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Iron and intrinsic deep level states in Ga$_2$O$_3$
Deep donors and acceptors in $\beta$-Ga$_2$O$_3$ crystals: Determination of the Fe$^{2+/3+}$ level by a noncontact method

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ABSTRACT

Electron paramagnetic resonance (EPR), infrared absorption, and thermoluminescence (TL) are used to determine the Fe$^{2+/3+}$ level in Fe-doped $\beta$-Ga$_2$O$_3$ crystals. With these noncontact spectroscopy methods, a value of $0.84 \pm 0.05$ eV below the conduction band is obtained for this level. Our results clearly establish that the E2 level observed in deep level transient spectroscopy (DLTS) experiments is due to the thermal release of electrons from Fe$^{2+}$ ions. The crystals used in this investigation were grown by the Czochralski method and contained large concentrations of Fe acceptors and Ir donors, and trace amounts of Cr donors. Exposing a crystal at room temperature to 325, 375, or 405 nm laser light converts neutral Fe$^{3+}$ acceptors to their singly ionized Fe$^{2+}$ charge state and, at the same time, converts a similar number of neutral Ir$^{3+}$ donors to the Ir$^{4+}$ charge state. The Fe$^{2+}$ EPR spectrum slowly recovers after the light is removed, as electrons are thermally released from Fe$^{2+}$ ions to the conduction band. Most of these released electrons recombine nonradiatively with holes at the deep Ir$^{4+}$ donors. Using a general-order kinetics model, the analysis of isothermal recovery curves for the Fe$^{2+}$ EPR signal taken between 296 and 310 K gives the activation energy for the decay of the photoinduced Fe$^{2+}$ ions. A TL peak, with emitted light having wavelengths longer than 500 nm, occurs near 349 K when a few of the electrons released from Fe$^{2+}$ ions recombine radiatively with holes at Ir$^{4+}$ and Cr$^{3+}$ donors. Photoluminescence and EPR verify the presence of Cr$^{3+}$ ions.

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I. INTRODUCTION

Single crystals of gallium oxide ($\beta$-Ga$_2$O$_3$), in bulk and thin-film form, are presently being developed for applications extending from power electronics to solar-blind detectors. To support these efforts, fundamental studies of deep donors and acceptors in this wide-bandgap semiconductor are needed. It is expected that the deep levels, when present, may influence the performance of emerging optical and electronic devices. The acceptors and donors receiving the most attention, thus far, are Fe, Mg, Cr, H, and Ir. In this paper, we describe the use of noncontact spectroscopy methods to characterize the behavior of Fe acceptors and Ir and Cr donors. Iron impurities appear at trace levels in many bulk $\beta$-Ga$_2$O$_3$ crystals (as a result of their unintentional presence in the starting materials used to grow the crystals). The Fe ions may be deliberately added to the starting materials to produce Fe-doped semi-insulating $\beta$-Ga$_2$O$_3$ crystals suitable for use as substrates for film growth. In addition to the Fe ions, significant concentrations of Ir ions may be present in bulk $\beta$-Ga$_2$O$_3$ crystals that are grown using iridium crucibles. Chromium ions are also often found in bulk $\beta$-Ga$_2$O$_3$ crystals at trace levels because of slightly impure starting materials.

Deep level transient spectroscopy (DLTS) experiments have revealed a level, labeled E2, in $\beta$-Ga$_2$O$_3$ crystals that is approximately 0.8 eV below the conduction band. This level also has been observed in Hall effect, steady-state capacitance, photoinduced current transients, and thermally stimulated current studies. These experimental techniques, however, do not provide information that directly identifies the microscopic and chemical nature of the responsible defect. As described by Ingebrigtsen et al., collecting data from a set of samples may allow a DLTS peak to be
correlated with the presence of a specific defect. For the E2 peak in β-Ga2O3, a possible link was established with the Fe content, determined using secondary ion mass spectrometry (SIMS), in a set of seven samples. In contrast, the earlier DLTS study by Irmscher et al. suggested that Fe is not responsible for the E2 peak. Thus, there is a need for a clear determination as to whether or not Fe is involved in this level near 0.8 eV in β-Ga2O3 crystals.

