Formation energies of antisite defects in $Y_3Al_5O_{12}$: A first-principles study

Bo Liu, Mu Gu,[a] Xiaolin Liu, Shiming Huang, and Chen Ni
Laboratory of Waves and Microstructure Materials, Pohl Institute of Solid State Physics, Tongji University, Shanghai 200092, People's Republic of China

(Received 15 February 2009; accepted 6 March 2009; published online 27 March 2009)

We perform the first-principles calculations for the formation energies of cation antisite defects in $Y_3Al_5O_{12}$. This method provides precise values of formation energy and thus allows us to estimate the defect concentration. The calculations show that $Y_{Al,16a}$ is the most predominant antisite defects at high temperature for the single crystal growth and its concentration significantly decreases at low temperature for the single-crystalline film preparation. The calculated defect concentrations are quantitatively accord with the experimental estimation. Al_Y has high formation energy even with excess Al_2O_3, which indicates Al_Y is energetically unfavorable and the defect process is not intrinsic but nonstoichiometry. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3109799]

Garnet $Y_3Al_5O_{12}$ (YAG) is an important host material with various applications in laser materials,[1] scintillation materials,[2,3] and phosphors.[4] Recently, it is also found that rare-earth ion doped YAG phosphors[5] are promising near-infrared luminescent materials in fiber optical communication.[6,7] In the application of scintillator Ce-doped YAG, the presence of lattice defects are responsible for the reduced light yield and slow components that prevent this promising material from a practical scintillator despite it have been proposed for more than 10 years. Many evidences show that the cation antisite defects in YAG are the most important defects that could form shallow electron traps and thus degrade the scintillation preference.[8,9]

Experiments such as x-ray diffraction (XRD) (Ref. 10) and x-ray absorption fine structure[11,12] revealed the presence of cation antisite defects. Despite the antisite defects include Y_{Al} (Y^{3+} at Al^{3+} site) and Al_Y (Al at Y site), however, only Y_{Al} have been experimentally observed.[13] Single-crystalline films (SCF) (Ref. 14) of YAG prepared at rather low temperature (~1000 °C) exhibit the extremely low concentration of antisite defects compared with the single crystals (SCs) obtained from the melt at considerable high temperature (~2000 °C), which indicates that the antisite defects are strongly temperature dependent.

Several calculations based on the pair-potential simulation techniques were performed and found that the cation antisite defects could be energetically favorable though different values of formation energies were obtained in those individual studies.[15–17] Nevertheless, the pair-potential simulation used in the studies mentioned above is typically less reliable for the quantitative calculation than the first-principles calculation based upon the density functional theory.

Therefore, it is necessary to perform a more precise first-principles calculation of the formation energies for the antisite defects in YAG. In the present work, we obtain the formation energies of antisite defects taking into account the different chemical environments, and thus the defects concentration deduced from the obtained formation energies.

The density functional theory calculations within the local-density approximation were performed using plane-wave pseudopotential code ABINIT.[18,19] Norm-conserving Troullier–Martins[20] type pseudopotentials for Y, Al, and O were used. The electronic wave functions were expanded in plane waves up to a kinetic energy cutoff of 30 hartree. A unit cell has eight YAG molecules and 160 atoms. We optimized the lattice constant of the unit cell with the experimental data ($a=12.0$ Å) as initial input. The calculated result ($a=11.9$ Å) is highly consistent with the experimental one. Brillouin zone integrations were made with a $2\times2\times2$ k-point mesh generated according to the Monkhorst–Pack scheme. All the atoms were allowed to relax using the Broyden–Fletcher–Goldfarb–Shanno algorithm until the maximum residual force was less than 5 meV Å^{-1}. For the calculations of the formation energy, we adopt a primitive cell with 80 atoms considering the calculation burden, assuming that the interaction between antisite defects in different periodically repeated cells could be ignored.

Since in the crystal growth the Al_2O_3 and Y_2O_3 are the raw materials, the defect formation energy of Y_{Al} is referred to the energy required for a Y ion from Y_2O_3 into YAG and an Al ion from YAG to Al_2O_3, described by the following formula:

$$\tfrac{1}{2}Y_2O_3 + nY_3Al_5O_{12} \rightarrow \tfrac{1}{2}Al_2O_3 + (nY_3Al_5O_{12} - Al + Y_{Al}), \tag{1}$$

where $n=4$ and $(nY_3Al_5O_{12}-Al+Y_{Al})$ denotes the Y_{Al}-containing YAG cell.

