Positron Lifetime Measurements of Vacancy Defects in Complex Oxides

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Native defects in complex oxides play a crucial role in determining their optical, electrical, and magnetic properties and it is difficult to identify and characterize them. Positron lifetime spectroscopy is a powerful technique to study vacancy defects; however its application to complex oxides has been limited. In this work we apply positron lifetime spectroscopy to study open volume defects in rare earth doped yttrium aluminum garnet (YAG) complex oxides grown in argon atmosphere. In YAG single crystals, positron lifetime measurements identified isolated aluminum vacancies and complexes of aluminum vacancy and neighbor oxygen vacancies. Thermoluminescence measurements were also performed to elucidate the interaction between trapping defects and luminescence centers. By combining positron lifetime and thermoluminescence, both the defect type and its effect on the optical properties of YAG crystals were revealed.

1. Introduction

There is considerable interest in complex oxides due to extraordinary optical, electrical, and magnetic properties [1]. However, most of their properties are affected by the presence of defects. $Y_3Al_5O_{12}$, yttrium aluminum garnet (YAG) is complex oxide with a wide range of applications in lasers, scintillation, and illumination devices [2–5]. Ce-doped YAG (Ce:YAG) single crystal for example has the potential to be an excellent scintillator for X- and γ-ray detection [6, 7]. However, its development to an efficient scintillator has been hindered by the presence of defects in the lattice [8]. These defects act as traps for charge carriers preventing or delaying them from reaching the luminescence centers. Hence investigation and control of defects is key to control the optical and scintillation properties of the crystal. Positron lifetime spectroscopy (PLS) [9] is an established tool for defect identification in metals and semiconductors; however its application to complex oxides has been limited.

2. Thermoluminescence experiment

In this work we combine PLS and thermoluminescence (TL) measurements to study point defects in undoped and RE doped YAG single crystals grown in Ar atmosphere. Wavelength-resolved TL measurements were carried out on undoped and Ce-doped YAG single crystals grown in Ar atmosphere to elucidate the interaction between defects and luminescence centers in the structure. The TL experimental setup is described elsewhere [10, 11]. The emitted light was recorded using a charge-coupled device detector over the range 200 to 800 nm between room temperature and 400 °C after irradiating each sample with ultraviolet (UV) light for 30 min using a pulsed xenon flash lamp.
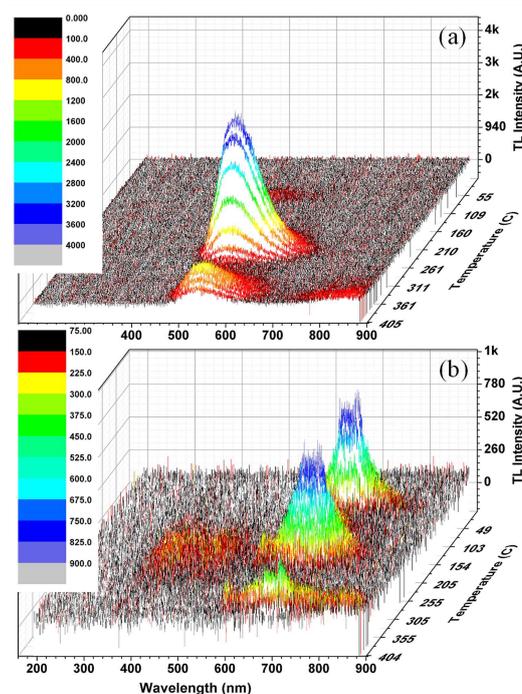

Fig. 1. TL spectra as a function of temperature and wavelength demonstrating the interaction between trapping defects and luminescence centers in single crystals of (a) Ce doped YAG, (b) undoped YAG.

Figure 1 displays 3-dimensional graphs of the intensity of light emitted as a function of temperature and wavelength for Ce doped (a) and undoped (b) YAG single crystals. These TL measurements confirm the presence of trapping defects and their significant effects on

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the luminescence properties of the crystals. Irradiating the sample with UV light generates excitons that can be rapped at crystal defects. Increasing the thermal energy of the crystal by heating releases the trapped excitons, which can then be captured by luminescence centers, producing light.
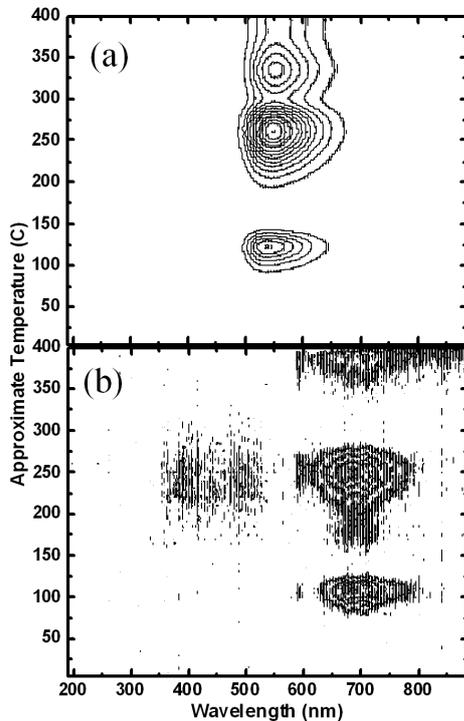

Fig. 2. Contour plot for the TL spectra shown in Fig. 1: (a) Ce doped YAG plotting luminescence intensity contours to a map of temperature versus wavelength. Each contour represents 1500 counts. (b) Undoped YAG, plotting luminescence intensity contours to a map of temperature versus wavelength. Each contour represents a step of 200 counts.