Electron paramagnetic resonance (EPR), infrared absorption, and thermoluminescence (TL) are used in the present study to determine the Fe²⁺/³⁺ level in an Fe-doped β-Ga2O3 crystal. We emphasize that these are noncontact methods used to identify and characterize donors and acceptors in semiconductors. EPR is an especially important part of our investigation as this experimental technique provides direct and unambiguous identification of specific charge states of many defects via the hyperfine and fine structure patterns appearing in their ground-state spectra. With EPR, we monitor the decrease of the Fe²⁺ spectrum during exposure to 325 nm laser light and the subsequent recovery of this spectrum when the laser light is removed. Isothermal recovery curves for the Fe²⁺ ions obtained near and just above room temperature place the Fe²⁺/³⁺ level at 0.84 eV below the conduction band. Infrared absorption and luminescence experiments provide additional insight into the movements of charge that occur during the photoinduced decrease of the Fe²⁺ EPR spectrum and its recovery in the dark. Infrared absorption monitors the production and decay of Ir⁴⁺ ions, thus identifying the primary charge compensating donor that accompanies the formation of the singly ionized Fe³⁺ acceptors. Thermoluminescence and photoluminescence (PL) experiments provide information about the radiative components of electron-hole recombination resulting from the release of electrons from the Fe²⁺ ions. Our thermoluminescence results are especially useful as they directly support the value of 0.84 eV for the Fe²⁺/³⁺ level obtained from EPR data.

As is the usual custom for transition-metal ions (i.e., ions with partially filled d shells), we use ionic notation for Fe, Ir, and Cr. An Fe²⁺ (3d⁵) ion replacing a Ga³⁺ ion is neutral with respect to the β-Ga2O3 lattice, whereas an Fe³⁺ (3d⁴) ion with one more d electron is negatively charged. In equivalent semiconductor notation, the neutral acceptor Fe²⁺ is [Fe]⁺, the singly ionized acceptor Fe³⁺ is [Fe]⁺, and the Fe²⁺/³⁺ level is the (−0/+) level.

II. EXPERIMENTAL

Bulk β-Ga2O3 crystals doped with Fe were obtained from Kyma Technologies (Raleigh, NC). They were grown by the Czochralski method with Fe₂O₃ added to the starting materials. The intensity of the EPR spectrum of the Fe³⁺ ions suggests that the concentration of this charge state of Fe in the as-grown crystals is approximately 2–3 × 10¹⁵ cm⁻³. Our estimate, valid within a factor of two, is based on a comparison to a standard EPR pitch sample provided by Bruker. The crystals also contain large concentrations of Ir ions and trace amounts of Cr ions. These impurities substitute for sixfold Ga³⁺ ions and are unintentionally present. The samples used in this study were rectangular b plates, approximately 3 × 4 mm² with a thickness of 0.37 mm. The EPR spectra of Fe³⁺ ions were obtained near room temperature using a Bruker EMX spectrometer operating at 9.39 GHz. Flowing nitrogen gas was used to control the temperature of the sample. The gas was contained within the glassware of an Oxford Instruments ESR-900 cryostat extending vertically through the center of the microwave resonator. To reach an equilibrium temperature in the 296–310 K range, the gas was preheated by passing through a small external furnace before reaching the crystal. The infrared absorption spectra of Ir⁴⁺ ions were taken with a ThermoScientific Nicolet 8700 FTIR spectrometer. A quartz tungsten halogen (QTH) white-light source (with a silicon wafer acting as a filter to remove wavelengths shorter than ∼1.1 μm), a GaF beam splitter, and a deuterated triglycine sulfate (DTGS) detector were used, along with an ultrabroadband (250 nm to 4 μm) fused-silica wire-grid polarizer from Thorlabs (Model WP25M-UB). Surface losses have been removed from the absorption spectra shown in this paper. The Fe³⁺, Ir⁴⁺, and Cr⁴⁺ charge states were produced near room temperature using a He-Cd laser (325 or 442 nm) or diode lasers (375 or 405 nm).

PL spectra were obtained with an Edinburgh FLS980 spectrometer. This spectrometer uses a xenon lamp as the excitation source, a cooled red-sensitive Hamamatsu R928P photomultiplier as a detector, and two double-grating Czerny-Turner monochromators to measure emission and excitation spectra. Thermoluminescence (TL) glow curves were taken with a Harshaw Model 3500 manual TL reader. An Electron Tubes 9125B photomultiplier tube (PMT) in this latter instrument monitors the total light output from the sample as the temperature increases at a constant rate.

