

Formation energies of point defects in Ti-doped YAG crystals: first-principles calculations

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Introduction

Yttrium aluminum garnet (YAG) is widely used in optics. When doped with various elements, YAG finds application in solid-state lasers and other optical devices, with impurities exerting a significant influence on its physical and optical properties.

Titanium is one of the less-studied YAG impurities. Nevertheless, several experimental studies suggest that Ti-doped YAG holds promise for practical applications. For instance, in work [1], it was found that Ti:YAG ceramics retain high optical quality after annealing in vacuum. Three absorption peaks were observed at wavelengths of 400, 498 and 586 nm, along with intense photoluminescence at 775 and 810 nm. Ceramics demonstrated transmittance of 70-80% in the visible light region and up to 80% in the infrared region. These findings led to the conclusion that this ceramic could be suitable for lasers. Similar results were reported for the YAG crystal grown in slightly reducing atmosphere [2]. It is reported in [1] for ceramic annealed in air and in [2] for crystals grown under oxidizing atmosphere that such samples had a larger number of inclusions.

The presence of Ti increases the gain of Nd:YAG laser crystals grown under reducing conditions and annealed in hydrogen or vacuum, according to [3]. At the same time, the associated increase in losses at 1064 nm is relatively minor compared to the gain. This makes Ti-doped YAG a potential candidate for pulsed laser systems. Furthermore, study [4] revealed that Ti impurities suppress the long-lived transient absorption observed in pure Nd:YAG. This absorption is known to cause thermal deformation of laser rods, which limits output power at higher pump levels. Therefore, Ti doping may also contribute to improved thermal stability in Nd:YAG-based lasers.

In all these works, the observed effects are attributed to Ti³⁺ ions. It is assumed in work [1] that oxidizing conditions cause greater number Ti⁴⁺ substitutions which imposes a stronger lattice distortion stress and can be the reason for new phases formation.

According to the experimental data presented above, it is of particular interest to investigate the properties of defects formed in Ti:YAG using the density functional theory (DFT) method. We present the results of a theoretical study of properties of point defects in the Ti:YAG crystal based on DFT calculations. The goal of this work is to find the predominant defects in Ti:YAG under different synthesis conditions and to determine the distribution of Ti among different types of defects.

Calculation methods

Defect formation energy calculations were performed using the SIESTA software package [5]. Pseudopotentials are generated with the Optimized Norm-Conserving Vanderbilt Pseudopotential (ONCVSP) approach [6].

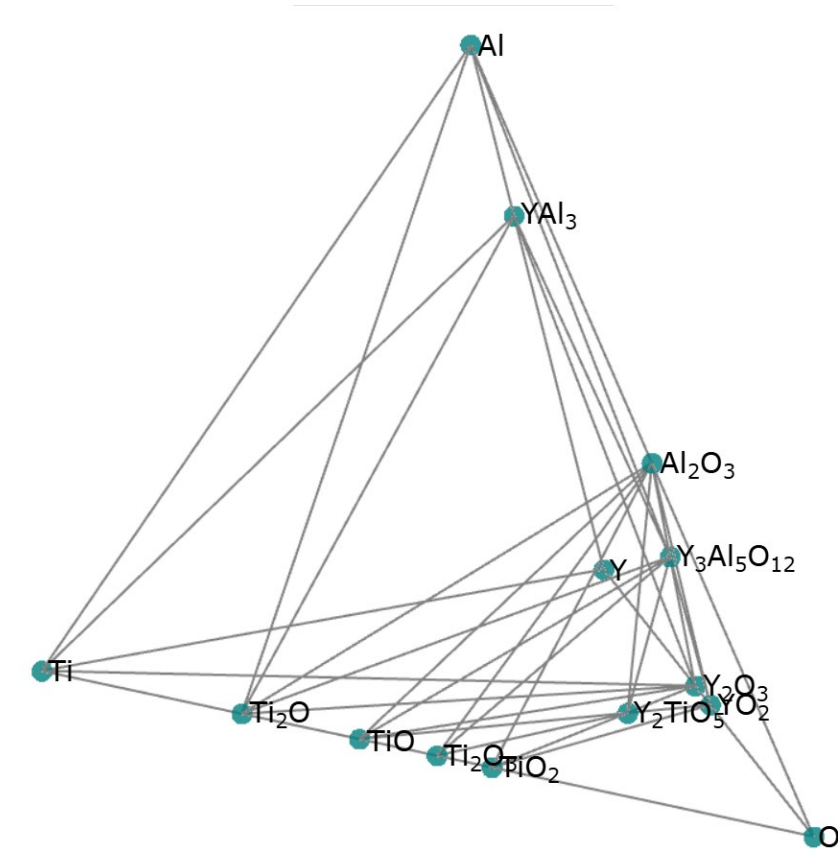
Formation energy of i-type defect is given by the equation[7,8]:

$$E_i = E_{def,i} - E_{perf} - \sum_x \mu_x p_{x,i} + \mu_e q_i + E_i^{(c)},$$

where $E_{def,i}$ is the total energy of a cell with i-type defect, E_{perf} is the total energy of a cell without any defects, μ_x and $p_{x,i}$ are the chemical potential and the number of x-type atoms that are added to (in such case $p_{x,i}$ is positive) or are removed from ($p_{x,i}$ is negative) cell, μ_e is the electron chemical potential, q_i is the defect electrical charge in elementary charge units, $E_i^{(c)}$ is the correction that excludes electrostatic interaction caused by periodic copying of charged defects in the calculations.