Figure 2 represents the contour plots of the luminescence measurements in Fig. 1 for (a) Ce doped YAG and (b) undoped YAG single crystals. They clearly demonstrate the interaction between trapping defects and luminescence centers. The strong luminescence in Ce doped YAG (Fig. 1a and Fig. 2a) is the well-known green emission of Ce^{3+} caused by transitions from $5d$ excited states to the $4f$ ground state of the Ce^{3+} ion [12]. Two emission bands are shown for undoped YAG in Figs. 1b and 2b. An ultraviolet emission at 400 nm has been known to be associated with self-trapped excitons [13] and a recently discovered photoluminescence emission at 700 nm. The 700 nm has been attributed to charge transfer between Fe^{2+} and Fe^{3+} impurities located on different sublattices in the matrix [14]. Careful inspection of the contour plots in Fig. 2 indicates that more than one type of traps exist in the YAG structure as Fig. 2b shows emission at 100 °C, 225 °C, and 375 °C. The presence of these traps in the undoped YAG crystal is an indication of their as-

sociation with native defects in the YAG structure. The contour plot of emission for Ce doped YAG crystal in Fig. 2a also shows three trapping defects. However, doping with Ce seems to cause a slight change in the energy level of defects as doping may induce defects with different structure as will be demonstrated by positron lifetime measurements below. These TL measurements confirmed that native defects in YAG structure greatly affect exciton dynamics and the scintillation properties of the crystals.

3. Experimental

PLS was applied to identify these defects that trap exciton in undoped YAG and in a number of RE (Ce, Nd, Tm, Yb) doped YAG single crystals. The measurements were performed using a conventional fast-fast time coincidence spectrometer [9] with two BaF_2 gamma-ray detectors mounted on photomultiplier tubes. A positron source was made by depositing $^{22}NaCl$ activity on an 8 μm thick kapton foil that was then folded and sandwiched between two identical samples. Several million counts were accumulated for a lifetime spectrum to obtain reasonable statistics. The lifetime spectrum was analyzed as a superposition of exponential decay components convoluted with three Gaussian functions that represent the instrumental timing resolution. Two lifetime components τ_1 and τ_2 were resolved in most samples. The one-defect simple trapping model (STM), which predicts two lifetime components was thus applied to analyze spectra for most samples. The bulk lifetime τ_B was calculated from the two measured lifetime components, τ_1 and τ_2, and their intensities, I_1 and I_2, via $\tau_B = (I_1/\tau_1 + I_2/\tau_2)^{-1}$ [9].

4. Results and discussion

Figure 3 shows the variation in the bulk lifetime τ_B and the defect characteristic lifetime τ_2 for undoped and RE doped YAG single crystals grown in neutral atmosphere of Ar. τ_B and τ_2 for Nd doped YAG are almost equal to those lifetimes in undoped YAG. This is probably because both Nd and Y ions can only be present in the trivalent state. On the contrary, Ce and Tm ions can be formed in both +3 and +4 states. τ_2 in Ce doped YAG is about 306 ps indicating the presence of more than single vacancy, which may be a result of the large size of Ce^{3+} (1.1 Å compared to 0.93 Å for Y^{3+}). With respect to Yb ion, it can be formed in both the divalent and trivalent states. The Yb^{2+} has a big size of 1.04 Å leading to knocking of neighbor oxygen atoms and the formation of vacancy complexes as indicating by large defect characteristic lifetime τ_2 of 340 ps. Anneal of Yb:YAG in air decreased τ_2 supports this interpretation since air anneal can oxidize Yb^{2+} and fills an oxygen vacancy according to the following reaction: Yb^{2+} + F^+ (an electron trap at an oxygen vacancy) + O → Yb^{4+} + O^{2-}.

The growth of Ce doped YAG in Ar atmosphere led to the formation of complex defect with more than one vacancy as indicated by the long lifetime 306 ps. This positron lifetime is longer than the defect lifetime in undoped YAG (the 282 ps component), which has been as-
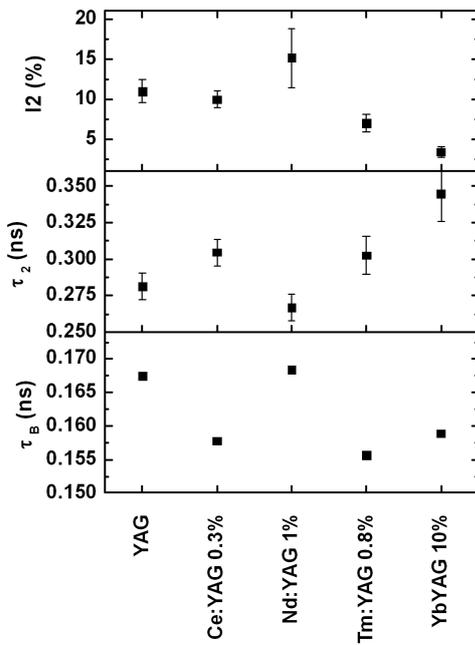
Fig. 3. Positron lifetime measurements in YAG single crystals grown in Ar atmosphere and doped with different rare earth metals. The graph shows the bulk lifetime, the defect lifetime and its intensity.