III. PRODUCTION AND THERMAL DECAY OF Fe²⁺ AND Ir⁴⁺ IONS

Figure 1 shows the EPR spectrum from Fe³⁺ (3d⁵) ions in an Fe-doped β-Ga2O3 crystal. These data were obtained at room temperature in a microwave field along the c direction and the microwave frequency is 9.393 GHz. All eight lines are from Fe³⁺ ions occupying sixfold Ga³⁺ sites.
temperature. The magnetic field was aligned near the c axis, the microwave frequency was 9.393 GHz, and no laser light was incident on the sample. Before acquiring the spectrum, the effects of previous illuminations were removed by holding the crystal near 525 K for several minutes. There are two dominant lines in Fig. 1 at 150.0 and 332.3 mT and six less intense lines at 102.0, 209.7, 257.6, 404.0, 667.9, and 756.8 mT. These lines, representing both allowed and forbidden transitions, are assigned to Fe$^{3+}$ ions at sixfold sites. $^{35}$ The Fe$^{3+}$ ions have the high-spin S = 5/2 ground state, with large zero-field splittings caused by the low-symmetry monoclinic crystal structure. As seen in Fig. 1, zero-field splittings often result in complex nonsymmetrical patterns in EPR spectra from transition-metal ions. $^{35}$ During the present study, no evidence was found that Fe$^{3+}$ ions occupy fourfold sites in Fe-doped β-Ga$_2$O$_3$ crystals grown by the Czochralski method. $^{37}$ This agrees with recent computational results that indicate Fe will preferentially incorporate on the octahedral Ga site. $^{35}$ Also, we note that no EPR spectrum has been reported, thus far, for Fe$^{3+}$ (3d$^5$) ions in β-Ga$_2$O$_3$ crystals. The Fe$^{3+}$ ions, a non-Kramers system, are best studied using optical methods. $^{36}$

The Fe$^{3+}$ EPR spectrum decreases in intensity when the Fe-doped β-Ga$_2$O$_3$ crystals are exposed at room temperature to below-bandgap laser light. This effect is easily produced using 325, 375, or 405 nm photons, with reductions in the Fe$^{3+}$ spectrum of approximately 25%–30% typically observed. Although they are less efficient, 442 nm photons also reduce the Fe$^{3+}$ concentration, whereas 532 nm photons have very little effect. A similar wavelength dependence has been reported for photocurrents and photo-EPR effects in Fe-doped β-Ga$_2$O$_3$ crystals. $^{17,31,39}$ Figure 2 shows the rapid decrease in the intensity of the Fe$^{3+}$ spectrum when 405 nm laser light is applied and the subsequent slow recovery of the Fe$^{3+}$ spectrum when the laser light is removed. These data were acquired at 296 K with the magnetic field set at the upper peak of the line at 150.0 mT in Fig. 1. The EPR spectrometer was operated in a kinetics mode (a time sweep with a fixed magnetic field), thus allowing the production and/or decay of a specific EPR line (representing one charge state of a defect) to be monitored.

Exposure of an Fe-doped β-Ga$_2$O$_3$ crystal at room temperature to below-bandgap laser light also affects the charge states of the iridium donors. Figure 3 shows the infrared optical absorption spectra taken at 296 K before and during illumination with 405 nm laser light. The band peaking at 5153 cm$^{-1}$ (1.94 μm), with a half-width near 17 cm$^{-1}$, has been assigned to Ir$^{4+}$ (5d$^3$) ions at sixfold Ga$^{3+}$ sites. $^{38}$ This band represents a d-d transition within the set of $t_2g$ orbitals. The lower red curve in Fig. 3 shows that Ir$^{4+}$ ions are not present before the illumination. At this stage, the iridium ions are all neutral Ir$^{3+}$ donors. This behavior (i.e., only Ir$^{4+}$ being present before illumination) indicates that the Ir$^{4+/3+}$ level is below the Fe$^{4+/3+}$ level in β-Ga$_2$O$_3$. The black curve in Fig. 3 shows that a large concentration of Ir$^{4+}$ ions is produced by the laser light. These Ir$^{4+}$ ions begin to thermally decay after the light is removed. The empirical relationship between concentration and peak absorption coefficient, N = $(2.4 \times 10^{19}$ cm$^{-2}$)α, obtained from Ref. 18 is used to determine the concentration of Ir$^{4+}$ ions formed by the laser light in our Fe-doped crystal. A value of absorbance of 0.0365 from Fig. 3 (corresponding to an absorption

