

# Modeling charge-state evolution of point defects in YAG from growth temperature to room temperature

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## Introduction

Yttrium aluminum garnet (YAG) is widely used in optics. Point defects, both native and impurity, play a significant role in its physical and optical properties. Although defect formation mechanisms, characteristics, and effects in YAG have been extensively studied ([1,2] and references therein), a comprehensive understanding of the stability of defect charge states and their evolution under varying growth and thermal conditions remains incomplete. In particular, the interplay between defect energetics, charge-state transitions, and defect concentrations during cooling from high-temperature synthesis requires further investigation.

The distribution of defect charge states depends on the differences in their formation energies and on temperature. Equilibrium charge-state populations at room temperature may differ substantially from those at crystal-growth temperatures. In addition, at the crystal-growth temperature equilibrium concentrations of electrons and holes are comparable to the concentrations of defects, and they make a significant contribution to the charge-neutrality equation. Upon cooling, free carrier concentrations decrease exponentially. Thus, cooling alters the relative populations of charge states while approximately preserving the total concentration of each structural defect. This recharging process shifts the Fermi level and results in a new low-temperature equilibrium in which charge neutrality is ensured primarily by oppositely charged defects rather than by free carriers.

This work quantitatively investigates cooling-induced charge transfer between native defects and its effects on defect charge states, the Fermi-level position, and charge neutrality in YAG.

## Calculation methods

Defect formation energy calculations were performed using the SIESTA software package [3]. Pseudopotentials are generated with the Optimized Norm-Conserving Vanderbilt Pseudopotential approach [4].

Formation energy of i-type defect is given by the equation[5,6]:

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

where  $E_{def,i}$  is the total energy of a cell with i-type defect,  $E_{prist}$  is the total energy of a cell without any defects,  $\mu_x$  and  $p_{x,i}$  are the chemical potential and the number of x-type atoms that are added to ( $p_{x,i} > 0$ ) or are removed from ( $p_{x,i} < 0$ ) cell,  $\mu_e$  is the electron chemical potential,  $q_i$  is the defect electrical charge (in units of  $|e|$ ),  $E_i^{(c)}$  is the correction that excludes electrostatic interaction caused by periodic copying of charged defects in the calculations.

## Calculation methods

Calculations were performed for the  $Al_2O_3$ -rich and  $Y_2O_3$ -rich conditions. The formation energies of defects under these conditions differ only slightly for most defects. In the following, **we present results for crystals grown in the  $Y_2O_3$ -rich environment**. To calculate the chemical potentials of atoms, the formation energies of  $Y_2O_3$  and Al were calculated. Structure data of compounds were taken from OQMD [7] and then optimized with SIESTA.

We considered the oxygen chemical potential varying from reducing conditions to oxidizing conditions.

The Madelung correction  $E_i^{(c)}$  is evaluated by using the method proposed in [8, 9] and applied in [10]. Specifically, we calculated the defect total energy  $E_{def,i}$  for the cubic unit cell and for two supercells (2 X 1 X 1) and (3 X 1 X 1) and extrapolate of this dependence to an infinite cubic cell. The obtained correction can be approximated by the general expression  $E_i^{(c)} \approx \alpha q^2$ , where  $\alpha = 0.13$  eV for simple defects and  $\alpha = 0.16$  eV for defect complexes.

Electronic band-structure calculations were performed using the Quantum ESPRESSO package [11] with the hybrid PBE0 exchange–correlation functional. Our calculations with a modified PBE0 with a mixing parameter of 0.32 yield  $E_g^{PBE0(m)} = 7.7eV$ , compared to the PBE functional result  $E_g^{PBE} = 4.58eV$ , with a downward shift of the valence-band maximum of  $\Delta E_{VBM} = 2.0eV$  and an upward shift of the conduction-band minimum of  $\Delta E_{CBM} = 1.1eV$  relative to the PBE values. The relative magnitudes of the downward and upward band-edge shifts follow a similar proportion, approximately  $\Delta E_{VBM}/\Delta E_{CBM} \approx 0.65/0.35$ . The band-structure calculations performed with the PBE functional using SIESTA yielded a band gap of  $E_g^{PBE} = 4.45eV$ . In the present work, we adopt this ratio for SIESTA and apply a rigid correction to achieve  $E_g = 7.7eV$ .