To calculate the chemical potentials of atoms, the formation energies of pure compounds consisting of the elements Ti, Y, Al, O were calculated. Structure data of compounds were taken from OQMD [9]. Based on formation energies data, the corresponding Ti-Y-Al-O phase diagram was constructed.

Figure 1. Ti-Y-Al-O phase diagram.



10 equilibrium points were taken for consideration from phase diagram:

- YAG, Al₂O₃, Al, Ti₂O;
- YAG, Al₂O₃, Ti₂O, TiO;
- YAG, Al₂O₃, TiO, Ti₂O₃;
- YAG, Al₂O₃, TiO, Y₂TiO₅;
- YAG, Al₂O₃, Ti₂O₃, Y₂TiO₅;
- YAG, Al₂O₃, Y₂TiO₅, YO₂;
- YAG, Y₂O₃, YAl₃, Ti₂O;
- YAG, Y₂O₃, Ti₂O, TiO;
- YAG, Y₂O₃, TiO, Y₂TiO₅;
- YAG, Y₂O₃, Y₂TiO₅, YO₂.

We considered the sum of the chemical potentials of the atoms in each compound to be equal to the chemical potential of that compound. And the system of such equations was solved for each equilibrium point.

Calculation methods

Concentration of Ti (in atomic percentage related to Al concentration) is given by the equation:

$$n_{Ti,i} = \frac{N_i}{N_{Al}} \exp\left(-\frac{E_i}{k_B T}\right) \cdot 100\%,$$

where N_i is the number of ways to place a given defect in the unit cell (different orientations of complex defects are considered as different ways), N_{Al}=40 is the number of Al atoms in the YAG unit cell. The temperature value was chosen to be 2023K, which corresponds to the sintering temperature of YAG ceramics.

To calculate the concentrations of defects the charge neutrality equation were solved for each equilibrium point.

Results and discussion

According to our calculations, Ti atoms enter into the crystals mainly in the form of Ti_{Al} substitutional defects. Ti can be in the Ti³⁺ and Ti⁴⁺ valence states (that corresponds to electrically neutral defects and charged defects with q=+|e|). A part of Ti_{Al} defects form complexes with each other and with cation vacancies (V_{Al}³⁻ and V_Y³⁻).

Under reducing conditions, Ti_{Al} substitutional defects are mainly Ti_{Al}⁰ defects, and under oxidizing conditions – Ti_{Al}¹⁺ (as shown on Figures 2,3, at.% means the ratio of the number of Ti atoms to the number of Al atoms). This finding is in agreement with the assumptions made in [1].

The dominance of substitution defects with titanium with a 4+ charge can be explained, among other things, by the fact that under oxidizing conditions a smaller number of positively charged defects and a larger number of negatively charged defects are formed, which makes it more energetically favorable to form substitution defects with titanium with a larger positive charge to ensure charge balance.

The properties we found are similar to those previously discovered for the laser material Ti:Al₂O₃ [10,11].

