I. INTRODUCTION

Complex oxides have optical, electrical, and magnetic properties that make them good candidates for applications as device materials and for fundamental studies of underlying defect physics. Garnets in particular have been developed for diverse applications. Garnets have the generic composition \( A_3B_2C_3O_{12} \). In yttrium aluminum garnet, \( Y_3Al_5O_{12} \) (YAG), Y occupies the \( A \) site (Wykoff notation \( c \)) and Al occupies the \( B(d) \) and \( C(a) \) sites, with \( A \), \( B \), and \( C \) sites having eightfold, fourfold, and sixfold coordination with oxygen atoms. Intrinsic point and extended defects strongly influence optical, magnetic, and electrical properties of garnet materials but little is known about the nature and structure of those defects. A variety of thermal and structural point defects occur in YAG single crystals as a consequence of deviations from stoichiometry, growth conditions at high temperature, subsequent annealing, and the presence of cation impurities such as Ce that may have variable charge states. These include vacancies on cation and anion sublattices, antisite atoms, and complexes of defects and impurities that may strongly influence optical properties. For example, anion and cation vacancies can act as electron and hole traps that degrade luminescence and scintillation properties.

Positron annihilation spectroscopy has particular sensitivity to open-volume defects such as vacancies and vacancy clusters. It has been applied since the 1970s to study defects in metals and semiconductors, but its application to oxide materials and complex oxides has been limited. A few studies of vacancy defects in YAG have been carried out using Doppler broadening of positron annihilation, but Doppler broadening can only provide detailed information about defect types when combined with theoretical calculations and positron lifetime measurements. In this paper, we report an investigation of defects in the YAG structure using positron lifetime spectroscopy (PLS). PLS resolves defects via characteristic positron lifetimes and provides unique insight into the nature of vacancy defects. In the experiments, defects were created in YAG samples by controlling growth and annealing atmospheres, and lifetimes were measured for aluminum vacancies (\( V_{Al} \)) and for complexes formed from an aluminum vacancy and neighboring oxygen vacancies.

This approach to the control and identification of vacancy defects can be extended to other garnets and, indeed, all complex oxides. Sample compositions were measured using wavelength-dispersive x-ray spectroscopy (WDS), which has the ability to detect light elements as well as heavy ones and has sensitivity an order of magnitude better than energy-dispersive x-ray spectroscopy.

II. EXPERIMENTAL DETAILS AND MEASUREMENTS

Growth conditions were chosen to enhance concentrations of different defect types. Single crystals of YAG, either undoped or doped with Ce impurities, were variously grown by the Czochralski method under (1) a reducing atmosphere of 40% hydrogen in argon, (2) a modestly oxidizing atmosphere of 100 ppm oxygen in nitrogen, or (3) an unreactive atmosphere of argon (crystal growth was carried out at Crytur Inc., Czech Republic and United Crystal Inc., USA). After growth, some samples were annealed in our laboratory at 1200 °C in air, in a hydrogen and Ar mixture, or in pure Ar to further modify the populations of defects. A few samples were also subjected to Al sputtering followed by annealing in Ar at 600 °C. WDS was used to measure mole fractions of Y, Al, and O and determine deviations from the stoichiometric composition. This analysis was carried out using a JEOL 8500F field-emission electron microprobe analyzer, with 15 keV accelerating voltage, 50 nA electron beam current, and 15 μm beam diameter. The electron beam hits the sample leading to the emission of characteristic x-ray radiation that can be used for chemical analysis. WDS utilizes Bragg diffraction from analyzing crystals to select x-ray wavelengths of interest and direct x-ray photons to gas flow proportional detectors. The JEOL instrument has five wavelength-dispersive spectrometers to cover the x-ray emission from all elements in the periodic table including light elements with high sensitivity. WDS measurements were carried out on YAG samples with well-polished surfaces and repeated at ten different points for each sample, after which mean values and standard deviations of mole fractions of Y, Al, and O were determined.

Positron lifetime spectroscopy is a highly informative technique for microscopic characterization of vacancy-type...
defects. Positrons injected into a solid annihilate with electrons, either from a delocalized state in the bulk or from a trapped state in an open-volume defect such as a lattice vacancy.\textsuperscript{11} When a material is free of positron traps, the positron annihilations in the bulk with only one lifetime $\tau_B$. When traps are present, annihilation leads to longer lifetimes $\tau_i$ and intensities $I_i$.\textsuperscript{11} Positron spectroscopies are typically sensitive to trapping at vacancy centers having concentrations as low as 0.1 ppm.