Equilibrium concentrations of defects are given by equation:

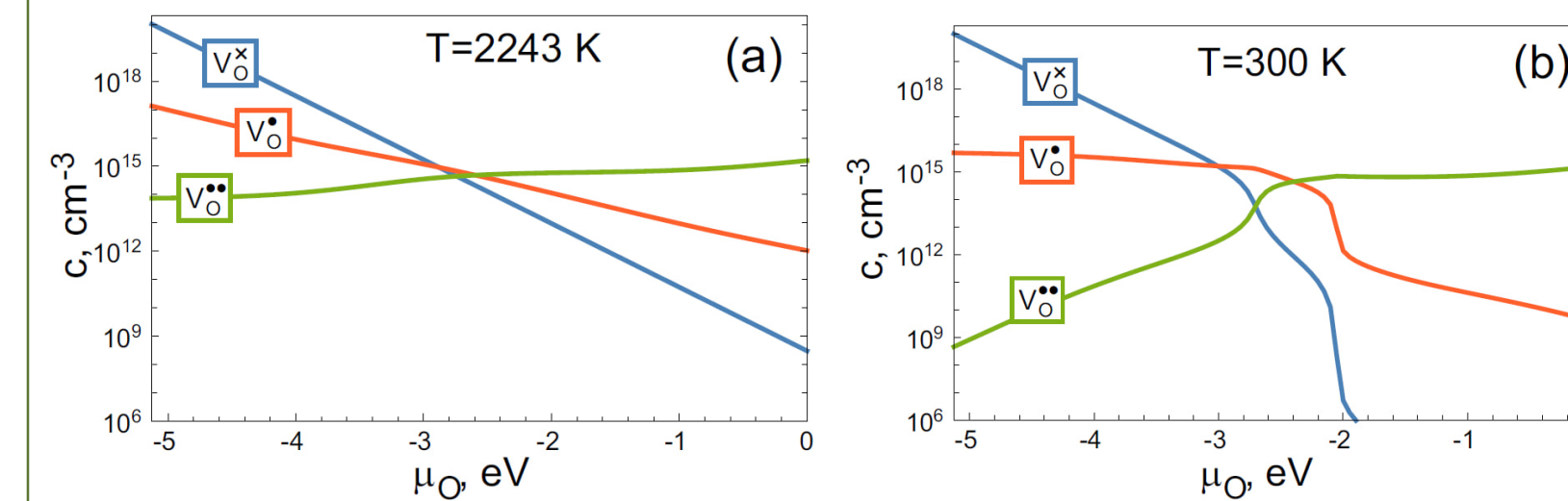
$$c_i = \frac{N_i}{V} \exp\left(-\frac{E_i}{k_B T}\right),$$

where  $N_i$  is the number of ways to place a given defect in the unit cell,  $V$  is the volume of the YAG unit cell.

To model the evolution of the charge states of point defects, we impose constraints on the concentrations of defect species summed over different charge states but do not fix their concentration for each charge state.