Thus, the formation energy (ΔH_f) of Y_{Al} can be determined by total energy calculations,

$$\Delta H_f = E(d) - E(p) + \tfrac{1}{2}[E(Al_2O_3) - E(Y_2O_3)] + \tfrac{1}{2}(\mu_{Al_2O_3} - \mu_{Y_2O_3}), \tag{2}$$

where $E(d)$ is the total energy of antisite-defect-containing YAG cell and $E(p)$ is the total energy of perfect YAG cell. $E(Al_2O_3)$ and $E(Y_2O_3)$ are the total energies of corundum Al_2O_3 and cubic Y_2O_3, respectively. $\mu_{Al_2O_3}$ and $\mu_{Y_2O_3}$ are chemical potentials of Al_2O_3 and Y_2O_3, which reflect the chemical environment in growth process.

Similarly, the formation energy of Al_Y can be expressed by

[a]Electronic mail: mgu@tongji.edu.cn.

TABLE I. The formation energies of antisite defects in YAG.

Defects	Formation energies (eV) Y$_2$O$_3$ rich and Al$_2$O$_3$ poor $\mu_{Y_2O_3}$=0 and, i.e., $\mu_{Al_2O_3}$=−0.48 eV	Al$_2$O$_3$ rich and Y$_2$O$_3$ poor $\mu_{Al_2O_3}$=0 and, i.e., $\mu_{Y_2O_3}$=−0.8 eV
$Y_{Al,16a}$	1.232	1.872
$Y_{Al,24d}$	1.606	2.246
Al_Y	3.629	2.989

$$\Delta H_f = E(d) - E(p) + \tfrac{1}{2}[E(Y_2O_3) - E(Al_2O_3)] + \tfrac{1}{2}(\mu_{Y_2O_3} - \mu_{Al_2O_3}). \quad (3)$$

In order to maintain a stable YAG compound rather than other structure such as $YAlO_3$, the chemical potentials are restricted by the following equilibrium conditions:

$$\tfrac{5}{2}\mu_{Al_2O_3} + \tfrac{3}{2}\mu_{Y_2O_3} = \Delta H(Y_3Al_5O_{12}) \quad (4)$$

is the equilibrium condition for formation of YAG.

$$\tfrac{1}{2}\mu_{Al_2O_3} + \tfrac{1}{2}\mu_{Y_2O_3} \le \Delta H(YAlO_3) \quad (5)$$

is required to prevent the formation of $YAlO_3$.

$$\mu_{Al_2O_3} \le 0 \text{ and } \mu_{Y_2O_3} \le 0 \quad (6)$$

are also needed to prevent the deposit of Al_2O_3 and Y_2O_3, respectively.

The enthalpies of formation of ΔH(YAG) and $\Delta H(YAlO_3)$ from Al_2O_3 and Y_2O_3 are −1.2 and −0.025 eV, respectively. Considering Eqs. (4)–(6), therefore, the chemical potentials can be determined as $\mu_{Y_2O_3}$=0 eV and $\mu_{Al_2O_3}$=−0.48 eV for Y_2O_3 rich and Al_2O_3 poor, and $\mu_{Al_2O_3}$=0 and $\mu_{Y_2O_3}$=−0.8 eV for Al_2O_3 rich and Y_2O_3 poor, which correspond to the excess Y_2O_3 nonstoichiometry and Al_2O_3 nonstoichiometry, respectively.

Let us discuss the calculated formation energies for the antisite defects. There are two types of Y_{Al} antisite defects (noted as $Y_{Al,16a}$ and $Y_{Al,24d}$) corresponding to the two Al sites (the 16*a* octahedral site and the 24*d* tetrahedral site) in the ideal crystal structure of garnet, while there is only one Y site. As a consequence, we calculate three types of antisite defects, i.e., $Y_{Al,16a}$, $Y_{Al,24d}$, and Al_Y.

The formation energies of Y_{Al} and Al_Y are summarized in Table I. The formation energy of $Y_{Al,16a}$ is lower than that of $Y_{Al,24d}$ by 0.374 eV, and thus it is indicated that $Y_{Al,16a}$ is energetically more favorable than that of $Y_{Al,24d}$. This result is consistent with the previous experiential investigations[11,12] study and calculated results[15–17] by atomistic simulation. The formation energy is strongly dependent on the chemical potentials of Y_2O_3 and Al_2O_3, which clearly indicates that the formation energy of $Y_{Al,16a}$ is low with excess Y_2O_3 nonstoichiometry and becomes somewhat high with excess Al_2O_3 nonstoichiometry. It is interestingly found that Al_Y has a considerably high formation energy even with excess Al_2O_3 (2.989 eV), compared with that of $Y_{Al,16a}$ (1.872 eV). Such high formation energy of Al_Y suggests that the formation of Al_Y antisite defect is predicted to be quite unlikely. Therefore, it is suggested that $Y_{Al,16a}$ antisite defects are always predominant regardless excess Y_2O_3 or excess Al_2O_3. It is in good agreement with the fact that only Y_{Al} rather than Al_Y were observed.