Positron lifetimes were measured using a conventional fast-fast time coincidence spectrometer\textsuperscript{10} with two BaF$_2$ detectors in a collinear geometry and with time resolution of \( \sim 200 \) ps. A positron source was made by depositing $^{22}$NaCl on an 8-micron-thick Kapton foil that was folded and sandwiched between two identical YAG samples. Several million counts were accumulated in each lifetime spectrum for good statistical precision. Each spectrum was analyzed as a superposition of exponential decay components convoluted with three Gaussian functions that represented the instrumental time resolution function.\textsuperscript{10} Decay components due to positron annihilation in the source and Kapton foil were subtracted from the total spectrum. These components were determined from independent measurements made on annealed defect-free Al samples, with the component from the Kapton foil having a lifetime of 384 ps and 10% intensity and the NaCl source component having a 430 ps lifetime and 1% intensity. After subtracting these components, lower variances were obtained for most of the spectra using a two-lifetime component fit. However, only one lifetime component was resolved for the samples grown under hydrogen. The variances of the fits were between 1.07 and 1.2. The longer lifetime $\tau_2$ in a two-component fit corresponds to the characteristic lifetime of the defect, with the shorter lifetime $\tau_1$ reduced below the bulk lifetime by an amount that depends on the defect trapping rate. The one-defect simple trapping model was applied to analyze spectra and the bulk lifetime $\tau_B$ was then calculated from the measured lifetime components $\tau_1$ and $\tau_2$, and their intensities $I_1$ and $I_2$: $\tau_B = (I_1/\tau_1 + I_2/\tau_2)^{-1}$.\textsuperscript{10,11} A slightly higher $\tau_B$ value observed for some samples was taken to indicate the presence of more than one defect type in these samples, so that the one-defect trapping model was less accurate. However, it is not possible to resolve two-lifetime components if they are too close. Fitted values of $\tau_1$, $\tau_2$, and derived values of the bulk lifetimes $\tau_B$ are listed for five samples of undoped and Ce-doped YAG single crystals in Table I and displayed in Fig. 1. Characteristic defect lifetimes $\tau_2$ can be seen to vary between 249 ps in O$_2$-grown YAG samples and 282 ps in Ar-grown YAG samples. After annealing the same Ar-grown YAG sample under air, $\tau_2$ decreased from 282 to 256 ps. Significantly, no defect-associated signal could be resolved in any of four samples grown under hydrogen.

III. DISCUSSION

Sample compositions obtained from the WDS measurements are included in Table I. Writing the mole fraction of element $X$ as $[X]$, measured ratios $3[Al]/5[Y]$ gave evidence of excess $[Y]$ in the range 0%–1% (see Table I). As explained below, the mole fraction of cation vacancies was much less, so that this yttrium excess is believed to be present as antisite atoms $Y_{Al}$ on the Al sublattices. Calculations indicate that the $Y_{Al}$ antisite atom is the intrinsic defect with the lowest energy in YAG\textsuperscript{18} but vacancies might also be present, either created during crystal growth or after annealing. From Table I it can be seen that \( \sim 0.5 \) at. % of O sites were vacant. In summary, the WDS results indicate that as-grown crystals contained a substantial concentration of oxygen vacancies and lesser amounts of $Y_{Al}$ antisite atoms and aluminum vacancies. In previous work, a Doppler broadening study of YAG showed that aluminum vacancies were abundant in crystals grown under nitrogen.\textsuperscript{16} Remarkably, the trap density for positrons was shown to be reduced by two orders of magnitude after Al was sputtered on the surface and diffused inside. The interpretation given was that the introduced Al atoms “filled up” nearly all Al vacancies. This treatment was repeated here on sample No. 1, as described in Table I, and lifetime measurements showed the absence of positron trapping after Al sputtering, consistent with the previous interpretation.

A. Oxygen vacancies

The gross deficiency in oxygen in the as-grown samples can only be explained by the presence of large mole fractions of oxygen vacancies, $V_0$. An \textit{ab initio} calculation\textsuperscript{19} of yttrium aluminum garnet has shown that the $+2e$ oxygen vacancy is the easiest to form and more stable than other charge states. Such a positively charged defect will repel positrons and be “invisible” to positron spectroscopies. Growth of YAG under hydrogen may be expected to lead to the creation of oxygen vacancies via the schematic reaction $\text{H}_2(g) + O_0 \rightarrow V_0 + H_2O(g)$. However, oxygen vacancies produced by such a reaction will not trap positrons and will go undetected. Therefore to confirm the presence of oxygen vacancies, we
undone thermoluminescence measurements (TL) on some samples in order to reveal the presence of oxygen-vacancy defects such as F centers. Undoped YAG single crystals grown under Ar were irradiated with ultraviolet (UV) light for 30 min under a pulsed xenon-flash lamp, after which light emission over the range 200–800 nm was recorded using a charge-coupled device detector during ramp heating of the sample from room temperature to 400 °C. UV light generates electron and hole charge carriers, some of which become trapped in metastable configurations at crystal defects such as oxygen vacancies. Subsequent heating leads to release of the trapped carriers, which can then migrate and transfer their energy at luminescence centers [provided by impurities in undoped YAG (Ref. 20), producing light (TL emissions). After annealing samples in air, TL emissions were dramatically suppressed, which is attributed to a large decrease in the number of oxygen vacancies owing to in-diffusion of oxygen anions and elimination of vacancies. These TL measurements and the WDS analysis confirm the presence of a large number of oxygen vacancies. The presence of YAl antisite atoms may explain in part the high concentration of oxygen vacancies. Since the radius of the Y3+ ion is much greater than the radius of an Al3+ ion, the strain interaction around a YAl antisite atom will be reduced when an oxygen vacancy forms next to it.