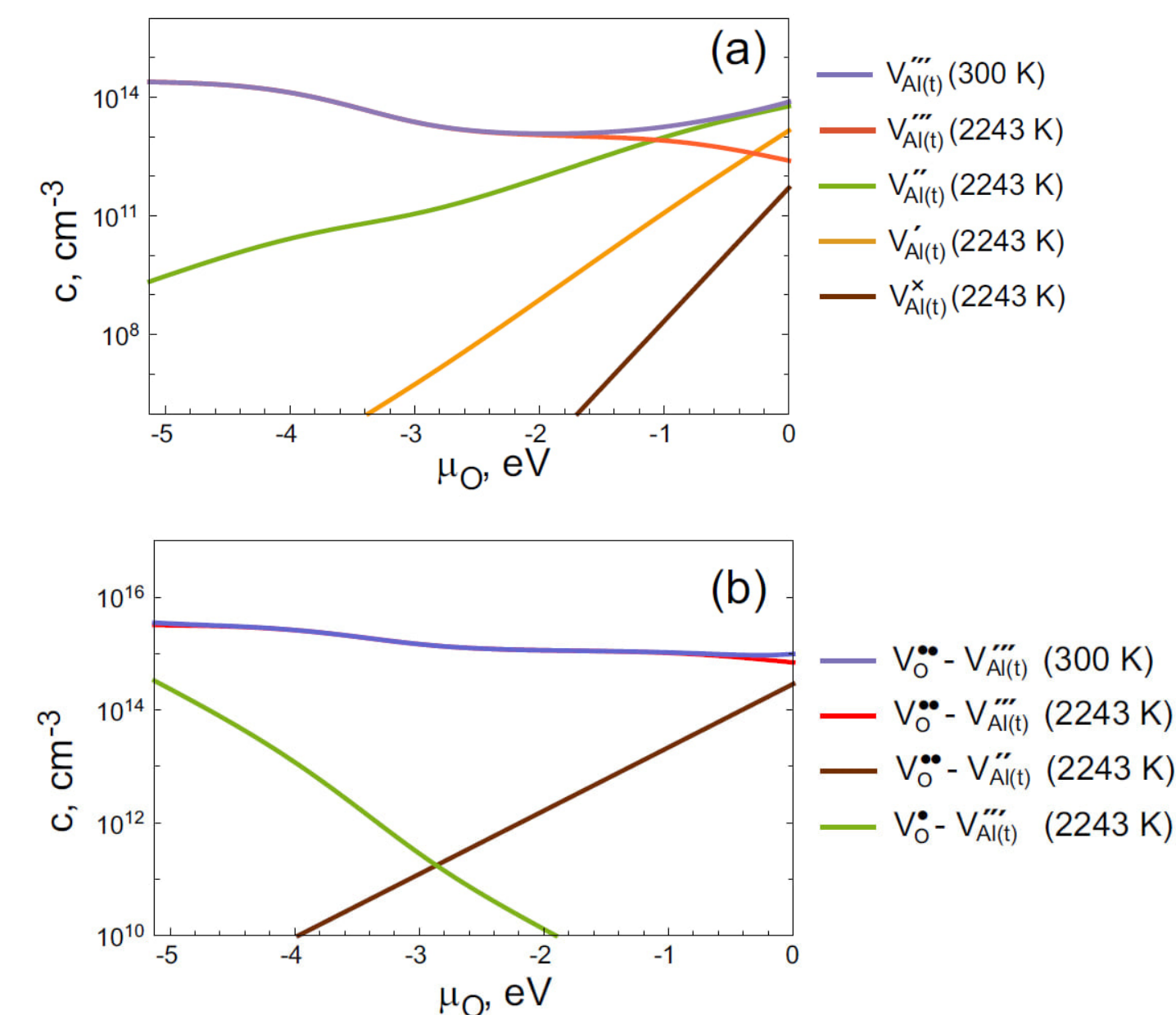
## Results and Discussion

Figure 1 indicates that charge transfer during cooling leads to a reduction in the concentration of  $V_O^{\bullet\bullet}$  defects in YAG grown under reducing conditions and to a reduction in the concentration of  $V_O^{\times}$  defects in YAG grown under oxidizing conditions. It is found that the oxygen interstitial defects in the charge states  $O_i^{\bullet}$  and  $O_i^{\times}$  disappear upon cooling in crystals grown under reducing conditions in similar way.



**Figure 1.** Concentrations of oxygen vacancies in different charge states at growth temperature (a) and at room temperature (b).

