principal values are close to 2.0 and one principal value is significantly greater than 2.0 (i.e., $g_{\parallel} > g_{\perp}$). Also, the principal-axis directions of the g matrix and the ^{63}Cu hyperfine matrix are roughly related to specific ion-to-ion directions in the LiGaO_2 crystal. Referring to Fig. 1, relevant directions in the regular (i.e., unperturbed) crystal are Li(1) to $\text{O}_{II}(1)$ and $\text{O}_{II}(2)$ to $\text{O}_I(1)$. The (θ, ϕ) pairs for these latter directions were obtained from the ion positions in Table 1 and are included in Table 2. A comparison of the (θ, ϕ) entries in Table 2

shows that the unique principal axes g_3 and A_3 are near the Li(1)–O_{II}(1) direction and the g_I and A_I axes are near the O_{II}(2)–O_I(1) direction. As expected, these observations are consistent with the Cu²⁺ ion occupying a Li⁺ site in LiGaO₂ with no defects nearby.

Following the earlier work on 3d⁹ ions in tetrahedrally bonded ZnO, GaN, and AgGaSe₂ [19-21], we suggest that the unpaired spin in the Cu²⁺ ion in LiGaO₂ occupies an $|xy\rangle$ -like orbital. With the Cu²⁺ ion at the Li(1) position in Fig. 1, the unique axis of the $|xy\rangle$ orbital would be along the Li(1)–O_{II}(1) direction and its lobes would be in the plane perpendicular to this Li(1)–O_{II}(1) direction. The relatively large magnitudes of g_3 and A_3 in Table 2 indicate that the unpaired spin is highly localized on the Cu²⁺ ion. This implies that the orbital contribution to the ground state Zeeman interaction in LiGaO₂ is not significantly reduced by the covalent sharing of charge with neighboring anions and cations. The commonly used orbital reduction factor k is expected to be between 0.75 and 1.0 for Cu²⁺ ions in LiGaO₂ instead of the 0.46 value reported for Cu²⁺ in ZnO [19] and the 0.25 (or 0.34) value reported for Cu²⁺ in GaN [20].

3.4. Thermoluminescence (TL)

A thermoluminescence (TL) glow peak is observed when a copper-diffused LiGaO₂ crystal is heated above room temperature at a constant rate after an exposure to 325 nm laser light at room temperature. As shown in Fig. 6, this TL peak (blue curve) occurs at 122 °C for a heating rate of 1 °C/s. The shape of the TL peak (a slower rise on the low temperature side and a more rapid decline on the high temperature side) suggests that first-order kinetics are involved. A weak 122 °C TL peak can often be seen in undoped LiGaO₂ crystals, but the peak is always much more intense in copper-diffused crystals. This, again, suggests that trace amounts of Cu⁺ are frequently present in as-grown undoped crystals. Additional glow peaks (other than the 122 °C peak) are not observed in the undoped or copper-diffused LiGaO₂ crystals.

An isochronal thermal annealing study shows that the photoinduced Cu²⁺ EPR signal in a copper-diffused LiGaO₂ crystal becomes unstable in the same temperature region as the TL peak. A crystal was initially heated to 400 °C for 10 minutes in a furnace to remove any photoinduced

defects produced during previous exposures to ultraviolet light (i.e., the crystal was “reset”). The crystal was then briefly illuminated at room temperature with 325 nm laser light and placed in the microwave cavity where the Cu^{2+} EPR spectrum was taken at 15 K. Next, the sample was again placed in the furnace (now preheated to 70 °C) and held at this temperature for 25 s before being returned to the microwave cavity where the EPR spectrum was taken at 15 K. This incremental annealing process was repeated at 90 °C and again in 20 °C steps above 90 °C with 25 s holding times at each elevated temperature (the equivalent constant heating rate was approximately 0.80 °C/s). After each step, the intensity of the EPR signal from the Cu^{2+} ions was recorded at the 15 K monitoring temperature. These thermal anneal results are plotted in Fig. 6. As can be seen in this figure, the TL peak near 122 °C coincides with the thermal decay of the EPR signal from the Cu^{2+} ions. The agreement is not exact since the effective heating rate in the EPR experiment was slightly different than the TL heating rate.