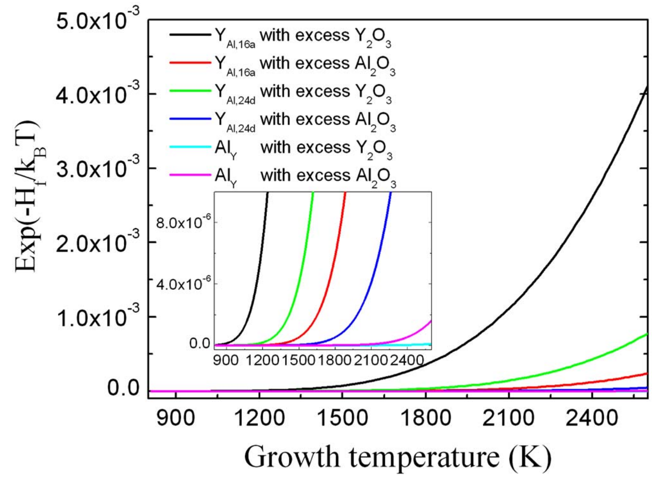

FIG. 1. (Color online) Percent concentration of antisite defects of $Y_{Al,16a}$, $Y_{Al,24d}$, and Al_Y with a function of growth temperature. The inset is a clear display at very small ordinate values.

The concentrations of native defects are mainly controlled by their formation energies and the growth temperature. Based on the precise formation energies by density functional method shown in Table I, we are allowed to estimate the equilibrium defect concentrations using the formalism by Zhang and Northrup as follows:[21]

$$[D] = N_{sites} \exp\left(-\frac{H_f}{k_B T}\right), \quad (7)$$

where $[D]$ represents the defect concentration, N_{sites} is the number of sites per unit volume of the YAG where antisite defects can be present, H_f is the formation energy, T is the growth temperature, and k_B is Boltzmann constant.

In the case of garnet, the values of N_{sites} for the formation of $Y_{Al,16a}$, $Y_{Al,24d}$, and Al_Y are 0.926, 1.39, and 1.39 $\times 10^{22}$ cm^{-3}, respectively. The percent concentrations [values of $\exp(-H_f/k_BT)$] of antisite defects, shown in Fig. 1, are plotted according to Eq. (7) and the calculated formation energies in Table I. The absolute concentrations could be easily obtained by multiplying with N_{sites}. The present calculated results predict that the percent concentration of $Y_{Al,16a}$ with excess Y_2O_3 reaches 0.185% when the samples are prepared from melt at 2000 °C, which is very close to the experimentally estimated value of 0.25%–0.5%.[22] At such high growth temperature, the percent concentration of $Y_{Al,24d}$ (0.0187%) is lower by one order of magnitude than that of $Y_{Al,16a}$. However, if the SCF samples prepared using liquid-phase epitaxy at low temperature of 1000 °C, the percent concentration of $Y_{Al,16a}$ is reduced to as small as 1.3 $\times 10^{-3}$%, which is hard to observe in experiment.[14]

It is very interesting that with excess Al_2O_3, the formation energies of $Y_{Al,16a}$ (1.872 eV) and $Y_{Al,24d}$ (2.246 eV) significant increase but still much lower than that of Al_Y (2.989 eV). This indicates that Y_{Al} antisite defect is always dominant and Al_Y is hard to form even with excess Al_2O_3 condition. It is consistent with the experimental results,[10] which show that with excess Al_2O_3, YAG and Al_2O_3 could coexist in sample and XRD measurement reveals the presence of Y-rich YAG. It could also be stated that Al-rich YAG is energetically unstable and tends to dissociate into Al_2O_3 and Y-rich YAG. Although with excess Al_2O_3, Y_{Al} is dominant with respect to Al_Y, the concentration of Y_{Al} is indeed decreased significantly since its relatively high formation energy.

