

First-Principles calculation of defect energetic in BaTiO₃ and SrTiO₃ : a possible relationship to grain growth behavior

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BaTiO₃ and SrTiO₃ are known to exhibit abnormal grain growth. Since electrical properties of these materials are strongly depend on the size and distribution of grain, the grain growth behavior of BaTiO₃ and SrTiO₃ have been extensively studied. Recent investigations have suggested the concentration of vacancies plays an important role in grain boundary morphology and grain growth behavior [1]. It is reported that Ti-excess BaTiO₃ specimen sintered in air show abnormal grain growth but same specimen sintered in H₂ atmosphere show normal grain growth [2]. So in this study, the defect formation energy in BaTiO₃ was calculated and compared with previously reported that in SrTiO₃ [3], and the relationship between the defect formation energetics and grain growth behavior will be discussed [4].

In this study, the formation energies of intrinsic vacancies in cubic-BaTiO₃ were studied by using a first-principles plane-wave-based pseudopotential using VASP code within local density approximation (LDA). The defect formation energies of neutral and charged vacancies are estimated by following equation with a charge state q :

$$E_f = E_T(\text{defect};q) - \{E_T(\text{perfect}) - n_{\text{Ba}}\mu_{\text{Ba}} - n_{\text{Ti}}\mu_{\text{Ti}} - n_{\text{O}}\mu_{\text{O}}\} + q(\varepsilon_F + E_{\text{VBM}}) \quad (1)$$

where $E_T(\text{defect};q)$ and $E_T(\text{perfect})$ are total energy of the supercell containing a vacancy and that of perfect supercell, respectively, n_{Ba} , n_{Ti} and n_{O} are the numbers of Ba, Ti, and O atoms removed from the perfect supercell. μ_{Ba} , μ_{Ti} and μ_{O} are the atomic chemical potentials, and ε_F is the Fermi energy measured from the VBM. The chemical potential of each element was calculated in a schematic phase diagram in Figure 1. The following reactions are considered: V_{O}^0 , V_{Ba}^0 , V_{Ti}^0 (electronic compensation), $V_{\text{Ba}}^{2-} + V_{\text{O}}^{2+}$, $V_{\text{Ti}}^{4-} + 2V_{\text{O}}^{2+}$ (Partial Schottky reactions), and $V_{\text{Ba}}^{2-} + V_{\text{Ti}}^{4-} + 3V_{\text{O}}^{2+}$ (Schottky reaction).

Figure 2 shows the defect formation energy of BaTiO₃ changing oxygen chemical potential. B,C,D, points in schematic phase diagram correspond to Ti rich condition and G, A points is Ba-rich condition. In oxidizing condition, $V_{\text{Ba}}^{2-} + V_{\text{O}}^{2+}$ Schottky defect formation energy is lower than other defect reaction and in reducing atmosphere V_{O} is the lowest defect formation energy. Moreover, the defect formation energy V_{O} in reducing atmosphere is lower than $V_{\text{Ba}}^{2-} + V_{\text{O}}^{2+}$ Schottky defect formation energy in oxidizing condition. This result seems to be consistent with the grain growth behavior results of Ti excess BaTiO₃ in different atmosphere.

To compare the defect formation energy in BaTiO₃ and SrTiO₃, the defect formation energy of BaTiO₃ as solid line and SrTiO₃ as dashed line plotted in Figure 3. The mean value of the lowest defect formation energy in BaTiO₃ is 2.48eV and that of SrTiO₃ is 2.03eV. Since the defect formation energy of $V_{\text{Sr}}^{2-} + V_{\text{O}}^{2+}$ in SrTiO₃ is lower than that of $V_{\text{Ba}}^{2-} + V_{\text{O}}^{2+}$ in BaTiO₃, overall dominant defect formation energy in SrTiO₃ is lower. This difference can explain the experimental difference of the grain growth behavior between BaTiO₃ and SrTiO₃. That is, BaTiO₃ preferentially exhibits abnormal grain growth compared SrTiO₃ because the cocentration of the vacancies in BaTiO₃ is less than SrTiO₃.

