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Antisite defect in nonstoichiometric yttrium aluminum garnet: Experimental and first-principles calculation

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Abstract

Antisite defects in nonstoichiometric yttrium aluminum garnet (YAG) were investigated systematically with experiments and first-principles calculation based on density functional theory. Transparent YAG ceramics with different deviations from stoichiometry have been prepared and the lattice constants increase with the increase of deviation. Calculations show that $Y_{Al,16a}$ is the most preferred antisite defect and the concentration of defects increases as the sintering temperature increased. High sintering temperature results in high concentration of Y_{Al} defects, however Y_{Al} defects may avoid secondary phase in Y_2O_3-rich YAG. It is found that formation energy of Al_Y antisite defect is very high, therefore the concentration of Al_Y antisite defects is very low even at high temperature. For Al_2O_3-rich YAG, it is impossible to avoid the formation of secondary phase. The deviation from stoichiometry has great influence on the transmittance and optical quality of transparent ceramics.

Keywords: Nonstoichiometry; Antisite defect; YAG; First principles; Transparent ceramics

1. Introduction

Yttrium aluminum garnet $Y_3Al_5O_{12}$ (YAG) is a well-known host material for solid-state lasers that has been studied for many years,[1–4] and shows a variety of applications in medicine, scientific research, and industries. Compared with YAG single crystal, transparent ceramics have attracted much attention for their excellent laser performance, low cost, large size, high doping concentration, and complex design structure.[5,6] Nowadays, many methods have been adopted to fabricate high quality RE:YAG transparent ceramics. In general, there are two typical methods: solid-state reactive sintering[6] and chemical precipitation with vacuum sintering.[7] It is believed that the composition distribution in transparent ceramics prepared with solid state reactive sintering is not homogenous compared with chemical precipitation method. On the other hand, for the chemical precipitation method, it is very important to choose a proper precipitating agent and control the pH value of the solution due to the different ionic depositing rates, which will result in the deviation from 3:5 for YAG in local sites.[8] Some researchers have done a few works to study the effects of pH values and aging time on the stoichiometry and transparency of transparent YAG ceramics.[9–11]

For optical applications, atomic scale defects may significantly affect the functional performance. It is well known that some native defects can be formed during the growth of YAG crystal. Previous investigations have found that the defects would act as shallow electron traps and affect the structure, scintillation performance, and other properties of pure and RE:YAG.[12–14] For this reason, a large number of researches have focused on the identification of the defects in YAG.[15–17] The crystal structure of YAG belongs to the space group of *I*a3d, which is shown as Fig. 1. In YAG structure, The Y atoms occupy the 24 (c) sites, the O atoms occupy the 96 (h) sites, and the Al atoms occupy the 16 (a) site and the 24 (d) sites. Among these defects, cation antisite defects are the predominant ones, as such $Y_{Al,16a}$ (Y on the 16a sites), $Y_{Al,24d}$ (Y on the 24d sites), and $Al_{Y,24c}$ (Al on the 24c sites). Extended x-ray absorption fine structure has indicated the existence of $Y_{Al,16a}$ antisites according to the bond lengths of Y–O.[18] Meanwhile, atomic

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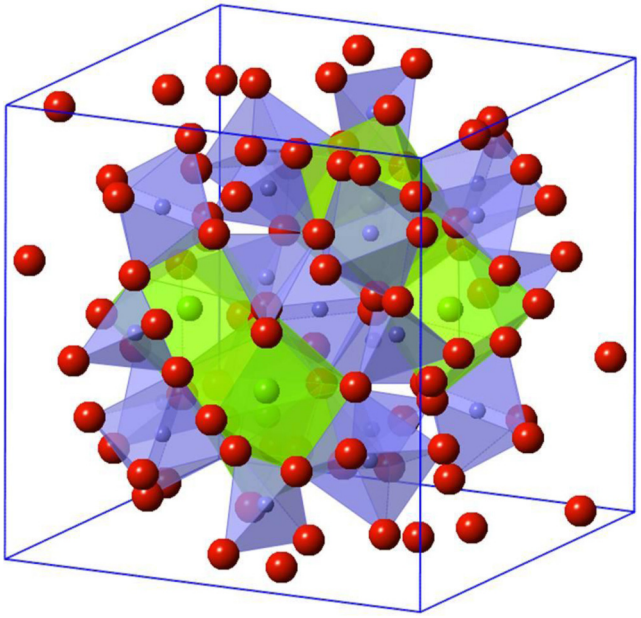

Fig. 1. The crystal structure of $Y_3Al_5O_{12}$ (space group: Ia3d, The Y atoms occupy the 24 (c) sites, the O atoms occupy the 96 (h) sites, Al atoms occupy the 16 (a) site and the 24 (d) sites).

simulations[19] have indicated that the formation energy of antisites in stoichiometry YAG is low, which means antisites are easily formed.