Fig. 7 shows the spectral dependence of the emitted light associated with the 122 °C TL peak. The spectral dependence of the PL emission (from Fig. 3) is also plotted in Fig. 7. These two emissions are similar and thus have a common origin. The slight differences are attributed to the different methods of collecting data (for the TL, a CCD array was used to collect all of the wavelengths simultaneously whereas, for the PL, a scanning monochromator and photomultiplier tube were used). In the intracenter PL process, the excitation light raises a Cu^+ ion to an excited state $(\text{Cu}^+)^*$ that then decays back to the ground state by emitting a photon near 530 nm. In the TL process, an electron is released from its trapping site (most likely a transition-metal ion on a Li^+ or Ga^{3+} site) and moves to a Cu^{2+} ion where the $(\text{Cu}^+)^*$ excited state of the copper is initially formed. This excited state, in turn, decays to the Cu^+ ground state. The common aspect of both the PL and TL is the formation of an excited state of the Cu^+ ion, followed by the emission of a photon near 530 nm as the $(\text{Cu}^+)^*$ returns to its ground state.

4. Discussion

The optical and magnetic resonance properties of copper ions in single crystals of LiGaO_2 are described in the present paper. It is useful to compare our results with those recently reported

for copper in LiAlO_2 crystals [15]. The crystals have similar structures, with tetrahedral bonding in both cases, and Cu^+ ions are easily diffused into both materials at high temperature. There are, however, two significant differences. First, the Cu^+ optical absorption band peaks near 277 nm in LiAlO_2 crystals and peaks near 350 nm in LiGaO_2 , a shift of 1.13 eV. Second, the Cu^+ ions in LiAlO_2 cannot be converted to Cu^{2+} ions with ultraviolet light, whereas the Cu^+ ions in LiGaO_2 are easily converted to Cu^{2+} ions with ultraviolet laser light near 325 nm. Although the reasons for this shift of the absorption band to lower energy and this change in photoionization behavior are not obvious, the smaller band gap of LiGaO_2 may be an important contributing factor. The optical absorption edge is near 236 nm in LiGaO_2 , whereas the absorption edge is below 190 nm in LiAlO_2 .

As described in Section 3.3, illuminating a copper-diffused LiGaO_2 crystal at room temperature with 325 nm laser light (i.e., light whose wavelength falls within the 350 nm absorption band) converts Cu^+ ions to Cu^{2+} ions. The simplest explanation for this phenomenon is to have the Cu^+ excited-state level near the conduction band. Once a Cu^+ ion has absorbed a photon and is in its excited state, the ion can radiatively return to its ground state by emitting a lower-energy photon, as happens in the PL experiments, or an electron can leave the ion and enter the conduction band. In the latter case, a Cu^{2+} ion is formed and the electron moves to a temporary trapping site (e.g., a transition-metal impurity such as Fe). This suggests that a significant portion of the Cu^+ ions can be photoionized with sufficiently intense ultraviolet light. A critical factor for this Cu^{2+} production mechanism to be efficient is having the excited state of the Cu^+ ion located close to the conduction band (within a few hundred meV or less), thus allowing an electron on the Cu^+ ion to have thermal access to the conduction band. If the excited state of the Cu^+ ion is close to the conduction band, then states associated with the bottom of the conduction band (primarily Ga 4s states) are expected to be mixed into the Cu^+ excited state. This, in turn, is related to the reduction in the transition energy for absorption from the Cu^+ ground state to the lowest Cu^+ excited state. In LiAlO_2 , with a larger band gap, the excited state of the Cu^+ ion is well separated from the conduction band and photoionization of Cu^+ and excited-state mixing effects are not observed.

5. Summary

Diffusion of Cu^+ ions into LiGaO_2 crystals is easily achieved in a nitrogen atmosphere at temperatures near 900 °C. These crystals have a wurtzite-like structure similar to GaN and ZnO and thus have potential as a versatile wide-band-gap semiconductor. In the diffused crystals, the Cu^+ ions occupy Li^+ sites and have a broad optical absorption band near 350 nm. Excitation in this band produces an intense broad green PL emission peak near 523 nm. Both of these optical bands are shifted to significantly longer wavelengths when compared to the Cu^+ bands in LiAlO_2 , a similar optical material having a larger optical band gap. An excited state of the Cu^+ ions near the conduction band in LiGaO_2 is proposed as the primary reason for these observed shifts of the PL and absorption bands. As shown with low-temperature EPR, exposing a Cu-diffused LiGaO_2 crystal at room temperature to 325 nm laser light converts Cu^+ ions to Cu^{2+} ions. This production of Cu^{2+} with ultraviolet light can also be explained by having a Cu^+ excited state located near the conduction band. The ground-state EPR spectra from these Cu^{2+} ions indicate that the unpaired spin is localized in an $|\text{xy}\rangle$ -like orbital whose unique axis points toward an O_{II} oxygen ion in the basal plane. Heating a copper-diffused crystal above room temperature at a constant rate after an illumination with 325 nm light produces a TL “glow” peak near 122 °C. The wavelength dependence of the PL and TL emissions are the same, thus verifying that the TL recombination occurs at Cu^{2+} ions.