In summary, the defect formation energy of intrinsic vacancies in BaTiO₃ is calculated using first-principles. The results obtained in this study can be summarized as following:

1. The lowest defect formation energy, V_O in reducing atmosphere is lower than V_{Ba}²⁻ + V_O²⁺ in oxidizing condition. It is consistent with the experiment result that normal grain growth occurs in H₂ atmosphere and abnormal grain growth do in air.
2. The overall defect formation energy in SrTiO₃ is lower than that in BaTiO₃ because the defect formation energy of V_{A(Sr, Ba)}²⁻ + V_O²⁺ is lower in SrTiO₃ than in BaTiO₃.

For further understandings of grain growth behavior, the consideration of other factors such as temperature, the existence of 2nd phase, twin, dopant also is necessary. However, it was found that the difference of the defect formation energetics between BaTiO₃ and SrTiO₃ can explain the difference of the grain growth behaviors.

References

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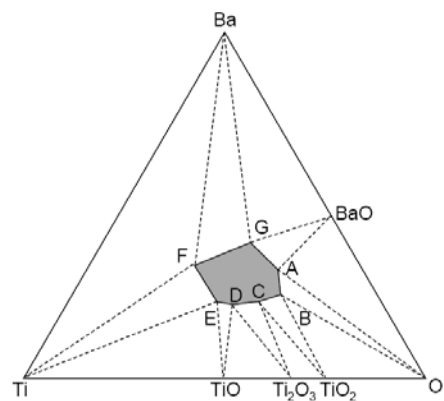


FIG. 1. Schematic phase diagram of the ternary system Ba-Ti-O

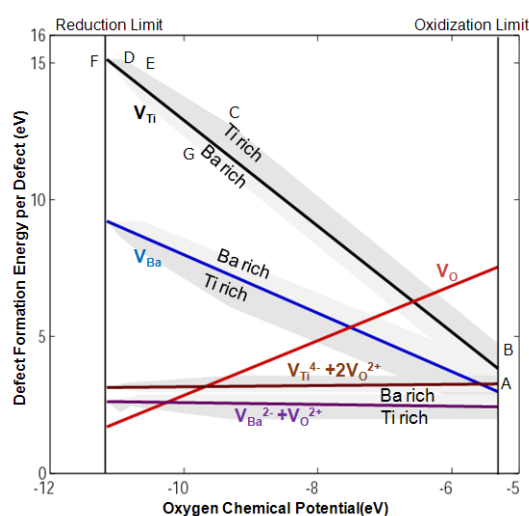


FIG. 2. Defect formation energy of vacancies in BaTiO₃ changing oxygen chemical potential

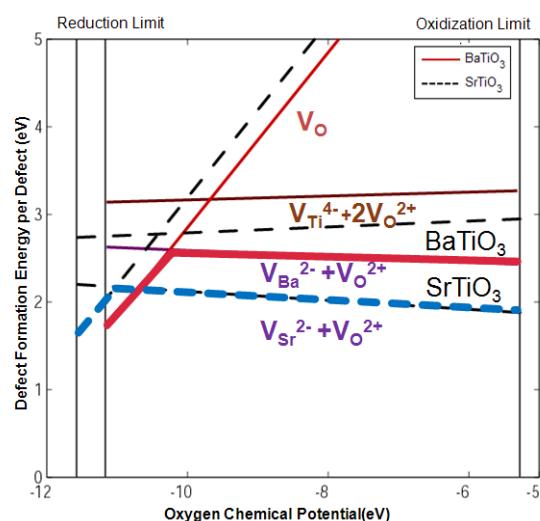


FIG. 3. Defect formation energy of V_{A(Sr, Ba)}²⁻ + V_O²⁺ and V_{Ti}⁴⁺ + 2V_O²⁺ and V_O in BaTiO₃ (solid line) and SrTiO₃ (dashed line)