Generally, it is very difficult to prepare YAG single crystal with stoichiometry, though it is thought to be a line compound from the Y_2O_3–Al_2O_3 phase diagram.[20] Whereas, for ceramics, the composition of grain boundary is deviated from the core of grain and the pH values (and other factors) also affect the stoichiometry of YAG during the co-precipitation. That means nonstoichiometry with excess Y_2O_3 or Al_2O_3 exists in YAG ceramics. Excess Y_2O_3 nonstoichiometry has been certified to form single YAG structure by Y_{Al} antisites and dramatically increases the concentration of these electron traps.[21] Although, Al_Y antisites were not directly observed in Al_2O_3-rich YAG, they still could be found through the analysis of antisite in stoichiometry YAG. So the presence of nonstoichiometry antisites in nonstoichiometry YAG is accepted. Some results have been obtained from experiments and simulations.[9,11,13,22] Sang et al.[22] studied the nonstoichiometry antisites in YAG nanoparticles by neutron and X-ray diffraction and did not find apparent antisites when the synthesis temperature is too low and the deviation of some samples is also too large. Patel et al.[13] studied the mechanisms of nonstoichiometry in YAG based on pair-potential simulations. The specific effects with limited deviation from stoichiometry need more investigation. As we know, the pair-potential simulation is less reliable for quantitative calculation than first-principles calculation based on the density functional theory. Therefore, a more precise first-principles calculation is needed to understand the effect of deviation in YAG crystal. Here, we studied the specific effects of deviation from stoichiometry in YAG ceramics by experimental investigation and first-principles calculations. It not only indicates the existence of nonstoichiometry antisites, but also shows the effects of defects on the YAG ceramics.

2. Experimental and calculation details

2.1. Experiments

High-purity α-Al_2O_3 (99.99%, Alfa Aesar Company) and Y_2O_3 (99.99%, Alfa Aesar Company) were used as the raw materials. These powders were blended with different Y/Al stoichiometric ratio (sample number 1–10: 0.5917, 0.5943, 0.5967, 0.5981, 0.5990, 0.5595, 0.6000, 0.6008, 0.6016, 0.6032, respectively) and ball milled with high-purity ZrO_2 balls for 12 h in ethanol, with 0.5 wt% tetraethyl orthosilicate (TEOS, 99.999%, Alfa Aesar Company) added as sintering aid. Then, the alcohol solvent was removed by drying the milled slurry at 90 °C for 12 h in oven. The dried powder mixture was sieved through 200 mesh screen. The mixed powders were dry-pressed into Φ15 mm with the pressure of 15 MPa and cold isostatically pressed at 200 MPa. The green pellets were preheated at 800 °C for 4 h in air to expel any organic materials. The pellets were sintered at 1780 °C for 10 h under high vacuum (1×10^{-5} Pa). The heating rate was 5 °C/min, and the cooling rate was 40 °C/min. After sintering, the pellets were annealed at 1450 °C for 10 h in air. And then the samples were mirror-polished on both surfaces.

Phase identification was performed via X-ray diffraction (XRD, D/max-2550, Rigaku CO., Tokyo, Japan). Microstructure of the raw powders and samples were determined by a field scanning electron microscopy (FESEM, LEO-1530, Carl Zeiss Co., Oberkochen, Germany). The density (up to 99.9%) of the samples was measured by the Archimedes method, using deionized water as the immersion medium. The density over 99.9% was determined by SEM images. Optical transmittance was determined by a Spectrophotometer (Lambda 950, Perkin-Elmer, America).

2.2. Calculation details

The calculations of formation energy at zero temperature were performed using the pseudo-potential plane-wave method within the framework of the density functional theory and implemented through the Cambridge Serial Total Energy Package (CASTEP) Program.[23] Vanderbilt-type ultra-soft pseudo-potentials[24] are employed to describe the electron–ion interactions. The effects of exchange correlation interaction are treated with local density approximation (LDA) of CA-PZ.[25] In YAG conventional unit cell, there are 160 atoms, so the electronic wave functions were expanded up to plane-wave cut-off energy of 600 eV. Pseudo-atomic calculations are performed for $O2s^2 2p^4$, $Al3s^2 3p^1$ and $Y4s^2 4p^6 4d^1 5s^2$. For the Brillouin zone sampling, the $6 \times 6 \times 6$ Monkhorst-Pack mesh[26] is adopted, where the self-consistent convergence of the total energy is at 1×10^{-5} eV/atom and the maximum force on the atom is below 0.01 eV/Å. Before energy calculations, all geometry optimizations have been performed.