Results and discussion

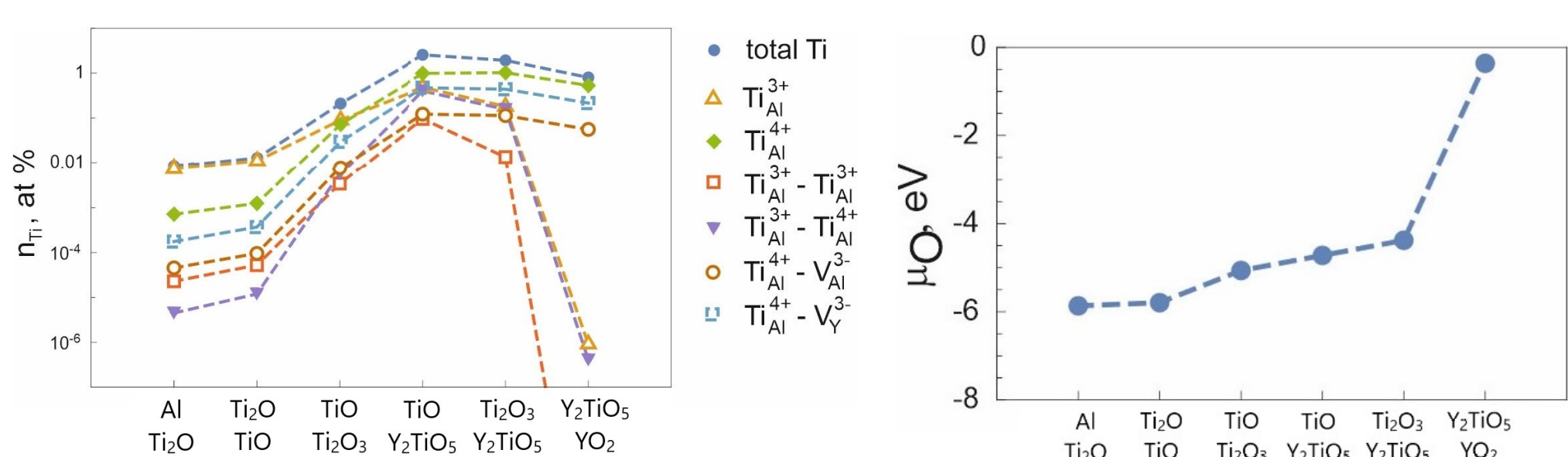


Figure 2. Ti concentration for YAG-Al₂O₃-X-Y equilibrium points (left) and oxygen chemical potential for these equilibrium points (right) (X and Y are the compositions indicated along the horizontal axis).

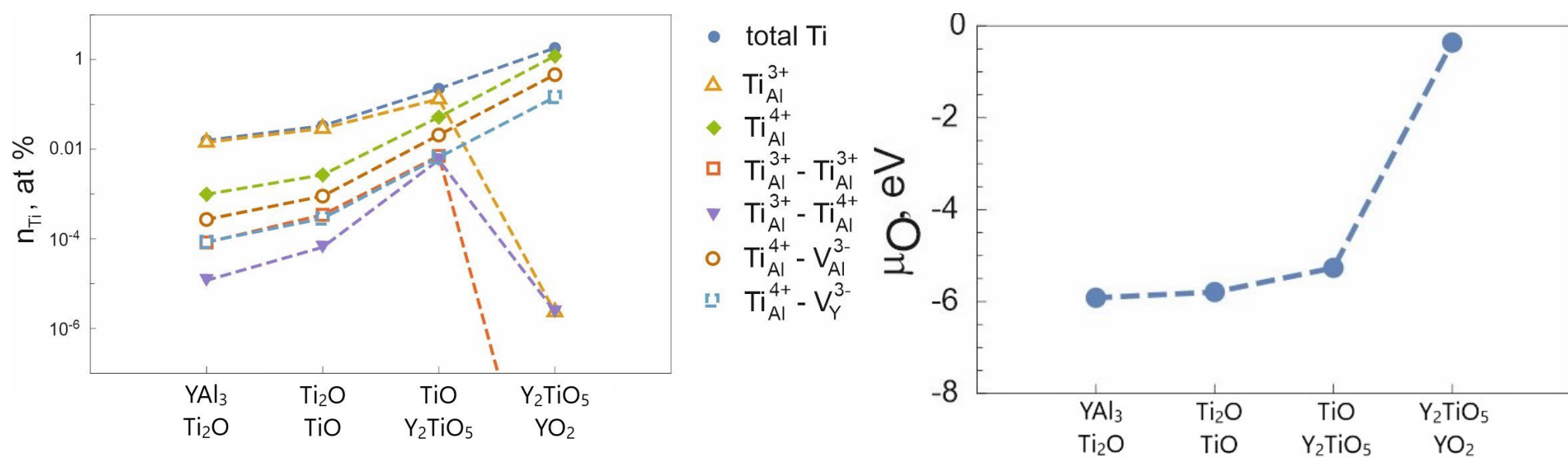


Figure 3. Ti concentration for YAG-Y₂O₃-X-Y equilibrium points (left) and oxygen chemical potential for these equilibrium points (right) (X and Y are the compositions indicated along the horizontal axis).

Conclusions

1. The highest equilibrium concentration of Ti is reached under intermediate and oxidizing conditions. In this case Ti is predominantly in the 4+ valence state and the ratio of isolated Ti_{Al}¹⁺ substitution defects and defects bound in pairs with cation vacancies is 2:1, i.e. such complexes play the role of charge compensator for defects Ti_{Al}¹⁺.

2. Under reducing conditions, the equilibrium concentration of Ti is two orders of magnitude smaller, but almost all Ti is in the 3+ valence state. In contrast, under oxidizing conditions, the concentration of Ti³⁺ is vanishingly small.

3. The relative fraction of Ti-Ti complexes becomes noticeable only under intermediate conditions.

4. Doping of Ti leads to an increase in the concentration of free cationic vacancies under reducing conditions, and a decrease in their concentration under oxidizing conditions. At the same time, the total concentration of such vacancies in oxidizing conditions increases.

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