signed to complex defect of an Al vacancy and O vacancy (V_{Al-O}) [15]. As explained above, the increase in the defect lifetime in Ce doped YAG reflects the formation of larger defect complexes as a result of the large size of Ce^{3+} ion. This defect lifetime value (305 ps) remained the same after annealing in air indicating no change in the defect structure. However its intensity declined to half, which is expected to be due to a change of some Ce^{3+} ions to Ce^{4+} around the vacancy after annealing and the subsequent reduction of positron trapping at the vacancy cluster because of the positive charge state. The TL luminescence data showed the increase of TL emission with increasing Ce concentration and the decline of TL emission after air-anneal. This is unambiguous indication for the increase of doubly charged oxygen vacancies V_O^{2+} with increasing Ce doping level and for their decrease upon annealing. These V_O^{2+} cannot be seen by positron and their concentration cannot be reflected in lifetime data because of their positive charge state.

The formation of V_{Al-O} complex in neutral growth conditions seems natural to help compensating charges. Their formation appears to depend on both the dopant valence state and size. Accordingly, the valence state of the dopants plays an important role in the formation of both F centers (oxygen vacancies) and defect complexes of cation vacancies and anion vacancies. Figure 3 shows that doping does not increase the defect density measured by positrons (represented by I_2). This result is a little surprising, however it could be because of the large

number of antisite defects in YAG single crystals as confirmed in parallel work [15] and the formation of oxygen vacancies which have +2 charge state and do not trap positrons.

5. Summary

We combined PLT and TL measurements to identify and characterize the native defects in undoped and RE doped YAG single crystals grown in Ar. Both the bulk positron lifetime and the defect characteristic lifetime of YAG single crystals were experimentally determined and the defect structures were predicted. Ion size and valency were found to play significant role on the defect structure around the dopant. These measurements show that positron lifetime spectroscopy can characterize vacancy defects in the garnets and provide some insight on how to control the defect structures in complex oxides which is of great interest in a broad range of fields.

Acknowledgments

References

[1] R. Ramesh, D.G. Schlom, *MRS Bull.* **33**, 1006 (2008).

[2] M. Grinberg, A. Sikorska, A. Śliwiński, J. Barzowska, Y.R. Shen, S.B. Ubizskii, S.S. Melnyk, *Phys. Rev. B* **67**, 045113 (2003).

[3] Shin-ichiro M. Nomura, T. Harada, K. Yoshikawa, *Phys. Rev. Lett.* **88**, 093903 (2002).

[4] Y.N. Xu, Y. Chen, S.D. Mo, W.Y. Ching, *Phys. Rev. B* **65**, 235105 (2002).

[5] A.G. Okhrimchuk, A.V. Shestakov, *Phys. Rev. B* **61**, 988 (2000).

[6] E. Zych, C. Brecher, J. Glodo, *J. Phys., Condens. Matter* **12**, 1947 (2000).

[7] S.R. Rotman, C. Warde, *J. Appl. Phys.* **58**, 522 (1985).

[8] F.A. Selim, D. Solodovnikov, M.H. Weber, K.G. Lynn, *Appl. Phys. Lett.* **91**, 104105 (2007).

[9] R. Krause-Rehberg, H.S. Leipner, *Positron Annihilation in Semiconductors*, Springer-Verlag, Berlin 1999.

[10] C.R. Varney, D.T. Mackay, A. Pratt, S.M. Reda, F.A. Selim, *J. Appl. Phys.* **111**, 063505 (2012).

[11] D.T. Mackay, C.R. Varney, J. Buscher, F.A. Selim, *J. Appl. Phys.* **112**, 2 (2012).

[12] D.J. Robbins, B. Cockayne, B. Lent, C.N. Duckworth, J.L. Glasper, *Phys. Rev. B* **19**, 1254 (1979).

[13] V. Babin, K. Blazzek, A. Krasnikov, K. Nejezchleb, M. Nilk, T. Savikhina, S. Zazubovich, *Phys. Status Solidi C* **2**, 97 (2005).

[14] C.R. Varney, S.M. Reda, D.T. Mackay, M.C. Rowe, F.A. Selim, *AIP Adv.* **1**, 042170 (2011).

[15] F.A. Selim, C.R. Varney, M.C. Taurn, M.C. Rowe, G.S. Collins, M.D. McClusky, *Phys. Rev. B* **88**, 174102 (2013).