It is also indicated from the present calculation that the percent concentration of Al_Y is very small and thus could be negligible even at high growth temperature of 2000 °C. This provides a clear explanation why the experiment cannot observe the presence of Al_Y.[13] Therefore, the concentrations of Y_{Al} and Al_Y are not equal. As a result, it is suggested that the defect process of antisite could not be intrinsic but a deviation from stoichiometry. The nonstoichiometry of YAG was experimentally demonstrated by Patel *et al.* using XRD measurements.[10]

In summary, the present calculated results indicate that the $Y_{Al,16a}$ rather than $Y_{Al,24d}$ is predominate at high temperature for SC growth. The calculated percent concentration of $Y_{Al,16a}$ with growth temperature of 2000 °C is consistent with the experimental estimate value and the concentration of $Y_{Al,16a}$ dramatically decreases to a very small value at 1000 °C. The formation of Al_Y antisite defect is unlikely even at very high growth temperature. It is suggested that Y_{Al} antisite defects could be removed by using low preparation temperature and thus the scintillation preference could be significantly improved. However, the application of SCF materials might be limited since the bulk SCs are required in many applications such as γ-ray detection in medical imaging or high energy physics experiment. Removing the antisite defects from YAG bulk SC is thus still an arduous and urgent task. Another alternative way to reduce Y_{Al} as possible is to prepare the sample with excess Al_2O_3. However, it might introduce the Al_2O_3 inclusions in the sample.

This work was supported by the National Natural Science Associated Foundation (NSAF) of China (Grant No. 10776024), the National Natural Science Foundation of China (Grant Nos. 50672068 and 10875085), the Shanghai Committee of Science and Technology (Contract No. 07DZ22302), and the Program for Young Excellent Talents in Tongji University.

[1]J. Dong, A. Shirakawa, K. Ueda, H. Yagi, T. Yanagitani, and A. A. Kaminskii, Appl. Phys. Lett. **89**, 091114 (2006).
[2]D. Solodovnikov, M. H. Weber, and K. G. Lynn, Appl. Phys. Lett. **93**, 104102 (2008).
[3]A. Moszynski, T. Ludziejewski, D. Wolski, W. Klamra, and L. Norlin, Nucl. Instrum. Methods Phys. Res. A **345**, 461 (1994).
[4]R. Kasuya, A. Kawano, T. Isobe, H. Kuma, and J. Katano, Appl. Phys. Lett. **91**, 111916 (2007).
[5]H. S. Jang, J. H. Kang, Y.-H. Won, S. Lee, and D. Y. Jeond, Appl. Phys. Lett. **90**, 071908 (2007).
[6]J. X. Meng, K. W. Cheah, Z. P. Shi, and J. Q. Li, Appl. Phys. Lett. **91**, 151107 (2007).
[7]J. X. Meng, J. Q. Li, Z. P. Shi, and K. W. Cheah, Appl. Phys. Lett. **93**, 221908 (2008).
[8]M. Nikl, Phys. Status Solidi A **202**, 201 (2005).
[9]M. Nikl, E. Mihokova, J. Pejchal, A. Vedda, Y. Zorenko, and K. Nejezchleb, Phys. Status Solidi B **242**, R119 (2005).
[10]A. P. Patel, M. R. Levy, R. W. Grimes, R. M. Gaume, R. S. Feigelson, K. J. McClellan, and C. R. Stanek, Appl. Phys. Lett. **93**, 191902 (2008).
[11]J. Dong and K. Lu, Phys. Rev. B **43**, 8808 (1991).
[12]C. Landron, S. Lefloch, M. Gervais, J. P. Coutures, and D. Bazin, Phys. Status Solidi B **196**, 25 (1996).
[13]Y. V. Zorenko, A. Voloshinovskii, V. Savhyn, T. Voznyak, M. Nikl, K. Nejezchleb, V. Mikhailin, V. Kolobanov, and D. Spasskii, Phys. Status Solidi B **244**, 2180 (2007).
[14]Y. Zorenko, V. Gorbenko, I. Konstankevych, A. Voloshinovskii, G. Stryganyuk, V. Mikhailin, V. Kolobanov, and D. Spassky, J. Lumin. **114**, 85 (2005).
[15]M. M. Kuklja, J. Phys.: Condens. Matter **12**, 2953 (2000).
[16]C. Milanese, V. Buscaglia, F. Maglia, and U. Anselmi-Tamburini, Chem. Mater. **16**, 1232 (2004).
[17]C. R. Stanek, M. R. Levy, K. J. McClellan, B. P. Uberuaga, and R. W. Grimes, Nucl. Instrum. Methods Phys. Res. B **266**, 2657 (2008).
[18]The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors (http://www.abinit.org).
[19]X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J. Y. Raty, and D. C. Allan, Comput. Mater. Sci. **25**, 478 (2002).
[20]N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[21]S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).
[22]Y. Zorenko, A. Voloshinovskii, I. Konstankevych, V. Kolobanov, V. Mikhailin, and D. Spassky, Radiat. Meas. **38**, 677 (2004).