![FIG. 2. Monitoring the intensity of the Fe$^{3+}$ EPR line at 150.0 mT in Fig. 1 before, during, and after exposure to 405 nm laser light. The temperature is 296 K. At 600 s, the light is turned on and the Fe$^{3+}$ signal decreases as Fe$^{2+}$ ions are formed. When the light is removed at 1400 s, the Fe$^{3+}$ signal slowly recovers as the Fe$^{2+}$ ions thermally convert back to Fe$^{3+}$ ions by releasing an electron.](image-url)

![FIG. 3. Infrared absorption from Ir$^{4+}$ ions in an Fe-doped β-Ga$_2$O$_3$ crystal. These spectra were obtained at room temperature. The spectrometer’s light beam propagated along the c direction of the crystal with the electric field vector E along the a direction. Sample thickness (i.e., optical path length) is 0.37 mm. The lower (red curve), 1, was taken before exposure to 405 nm laser light and the upper (black curve), 2, was taken during exposure to the 405 nm laser light.](image-url)
coefficient \( \alpha = 2.27 \text{ cm}^{-1} \) gives a value of \( N = 5.4 \times 10^{18} \text{ cm}^{-3} \) for the concentration of \( \text{Ir}^{4+} \) ions.

The photoinduced results in Figs. 2 and 3 demonstrate that the iridium ions lose electrons and the iron ions gain electrons during an illumination at room temperature. Specifically, laser light converts neutral \( \text{Ir}^{3+} \) donors to singly ionized \( \text{Ir}^{4+} \) donors and, at the same time, converts neutral \( \text{Fe}^{3+} \) acceptors to singly ionized \( \text{Fe}^{4+} \) acceptors. Figure 4 describes the decay of the \( \text{Ir}^{4+} \) ions (discrete points) and the recovery of the \( \text{Fe}^{4+} \) ions (solid curve) at 296 K after the laser light is removed. To allow a direct comparison, the \( \text{Fe}^{2+} \) decay is plotted in Fig. 4. Recovery of the \( \text{Fe}^{3+} \) ions is directly related to the decay of the \( \text{Fe}^{4+} \) ions; thus, we invert (i.e., turn upside down) the \( \text{Fe}^{2+} \) recovery curve to obtain the \( \text{Fe}^{2+} \) decay curve. The decay of the \( \text{Ir}^{4+} \) absorption band in Fig. 4 occurred after an illumination with 405 nm laser light, while the recovery of the \( \text{Fe}^{4+} \) spectrum followed an illumination with 325 nm laser light. The similarity of the two curves in this figure shows that the decay of the \( \text{Ir}^{4+} \) ions and the recovery of the \( \text{Fe}^{4+} \) ions are correlated. Although the two sets of data in Fig. 4 were acquired in quite different experiments (infrared absorption vs EPR), the agreement between them is good. From the change in the concentration of \( \text{Ir}^{4+} \) ions determined in the previous paragraph, it now follows that the concentration of photoinduced \( \text{Fe}^{2+} \) ions at 296 K must also be approximately \( 5.4 \times 10^{18} \text{ cm}^{-3} \). Before an exposure at room temperature to laser light, a few percent of the Fe ions in the crystals may already be in the \( \text{Fe}^{2+} \) charge state because of the presence of shallow donors such as Si.

Two possible mechanisms by which laser light produces the \( \text{Ir}^{4+} \) and \( \text{Fe}^{2+} \) ions in the Fe-doped \( \beta\text{-Ga}_{2}\text{O}_{3} \) crystals are (1) excitation of electrons from \( \text{Ir}^{3+} \) ions to the conduction band with the subsequent trapping of the electrons by \( \text{Fe}^{3+} \) ions or (2) excitation of electrons from the valence band to the \( \text{Fe}^{4+} \) ions with the holes left in the valence band being trapped on \( \text{Ir}^{4+} \) ions. Both optical absorption processes may be contributing to the photoinduced production of the \( \text{Fe}^{2+} \) and \( \text{Ir}^{4+} \) ions when the 325 nm (3.81 eV) laser is used. Process (1), however, is expected to dominate when the 375 nm (3.30 eV), 405 nm (3.06 eV), and 442 nm (2.80 eV) lasers are used. After the \( \text{Fe}^{2+} \) and \( \text{Ir}^{4+} \) ions are formed, the subsequent recovery mechanism that restores the crystal to its preilluminated state is the thermally activated release of trapped electrons from the \( \text{Fe}^{2+} \) ions and not the thermally activated release of trapped holes from the \( \text{Ir}^{4+} \) ions. Simply stated, the \( \text{Ir}^{4+/3+} \) level is significantly farther from the valence band than the \( \text{Fe}^{2+/3+} \) level is from the conduction band. This is in agreement with recent computational results that place the \( \text{Ir}^{4+/3+} \) level 2.60 eV above the valence band.19

