

# Comparative study of vacancy formation energies in $\text{PbTiO}_3$ and $\text{BaTiO}_3$

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$\text{BaTiO}_3$  and  $\text{PbTiO}_3$  are two paradigm examples of ferroelectrics due to their distinct ferroelectric properties. With respect to  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$  displays a far larger  $c/a$  strain, stronger spontaneous polarization, and a deeper potential well of FE instability. While there have been numerous studies devoted to these structural differences, far fewer studies are conducted to understand difference and/or similarity of these two materials in terms of tendency for forming vacancy (in fact, theoretical studies of defects in ferroelectrics are rather limited in general[1–4]). For example,  $\text{TiO}_6$  octahedra exist in both substances and have similar structure. Does it indicate that the formation energy for oxygen vacancy, under oxygen-poor condition, be close in two materials? (Under oxygen-rich condition, this question is of less interest since oxygen vacancies will not take place.) On a separate issue, the strong tetragonality (that exists in  $\text{PbTiO}_3$  but to a considerably less extent in  $\text{BaTiO}_3$ ) results in two non-equivalent oxygen sites. What difference will this tetragonality lead to the formation energy of oxygen vacancy? Another question concerns the A-site vacancy. It is well known that in  $\text{PbTiO}_3$  there is a strong covalent hybridization between Pb atom and O atom. Because of this hybridization shall we expect a larger formation energy for  $V_{\text{Pb}}$  in  $\text{PbTiO}_3$  than for  $V_{\text{Ba}}$  in  $\text{BaTiO}_3$ ? Furthermore, how does the consideration of chemical potentials alter the conclusion?

Formation energy of vacating atom  $j$  is, as described above, the energy required to move this atom from the  $\text{ABO}_3$  solid into the gas-phase reservoir. This energy, denoted as  $\Delta E_f^v(j)$  can be written as a function of the atomic chemical potential as follows:

$$\Delta E_f^v(j) = E_{\text{tot}}(\text{ABO}_3, [j]) + E_{\text{tot}}(j) + \mu_j - E_{\text{tot}}(\text{ABO}_3) \quad (1)$$

where  $E_{\text{tot}}(\text{ABO}_3)$  and  $E_{\text{tot}}(\text{ABO}_3, [j])$  are the total energy of the perfect perovskite solid and the solid containing one  $j$ -specie vacancy.  $E_{\text{tot}}(j)$  is the total energy per atom in elemental solid, and  $\mu_j$  the chemical potential of this specie. The first three terms in the right side of Eq.(1) is the total energy of the system after the vacancy is created. For convenience, Eq.1 can be also written as  $\Delta E_f^v(j) = \Delta G(j) + \mu_j$ , where  $\Delta G(j) = E_{\text{tot}}(\text{ABO}_3, [j]) - E_{\text{tot}}(\text{ABO}_3) + E_{\text{tot}}(j)$  is the vacancy formation energy when chemical potential  $\mu_j$  is zero.

Using density functional total-energy calculations and structural minimization we determined the formation enthalpy of various compounds, and critical quantity  $\Delta G$  which is associated with the energy of creating a vacancy in the host solid and the vacated atom is placed in the lattice site of the relevant elemental solid. We further ob-

tained analytically, according to thermodynamical laws, the formulae that specify the valid chemical-potential range of gas-phase reservoirs in equilibrium with the ferroelectric solids. Both the formation enthalpy of compounds and the valid chemical potentials, as determined here in this study, will be fairly helpful for investigating other types of defects and related properties. By combining the studies of  $\Delta G$  and chemical potentials, formation energies of neutral vacancies under different environment conditions are calculated for all species. Comparing vacancies in  $\text{PbTiO}_3$  and  $\text{BaTiO}_3$  further reveals interesting differences of defect energetics in these two paradigm ferroelectrics. Our specific conclusions are summarized as follows.

(i) The oxygen gas reservoir in equilibrium with  $\text{BaTiO}_3$  can vary its chemical potential over a much wider range than the oxygen reservoir in equilibrium with  $\text{PbTiO}_3$  can, and more quantitatively,  $-5.87 \leq \mu_{\text{O}} \leq 0$  eV in the BT system, while  $-2.98 \leq \mu_{\text{O}} \leq 0$  eV in the PT case. (ii) For a fixed  $\mu_{\text{O}}$ ,  $\mu_{\text{Pb}}$  and  $\mu_{\text{Ti}}$  of gas reservoirs in  $\text{PbTiO}_3$  system must be carefully adjusted in order to avoid the occurrence of secondary phases, since the valid region of  $\mu_{\text{Pb}}$  or  $\mu_{\text{Ti}}$  has a narrow width of only 0.39 eV. This is different in  $\text{BaTiO}_3$ , where  $\mu_{\text{Ba}}$  or  $\mu_{\text{Ti}}$  can be adjusted over a significant range of 1.62 eV. (iii)  $\Delta G$  is predicted to be on the order of about 4.5, 6.0, 9.5, and 15.0 eV for Pb, O, Ba, and Ti vacancies, respectively. Thus,  $\Delta G(\text{Pb}) < \Delta G(\text{O}) < \Delta G(\text{Ba}) < \Delta G(\text{Ti})$ . (iv) While Pb and Ba are both predominantly ionic in ferroelectric solids (Pb-O bonds have some covalent character), their vacancy formation energies  $\Delta G$  are dramatically different, however, and  $\Delta G(\text{Pb})$  is about 5 eV smaller than  $\Delta G(\text{Ba})$ . Furthermore, although O atoms form strong covalent bonds with Ti, its  $\Delta G(\text{O})$  is surprisingly smaller than the  $\Delta G$  of Ba. (v) The strong tetragonality in  $\text{PbTiO}_3$  does not introduce significant effect to the vacancy formation energy of two non-equivalent oxygen atoms. (vi) Oxygen chemical potential can be effectively used to modify the vacancy formation energy (and thus the vacancy concentration) of oxygen specie and *other* species. For instance, our calculations show that by varying  $\mu_{\text{O}}$ ,  $\Delta E_f^v(\text{Ti})$  of a Ti vacancy can be drastically reduced from 15.65 eV to 3.67 eV, while  $\Delta E_f^v(\text{Ba})$  changes from 9.69eV to merely 2.43 eV. (vii) Under oxygen-rich condition, formation of a Pb vacancy in  $\text{PbTiO}_3$  needs an energy within the range of [1.47,1.86] eV, while formation of a Ba-site vacancy takes [2.43, 4.05] eV. The comparable and small formation energies of A-site vacancies thus indicate that, when oxygen is rich, both Pb and Ba vacancies are very likely to appear in corresponding ferroelectrics. (viii) For the limiting case when oxygen is poor, our calculations predict that in  $\text{BaTiO}_3$  formation of an

O vacancy needs only 0.43 eV, and the concentration of  $V_O$  is thus to be exceedingly high.

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