Prediction of Order-disorder Transition Temperature of δ-Bi_2O_3 by Systematic First-principles Calculations

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δ-Bi_2O_3 with a defective fluorite structure represents a good oxygen conductivity of nearly 1 S/cm at high temperatures [1]. However, the phase transition to α-phase involves a dramatic decrease of the oxide ion conductivity. Although some rare-earth-alloyed Bi_2O_3 keeps the cubic-phase even at room temperature, they show much lower conductivity at room temperature with the deflection of ionic conductivity than that can be expected by a simple Arrhenius extrapolation of the high temperature data [2]. This has been ascribed to the ordering of the oxygen sublattice. Therefore, the prediction of the order-disorder transition is a key issue to utilize the high conductivity for practical applications. In this work, we propose an efficient procedure based on systematic first-principles calculations to predict the order-disorder transition temperature T_c. Then we apply the method to the prediction of the order-disorder temperature in rare-earth-alloyed Bi_2O_3.

In the proposed method, free energies of ordered and disordered structures are approximately evaluated for predicting the transition temperature. The ordered structure is explored using an idea of "special structures", which is based on the cluster expansion method. The internal energy of the disordered structure is evaluated by averaging internal energies of random structures with a large supercell. The entropy of the disordered structure is expressed with the point approximation.

Firstly, we compare the internal energies of "special structures" with those of all possible configurations within a supercell to demonstrate the predictive power of "special structures" search. Figure 1 shows the internal energies of "special structures" and all possible configurations in undoped Bi_2O_3. As can be seen in Fig. 1, the structure with minimum energy is included in the special structures, hence the ground state structure can be obtained by the calculations only for special structures. Using the energy of the ground state structure, T_c is predicted to be 1070 K. It is close to the experimental β-δ transition temperature of around 900 K, which can be regarded as the order-disorder temperature [3]. This result implies that our procedure is a good approximation to predict T_c.

Then, we predict the order-disorder temperatures in rare-earth-alloyed Bi_2O_3. Figure 2 shows the concentration dependence of the predicted T_c in the Bi_2O_3-Gd_2O_3 system. The reported deflection point of ionic conductivity [4] is regarded as the experimental T_c. The predicted T_c is consistent with the experimental ones. Also in the other rare-earth-alloyed Bi_2O_3, the prediction of T_c agrees with experiments. These results support the presumption that the deflection of ionic conductivity of rare-earth-alloyed Bi_2O_3 is ascribed to the order-disorder transition of the oxygen sublattice.

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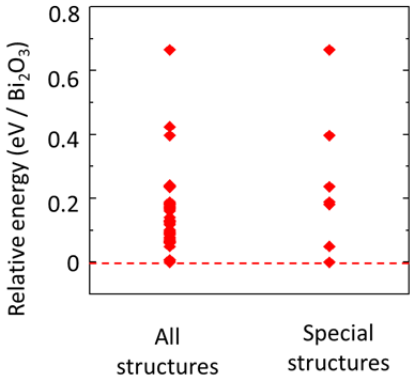

Fig. 1. The energy of undoped Bi_2O_3. Left is for all structures and right is only for the special structures.

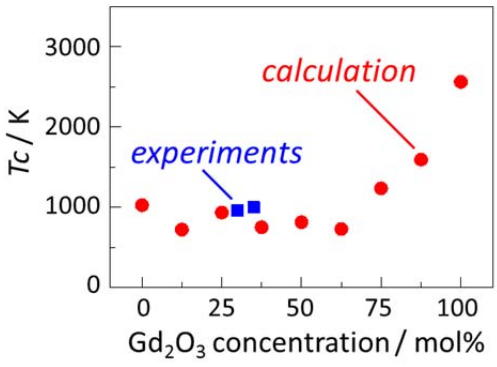

Fig. 2. Predicted order-disorder transition temperature T_c of Bi_2O_3-Gd_2O_3. Squares are deflection point of ionic conductivity.