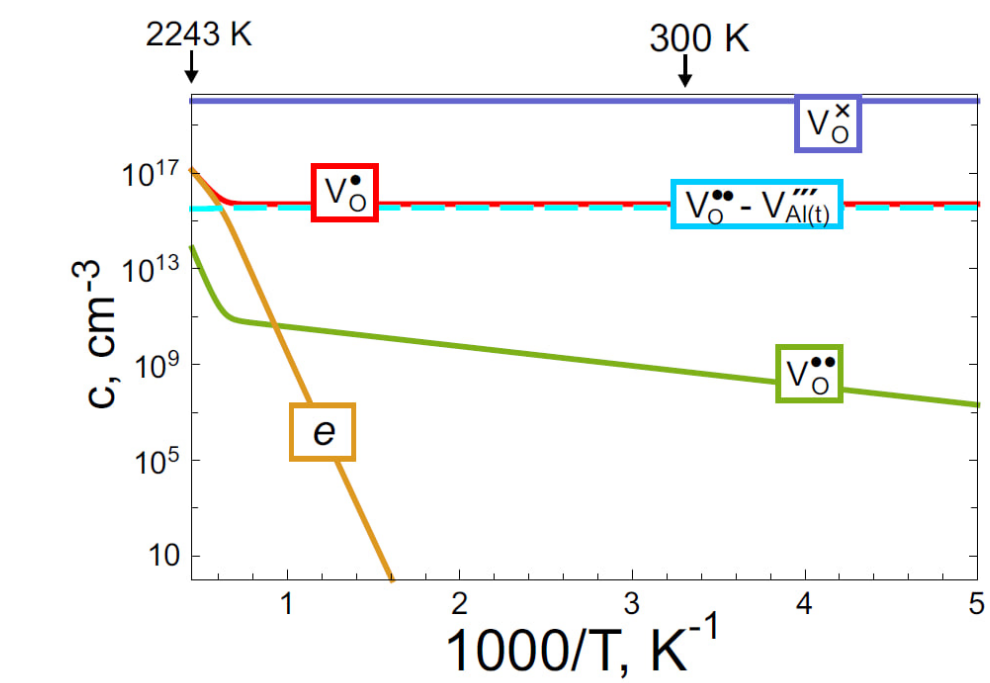
Figure 2 shows that only the charge states  $V_{Al}^{\bullet\bullet}$ , and  $V_O^{\bullet\bullet} - V_{Al}^{\bullet\bullet}$  remain populated upon cooling to room temperature.



**Figure 2.** Concentrations of Al (a) and complexes of Al and O vacancies (b) in different charge states at growth temperature and at room temperature.

## Results and Discussion

In Figure 3, we present the evolution of the charge states of oxygen vacancies and free electrons upon cooling in YAG grown under reducing conditions ( $\mu_O = \mu_O^{\min}$ ). At  $T < 1000$  K the charge neutrality condition is mainly maintained by the balance between the concentrations of  $V_O^{\bullet}$  and  $V_O^{\bullet\bullet} - V_{Al}^{\bullet\bullet}$  complexes.



**Figure 3.** Evolution of the concentrations of  $V_O$ , free electrons, and complexes of  $V_O$  with  $V_{Al}$  during cooling from the crystal-growth temperature to  $T = 200$  K in YAG grown under reducing conditions.

In crystals grown under oxidizing conditions, charge neutrality is maintained by the balance between  $V_O^{\bullet\bullet}$  vacancies,  $O_i^{\bullet}$  interstitial defects, and the complexes  $V_O^{\bullet\bullet} - V_{Al}^{\bullet\bullet}$ . The concentration of free holes drops from  $10^{15} cm^{-3}$  at growth temperature to negligible values upon cooling. The association of  $V_O$  with  $V_{Al}$  occurs under both reducing and oxidizing conditions, and such complexes play the major role in charge compensation at room temperature.

## Conclusions

**1.** Shown, that charge neutrality upon cooling is increasingly maintained through charge transfer between defect centers. In this process electrons or holes are captured by defects, which leads to a redistribution of defect populations among their possible charge states while the total concentration of each structural defect remains approximately constant.

**2.** Cooling leads to a strong stabilization of only a limited number of charge states for each defect type. Other charge states that are populated at high temperatures become strongly suppressed at room temperatures.

**3.** The presence of a significant number of  $V_{Al}$  and complexes of  $V_{Al}$  with  $V_O$  at room temperature yielded a result that is in good agreement with the experimental data [1,2,12,13], suggesting that such defects are predominantly in the specified charge state.

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