The electron-release recovery mechanism is also supported by the DLTS results of Irmscher et al.21 and Ingebrigtsen et al.25 where the E2 peak near 350 K is attributed to electron release. Our thermoluminescence data for Cr, reported in Sec. V, provide further evidence that the recovery of the \( \text{Fe}^{3+} \) ions occurs when electrons are thermally released from the \( \text{Fe}^{2+} \) ions.

Isothermal recovery curves for the \( \text{Fe}^{3+} \) EPR signal in an Fe-doped \( \beta\text{-Ga}_{2}\text{O}_{3} \) crystal were obtained at 296.6, 303.0, and 310.0 K, after illumination with 325 nm laser light. The recovery of the \( \text{Fe}^{3+} \) ions corresponds to the decay of the photoinduced \( \text{Fe}^{2+} \) ions; thus, the data are plotted as normalized decay curves in Fig. 5. These data were obtained by monitoring the intensity of the \( \text{Fe}^{3+} \) EPR line at 150.0 mT when the magnetic field is along the c direction (see Fig. 1). Prior to recording a recovery curve, the crystal was exposed to 325 nm laser light until a reduced equilibrium concentration was established for the \( \text{Fe}^{3+} \) ions. Then the intensity of the EPR line was monitored as a function of time after removing the laser light. This is the procedure illustrated in Fig. 2. While acquiring a recovery curve, the temperature varied by less than 0.1 K. The kinetics model and the process used to extract an activation energy from the set of decay curves in Fig. 5 are described in Sec. IV.

**IV. ANALYSIS OF THERMAL DECAY CURVES**

Thermally stimulated processes, such as those illustrated in Fig. 5, can be analyzed using methods developed over many years by the thermoluminescence (TL) community and described in detail in two comprehensive research monographs.40,41 Our present situation provides a unique application of these methods, in that we analyze isothermal decays following an excitation instead of a glow peak obtained by increasing the temperature at a constant rate. After removing the laser light incident on our \( \beta\text{-Ga}_{2}\text{O}_{3} \) crystal, we monitor the thermally stimulated release of electrons from \( \text{Fe}^{4+} \) ions to the conduction band. Once in the conduction band, these electrons can either recombine with holes at \( \text{Ir}^{4+} \) ions or be retrapped at \( \text{Fe}^{4+} \) ions. Retrapping is important since the individual isothermal curves in Fig. 5 are not single exponentials. Thus, a general-order kinetics model from the TL literature,42–48 which

![Fig. 4. Comparison of the decay of the \( \text{Ir}^{4+} \) infrared absorption spectrum (discrete points) and the recovery of the \( \text{Fe}^{4+} \) EPR spectrum (solid curve). Data were taken at 296 K after the laser light was removed. The inverted \( \text{Fe}^{2+} \) recovery curve is plotted to allow easier comparison.](image-url)
electron thermally released from the Fe$^{3+}$ ions. This suggests that the kinetics of the Fe$^{2+}$ decay curves in Fig. 5 will fall between first and second order.

The solution to Eq. (1), for $b > 1$, is

$$n(t) = n_0[1 + s' n_0^{b-1}(b - 1) \exp(-E/kT)t]^{-1/b},$$

where $n_0$ is the initial concentration of photoinduced Fe$^{2+}$ ions at $t = 0$ (when the laser light is removed). Equation (2) is rewritten in the following form:

$$\left(\frac{n}{n_0}\right)^{1/b} = 1 + s' n_0^{b-1}(b - 1) \exp(-E/kT)t.$$  

The next step in the analysis is to use the three experimental decay curves in Fig. 5 to separately plot the quantity $(n/n_0)^{1/b}$ vs time. For each plot, the value of $b$ is adjusted between 1 and 2 until a straight line emerges. There was a variation of approximately 15% in the resulting values of $b$ with the average being 1.87. In general, $b$ is not expected to be constant. This averaged value of $b$ indicates that the kinetics is close to second order. The three straight lines, corresponding to the three decay curves in Fig. 5, have different slopes. From Eq. (3), these slopes are