B. Cation vacancies detected after growth under oxygen or argon

Positron trapping centers are assumed to be cation vacancies since bare vacancies have a relative negative charge that attracts positrons. After growth in oxygen or after growth in argon followed by annealing in air, a defect having a long positron lifetime was observed (Table I) that varied between 240 and 280 ps. Because trapping centers must be negatively charged, they are attributed to cation vacancies and, based on yttrium excess shown in the WDS measurements, they are identified as aluminum vacancies. The range of observed second lifetime values may be due to the presence of two Al sites with different coordination in YAG and also to the possible role of oxygen vacancies. The decrease of the defect lifetime and the increase in its intensity after air anneal in Ar-grown samples support the presence of oxygen vacancies next to Al vacancies. From the intensities $I_2$ for annihilation of trapped positrons shown in Table I, the cation vacancy mole fractions for undoped YAG grown in O2 were estimated to be of order 0.1 ppm, assuming a trapping rate in the range 0.5–2.0 × 1013 Hz.10 Such a low concentration of Al vacancies is consistent with the much-greater assumed presence of YAl antisite defects.

C. Elimination of oxygen vacancies by annealing in air

From Table I, it can be seen that there was a decrease from a defect lifetime of 279 ps for the sample grown in Ar, to 256 ps after a subsequent anneal in air. In addition, it can be seen that annealing in air led to an increase in the trapped positron intensity $I_2$ by a factor of 50%. This may be attributed to annihilation of oxygen vacancies in the defect complexes, increasing the nominal charge of the trapping centers and decreasing their size. In addition, a reduction in the density of isolated oxygen vacancies should increase the mobility of positrons in the matrix. Elimination of oxygen vacancies is also supported by the suppression of TL emission after air anneal for this sample.

D. Hydrogen decoration and passivation of cation vacancies

Complete absence of positron trapping was observed for samples grown under hydrogen (see Table I). Since WDS measurements did not show appreciable differences in composition depending on the growth atmosphere, it is assumed that cation vacancies still existed in such samples, but that hydrogen had also been incorporated in samples during growth and was responsible for elimination of trapping at the cation vacancies. This is because there is no obvious hydrogen reaction that might eliminate Al vacancies. As an explanation, it is proposed that significant amounts of hydrogen enter the lattice as
interstitial cations during crystal growth under H₂ and then diffuse to and trap in the Al vacancies. A hypothetical reaction leading to complete compensation of the negative charge of an aluminum vacancy is \( \frac{3}{2} \text{H}_2(g) \rightarrow 3\text{H}^+ + 3e^- + V_{\text{Al}}/3 \rightarrow [V_{\text{Al}}/3 + 3\text{H}^+]^+ + 3e^- \), using the Kröger-Vink notation for defect charges, in which \( \text{H}^+ \) identifies mobile hydrogen interstitial cations and the bracket indicates a bound complex of an Al vacancy with three hydrogen cations. Such “decoration” with hydrogen cations compensates the \(-3e^-\) charge of a “bare” Al vacancy and thereby blocks the ability to trap positrons.

Since growth under hydrogen completely suppresses positron trapping, it is reasonable to assume that 2-3 hydrogen cations have been trapped in each aluminum vacancy. In order to test this hypothesis, several samples that had been grown under hydrogen were annealed under air for several hours. This did not cause the appearance of the long lifetime associated with Al vacancies. However, longer annealing in air for a few days at 1200 °C led to the appearance of long lifetime components such as represented for sample No. 1 in Table I. Further support for this passivation mechanism comes from experiments on sample No. 2 that had been grown under oxygen, before and after subsequent annealing in hydrogen and Ar at 1200 °C (see Table I). As can be seen, annealing in hydrogen and Ar dramatically decreased the lifetime of trapped positrons suggesting partial decoration of cation vacancies by hydrogen. (The large uncertainty in the intensity \( I_2 \) is due to the close values of \( \tau_B \) and \( \tau_2 \), and therefore, poor resolution, but the fitting definitely showed the existence of two lifetimes.) Compared with the effects of annealing in hydrogen at 1200 °C observed here, the original crystal growth under hydrogen at \( \sim 1900 \) °C should be expected to have been much more effective at introducing H cations. After that, sample No. 2 was again annealed under Ar in an attempt to outgas hydrogen from the sample. This led to the appearance of a long lifetime component of 208 ps, as shown in Table I. These experiments on sample No. 2 show reversible effects on positron trapping that strongly support the interpretation that hydrogen cations trap in and passivate cation vacancies.