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Table 1. Positions of ions in LiGaO_2 (for an arbitrary origin). All of the ions shown in Fig. 1 are included in this table and the same ion labeling scheme is used. Units are Å. These positions are based on the room-temperature lattice parameters reported by Marezio (Reference 13).

Ion	x	y	z
Li(1)	3.1305	5.5647	−0.0320
Li(2)	0.4285	3.9933	−0.0320
Li(3)	2.2735	7.1793	−2.5355
Li(4)	2.2735	7.1793	2.4715
Ga(1)	3.1457	2.3812	0.0000
Ga(2)	2.2583	3.9908	−2.5035
Ga(3)	4.9603	5.5672	−2.5035
Ga(4)	0.4437	7.1768	0.0000
Ga(5)	3.1457	8.7532	0.0000
Ga(6)	2.2583	3.9908	2.5035
Ga(7)	4.9603	5.5672	2.5035
O _I (1)	2.1973	7.2564	−0.5373
O _I (2)	3.2067	5.4876	1.9662
O _{II} (1)	5.0273	5.6577	−0.6469
O _{II} (2)	2.3253	3.9003	−0.6469

Table 2. Spin-Hamiltonian parameters for Cu^{2+} ions diffused into LiGaO_2 crystals. Values for the ^{63}Cu hyperfine interactions were obtained from experiment (multiplying the ^{63}Cu values by 1.0692 gives the ^{65}Cu values). Estimated error limits are ± 0.001 for the g values, ± 3.0 MHz for the A values, and $\pm 1^\circ$ for the angles. The θ, ϕ values for two relevant crystallographic directions are also included as the last entries in the table.

Principal value		Principal-axis direction	
		θ	ϕ
<hr/>			
g matrix			
g_1	1.9998	87.9°	99.5°
g_2	2.1538	20.6°	4.1°
g_3	2.7796	110.5°	10.3°
^{63}Cu hyperfine matrix			
A_1	261.5 MHz	70.4°	91.5°
A_2	192.0 MHz	44.1°	339.9°
A_3	667.7 MHz	127.6°	17.4°
crystallographic directions			
$\text{O}_{\text{II}}(2)$ to $\text{O}_{\text{I}}(1)$		88.1°	92.2°
$\text{Li}(1)$ to $\text{O}_{\text{II}}(1)$		107.9°	2.8°
<hr/>			

Figure Captions

Figure 1. A view looking along the a axis (i.e., the $[100]$ direction) in the orthorhombic LiGaO_2 crystal structure. Lithium ions are green, gallium ions are violet, and oxygen ions are red.

Figure 2. Optical absorption from LiGaO_2 crystals. These data were taken at room temperature with unpolarized light propagating along the $[001]$ direction. The upper (red) curve is from a copper-diffused crystal. The lower (blue) curve is from a crystal heated to 900°C without being wrapped in copper foil.

Figure 3. Normalized PL and PLE spectra acquired at room temperature from a copper-diffused LiGaO_2 crystal. The PL spectrum (red curve) was taken with 355 nm excitation light and the PLE spectrum (blue curve) was obtained by monitoring the emission at 525 nm .

Figure 4. Photoinduced EPR spectrum of Cu^{2+} ions in a copper-diffused LiGaO_2 crystal. These data were taken at 15 K after exposing the crystal at room temperature to 325 nm laser light. The magnetic field is along the $[100]$ direction and the microwave frequency is 9.401 GHz .

Figure 5. EPR angular dependence of Cu^{2+} ions in a LiGaO_2 crystal. Data for the ^{63}Cu isotope were taken in three high-symmetry planes. The discrete points are experimental results and the solid curves are computer-generated using the parameters in Table 2.

Figure 6. Thermoluminescence (blue curve) from a copper-diffused LiGaO_2 crystal. The TL peak occurs at 122°C . The red curve (with discrete data points) represents the thermal decay of the Cu^{2+} EPR signal. Both sets of data are from the same crystal.

Figure 7. Normalized spectral dependence of the emission associated with the 122°C TL peak (blue curve) from a copper-diffused LiGaO_2 crystal. The PL band (red curve) from Fig. 3 is included for comparison.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7