$$m_i' = s' n_0^{b-1}(b - 1) \exp(-E/kT_i).$$

The index $i = 1$ to 3 corresponds to the three temperatures where decay curves were obtained. Although normalized in Fig. 5, each decay curve has a different value of $n_0$. These initial concentrations of Fe$^{2+}$ ions represent an equilibrium value reached when the production rate (which depends on the intensity of the laser light) equals the decay rate (which depends on the temperature). For a constant intensity of excitation light, the initial concentration of photoinduced Fe$^{2+}$ ions is larger at lower temperatures. For our three decay curves, the initial concentrations are expressed as $n_{0i} = c_i N_0$, where the values of $c_i$ are 1.00, 1.04, and 1.06 for the 310.0, 303.0, and 296.6 K decay curves, respectively. The quantity $N_0$ represents the initial concentration for the 310 K decay curve. Equation (4) then becomes

$$m_i = \frac{m_i'}{(c_i^{b-1})} = s' N_0^{b-1}(b - 1) \exp(-E/kT_i).$$

Equation (5) is rewritten in the following form by taking the natural logarithm of each side:

$$\ln(m_i) = \ln[s' N_0^{b-1}(b - 1)] - \frac{E}{kT_i}.$$  

The final step is to construct a plot of $\ln(m_i)$ vs $1/T_i$. This plot contains three points, one for each decay curve, and is shown in the inset in Fig. 5. From Eq. (6), the slope of the best-fit straight line in the inset is $-E/k$. Our general-order kinetics analysis gives...
an activation energy of $E = 0.84$ eV for the thermal decay of photoinduced Fe$^{2+}$ ions in $\beta$-Ga$_2$O$_3$ crystals. The uncertainty in this value of $E$ is $\pm 0.05$ eV. Our result for the Fe$^{2+/3+}$ level is in agreement with experimental values previously reported for the E2 level. Earlier results from DLTS experiments are 0.78 eV ($\pm 0.04$ eV),$^{27}$ 0.82 eV,$^{28}$ and 0.81 eV.$^{29}$ Hall effect measurements gave 0.86 eV,$^{30}$ steady-state capacitance spectroscopy gave 0.81 eV ($\pm 0.005$ eV),$^{31}$ and thermally stimulated current spectroscopy gave 0.84 eV.$^{32}$ For comparison, recent computational results$^{33-35}$ predict that the Fe$^{2+/3+}$ level is approximately 0.61 eV below the conduction band.

We would have preferred to have Fe$^{2+}$ isothermal decay curves in Fig. 5 that spanned a larger temperature range, but experimental constraints were a limitation in our laboratory. We were unable to maintain a sufficiently constant sample temperature within the EPR resonator in the region above 310 K. Data below room temperature were not obtained because of the longer decay times and also the added complexity of introducing liquid nitrogen to cool the gas passing by the crystal. To ensure the validity of our Fe$^{2+/3+}$ activation energy obtained from the Fe$^{2+}$ EPR results, we acquired complementary thermoluminescence data that also describe the thermal release of electrons from Fe$^{2+}$ ions. The temperature range for the TL data was greater than 40 K (i.e., the half-width of the TL peak).

As described in Sec. V, these TL data are in excellent agreement with the results extracted from the EPR isothermal decay curves.

V. LUMINESCENCE RESULTS

Thermoluminescence, representing the radiative component of electron-hole recombination, is observed near 349 K in the Fe-doped $\beta$-Ga$_2$O$_3$ crystals. This agrees with the 354 K position of the E2 peak in DLTS measurements.$^{23}$ The experimental TL peak (discrete points) shown in Fig. 6 was obtained with a heating rate of $\beta = 1$ K/s after the crystal was exposed at room temperature to 325 nm laser light for 5 min. This TL peak is directly associated with the thermal release of electrons from the photoinduced Fe$^{2+}$ ions and, thus, is described by the kinetics parameters determined in Sec. IV. Verification of this association comes from the good agreement between the simulated TL peak (solid line) in Fig. 6 and the experimental peak. The simulated TL peak was generated using Eqs. (7) and (8),$^{36}$ with the slope and the vertical intercept from the inset in Fig. 5 providing input values. As described in Ref. 49, the following equations are obtained from the general-order kinetics model introduced in Sec. IV:

$$I_{\text{TL}} = s' n_0 \exp\left(\frac{-E}{kT}\right) \left[1 + \frac{s''}{b} \int_{T_0}^{T} \exp\left\{-\frac{E}{kT}\right\} \frac{dT}{\theta} \right]^{-\frac{1}{s''}},$$