E. Infrared spectroscopy

To provide more direct evidence for the presence and incorporation of H₂, IR absorption measurements were performed on the H₂-grown and O₂-grown YAG samples using a Bomem DAS Fourier transform infrared spectrometer with a globar light source, a KBr beam splitter, and a liquid-nitrogen-cooled InSb detector. Samples were maintained at liquid-helium temperatures (\( \sim 10 \) K) in a Janis continuous-flow cryostat. The spectral range of the spectrometer covers from 1800 to 7000 cm\(^{-1}\) and its resolution is 0.2 cm\(^{-1}\). Figures 2(a) and 2(b) show the measured IR absorption spectra of O₂-grown YAG and H₂-grown YAG, respectively. Two peaks were identified at 3335 and 3370 cm\(^{-1}\) in the sample grown in O₂ atmosphere. These two peaks were reported to be associated with O-H bond stretching vibrational modes. They represent hydrogen atoms located at two different interstitial sites. These two peaks did not appear in the IR absorption spectrum of YAG samples grown in H₂. Instead, a peak at 3416 cm\(^{-1}\) is observed at liquid-helium temperature. We attribute this new O-H mode to a passivated Al vacancy for the following reasons. First, hydrogen passivation of Al vacancies explains the absence of positron trapping. Second, the observation of one IR peak is consistent with a fully passivated cation vacancy such as \( V_{\text{In}}/4 \) in InP. The high symmetry of such a complex results in one IR-active peak. In contrast, vacancy complexes decorated with two hydrogen atoms have a lower symmetry, resulting in two IR peaks. Finally, the relatively high vibrational frequency is common for a vacancy decorated with multiple hydrogen atoms in which the atoms are crowded and the bonds are compressed.

IV. CONCLUSIONS

In summary, a positron lifetime study was made of YAG single crystal samples that had been grown and/or annealed under different atmospheres. Trapping was observed at cation
HOLES AND COMPLEXES OF CATION VACANCIES AND NEIGHBORING OXYGEN VACANCIES. COMPLETE CHARGE COMPENSATION OF CATION VACANCIES WAS OBSERVED AFTER GROWTH UNDER HYDROGEN, ELIMINATING ALL POSITRON TRAPPING, AND PARTIAL CHARGE COMPENSATION WAS OBSERVED AFTER ANNEALING UNDER HYDROGEN. WE EMPHASIZE THAT THERE IS NO REASON TO SUPPOSE THAT CRYSTAL GROWTH UNDER HYDROGEN SHOULD HAVE ELIMINATED CATION VACANCIES IN THE SAMPLES GROWN UNDER HYDROGEN. THEREFORE, GROWTH UNDER HYDROGEN APPEARS TO HAVE INTRODUCED SUFFICIENT, MOBILE HYDROGEN INTERSTITIALS TO DIFFUSE THROUGH THE OXIDE AND TO TRAP AT AND COMPENSATE NEGATIVE-CHARGE DEFECT CENTERS COMPLETELY, IN PARTICULAR, CATION VACANCIES. IR ABSORPTION SPECTROSCOPY PROVIDES STRONG DIRECT EVIDENCE FOR THE PRESENCE OF HYDROGEN. THIS KIND OF “HYDROGEN PASSIVATION” OF NEGATIVELY CHARGED CATION VACANCIES AND OTHER DEFECT CENTERS IS SUGGESTED AS A COMMON MECHANISM IN GARNETS AND OTHER COMPLEX OXIDES. PASSIVATION OF CATION VACANCIES CERTAINLY HAS A MAJOR IMPACT ON THE OXIDE PROPERTIES. HYDROGEN HAS BEEN KNOWN TO HAVE SIGNIFICANT EFFECTS ON THE PROPERTIES OF MANY SEMICONDUCTORS. THE CONCLUSION DRAWN FROM THE PRESENT STUDY SUGGESTS THAT HYDROGEN MAY ALSO HAVE SIGNIFICANT EFFECTS ON THE PROPERTIES OF INSULATING OXIDES.

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