(7)

$$s'' = s' b^{-1}.$$  

(8)

The input parameters are $E = 0.84$ eV, $b = 1.87$, $n_0 = 5.4 \times 10^{18}$ cm$^{-3}$, $s' = 9.5 \times 10^{19}$ s$^{-1}$, and $\beta = 1$ K/s. The starting temperature for the integral is $T_0 = 293$ K. A Mathematica subroutine is used to generate values of the integral. The series of data points plotted for the simulated TL curve in Fig. 6 are generated by stepping the upper limit of the integral in Eq. (7) from 293 to 448 K in increments of 0.1 K. In Fig. 6, the peak positions of the experimental and simulated TL peaks are extremely close. The low-temperature side of the experimental curve is slightly higher than the simulated curve because of the small delay in time (a few seconds) that occurs between the end of the exposure to the 325 nm light and the beginning of the TL measurement. This means that a small portion of photoinduced Fe$^{2+}$ ions are already decaying and, thus, emitting light, before the temperature ramp begins in the Harshaw TL reader.

The wavelengths of the light emitted by the TL peak at 349 K were determined to be longer than 500 nm by using two long pass filters to narrow the range of wavelengths incident on the photomultiplier tube (PMT) in the TL reader. These results are shown in Fig. 7. Before acquiring each TL curve, the crystal was first heated to near 500 K to remove any effect of previous illuminations and then was exposed at room temperature for 5 min to 325 nm laser light. For curve (a) in Fig. 7, no filter was placed between the sample and the PMT and the most intense TL peak was obtained with all emitted wavelengths contributing. For curve (b), a 500 nm long pass filter (Hoya Y-50) was inserted between the sample and the PMT. The intensity of the TL peak was only slightly reduced by this filter, suggesting that at least 80% of the emitted light has wavelengths longer than 500 nm. For curve (c), a 600 nm long pass filter (Hoya R-60) was placed between the sample and the PMT. This latter filter significantly reduced the intensity of the TL peak, suggesting that 90% of the emitted light has wavelengths shorter than 600 nm.

The electrons thermally released from the singly ionized Fe$^{2+}$ acceptors near 349 K recombine, either radiatively or nonradiatively, with the singly ionized Ir$^{4+}$ and Cr$^{4+}$ donors that were initially produced by the 325 nm excitation light. Most of the
recombination takes place at Ir$^{4+}$ ions, as they are present in a much larger concentration than the Cr$^{4+}$ ions. In the next paragraphs, radiative recombination of electrons with Cr$^{3+}$ ions is shown to produce both broad and sharp line emission in a region near 690 nm. Thus, the portion of the TL light emitted at wavelengths longer than 600 nm in Fig. 7 is attributed to recombination of electrons with Cr$^{3+}$ ions. The larger portion of the emitted TL light in Fig. 7, with wavelengths between 500 and 600 nm, is assigned to recombination of electrons with Ir$^{4+}$ ions. This latter emission range is consistent with the Ir$^{4+/3+}$ level being between 2.0 and 2.5 eV below the conduction band, as the midpoint of this energy range corresponds approximately to 550 nm photons. The weak intensities (i.e., low signal-to-noise ratio) of the TL peaks in Fig. 7 suggest that the recombination at the Ir$^{4+}$ ion is primarily nonradiative.

Galazka et al. have observed that the electrical properties of Cr-doped β-Ga$_2$O$_3$ crystals are similar to those of undoped crystals grown under the same conditions. This indicates that Cr acts as a deep donor in β-Ga$_2$O$_3$ and is present as Cr$^{3+}$ ions in unintentionally doped n-type crystals. If Cr were an acceptor, doping with Cr would have produced semi-insulating β-Ga$_2$O$_3$ and, thus, quite different electrical properties. Additional evidence that Cr is a donor in this material comes from EPR. Galazka et al. simultaneously observed signals from shallow donors and Cr$^{3+}$ ions in EPR spectra taken at 6 K from an undoped n-type β-Ga$_2$O$_3$ crystal, a behavior only possible if Cr is a donor. In Ref. 50, the model angular dependence of the “defect” EPR signal clearly links it to Cr$^{3+}$ ions. We also routinely observe a Cr$^{3+}$ EPR signal (from trace amounts of Cr) in nominally undoped n-type β-Ga$_2$O$_3$ crystals at temperatures below approximately 20 K where carrier freeze-out typically occurs. The strong nonresonant absorption of microwaves by free carriers prevents observation of the Cr$^{3+}$ EPR spectrum at higher temperatures in the n-type crystals. In contrast, the lack of free carriers in semi-insulating β-Ga$_2$O$_3$ crystals allows the Cr$^{3+}$ donor EPR spectrum to be observed at room temperature.

A Cr$^{3+}$ EPR spectrum can be seen at room temperature in our semi-insulating Fe-doped β-Ga$_2$O$_3$ crystals, thus demonstrating the presence of a small concentration of neutral Cr donors. The intensity of the Cr$^{3+}$ spectrum is much less than the intensity of the Fe$^{3+}$ spectrum, as expected if Cr donors are present only because of the impure starting materials used in growth. When the Fe-doped crystals are exposed at room temperature to 325 nm laser light, the Cr$^{3+}$ EPR spectrum decreases slightly in intensity and Cr$^{3+}$ ions are formed at the same time Fe$^{3+}$ ions are formed. These Cr$^{3+}$ ions serve as recombination sites when electrons are thermally released from Fe$^{3+}$ ions. The electron returning to a Cr$^{3+}$ ion first forms a Cr$^{4+}$ ion in an excited state, with emission then occurring near 700 nm as the excited Cr$^{4+}$ ion returns to its ground state. This accounts for the portion of the TL emission having wavelengths longer than 600 nm when the crystal is heated above room temperature (see Figs. 6 and 7).

The photoluminescence spectrum shown in Fig. 8 verifies that Cr$^{3+}$ (3d$^3$) ions are present in our Fe-doped β-Ga$_2$O$_3$ crystals. This PL spectrum was taken at room temperature with 265 nm excitation. In recent years, numerous investigations of the PL from Cr$^{3+}$ ions in Ga$_2$O$_3$ have been reported. The primary features in these spectra are the well-known R$_1$ and R$_2$ lines at 696.8 and 690.0 nm (with the R$_3$ line dominating at room temperature). These R lines are $^2$E to $^4$A$_2$ transitions of the Cr$^{3+}$ ion, whereas the broader underlying band in Fig. 8 is attributed to the $^4$T$_2$ to $^4$A$_2$ transitions of the Cr$^{3+}$ ion.
transition. This latter transition is vibronic broadened and is relatively large at room temperature because of the thermal population of the $^4\text{T}_2$ level from the $^5\text{E}$ level. Recently, a photoluminescence study$^{3}$ and a thermoluminescence study$^5$ have suggested that Fe is responsible for narrow emission peaks near 700 nm in $\beta$-Ga$_2$O$_3$ crystals. We believe it is likely that the 700 nm emissions reported in those studies are due to Cr$^{3+}$ impurities.

VI. SUMMARY

The E2 level often observed in $\beta$-Ga$_2$O$_3$ crystals is conclusively shown to be associated with Fe impurities at sixfold Ga sites. Electron paramagnetic resonance (EPR), a noncontact experimental technique, is used to obtain a value of 0.84 eV for the Fe$^{2+}$ level in Fe-doped crystals grown by the Czochralski method. Neutral Fe$^{3+}$ acceptors and neutral Ir$^{4+}$ donors in the as-grown crystals are converted to their Fe$^{2+}$ and Ir$^{4+}$ charge states during an exposure near room temperature to laser light with wavelengths ranging from 325 to 405 nm. An activation energy is then extracted from the Fe$^{3+}$ isothermal recovery curves obtained when the light is removed and electrons are thermally released from the singly ionized Fe$^{2+}$ acceptors. A general-order kinetics model is used to analyze these recovery curves. A thermoluminescence curve peaking at 349 K is also produced when a small portion of the electrons released from the Fe$^{3+}$ ions recombine radiatively at Ir$^{4+}$ and Cr$^{4+}$ donors. A simulation of this TL peak, using parameters obtained from the isothermal EPR recovery curves, agrees well with experiment and directly supports the value of 0.84 eV for the Fe$^{3+}$ level. Photoluminescence spectra from the Fe-doped $\beta$-Ga$_2$O$_3$ crystals show the R lines near 690 nm that are characteristic of neutral Cr$^{3+}$ donors.

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