Effect of charge on point defect size misfits from ab initio: Aliovalently doped SrTiO$_3$

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A B S T R A C T

We demonstrate a computationally efficient method to calculate size misfits of point defects in aliovalently doped SrTiO$_3$ using density functional theory. The size misfits of neutral and charged single point defects are calculated and linearly combined to estimate the effective size misfits of multiple point defects in aliovalently doped SrTiO$_3$. The charge state has a demonstrable effect on point defect size misfits for both isolated and multiple defects. We attribute this to the different charge localization between the defective systems. The extra electron or hole for the charged isolated point defects compensates the difference of charge localization between the neutral point defects and aliovalently doped system. The sum of size misfits of charged isolated point defects accurately estimates size misfits for aliovalently doped SrTiO$_3$, without charge correction which was possibly required due to the additional charge state of point defect.

1. Introduction

The perovskite material strontium titanate (SrTiO$_3$) is used in a wide range of applications including buffer layers for epitaxial thin films, microwave resonators, and catalysts [1–3]. The dielectric properties of SrTiO$_3$ depend on its structural parameters such as lattice constants and the tolerance factor [4]. Many theoretical and empirical models predict the structural parameters based on the composition of perovskites [5–7]. However, these models do not account for the effects of dopants or vacancies on the structural parameters, despite the fact that SrTiO$_3$ is commonly doped by metals or trivalent rare earth elements to improve the dielectric properties [8]. Recently, Ubic et al. [9] controlled the Sr vacancy concentration in SrTiO$_3$ by doping with the trivalent atoms (La, Ce, and Nd), and measured the lattice constants according to the vacancy concentration. The authors suggest an improved empirical model to evaluate the pseudo-cubic lattice parameter and tolerance factor of aliovalently doped SrTiO$_3$ by accounting for the effective size of a vacancy at a Sr site.

Calculating formation volumes and energies of charged point defects using density functional theory (DFT) requires a careful approach to account for electrostatic interactions within the periodic cell and the potential shift [10–12]. In silicon, Bruneval and Crocombette [13] described the potential bias caused by the charge

state of point defects that significantly changes the formation volume and requires correction. They found that the corrected formation volume weakly depends on the defect type and charge state. Density functional theory studies of perovskites studies have focused on charged or neutral oxygen vacancies and their formation energies or electronic properties [14,15], but not on formation volumes. The formation energy calculations for charged point defects require a charge correction to account for the potential shift in perovskites as well. These results suggest that the charge state could affect formation volume, and aliovalently doped SrTiO$_3$ with experimentally measured lattice constants [9] provides an ideal system to answer this question. Aliovalently doped SrTiO$_3$ contains two substitutional atoms (Ln$_{Sr}$, Ln = La, Nd, Ce) with a single vacancy (V_{Sr}) at Sr atomic sites given by

$$Ln_2O_3 \xrightarrow{SrTiO_3} 2Ln^\bullet_{Sr} + V''_{Sr} + 3O^\times_O. \quad (1)$$

These trivalent substitutional elements have a +1 charge, compensated by the −2 charge of the Sr vacancy. Shanthi and Sarma computed charge distributions in perfect SrTiO$_3$ and in neutral SrTiO$_3$ with a substitutional La solute on the Sr sublattice [16]. They find that the La does not yield midgap states, which is attributed to the La-derived electronic states occurring far below the Fermi energy. However, they didn't investigate the redistribution of charge in systems with multiple defects – i.e., aliovalently doped SrTiO$_3$ – or the effect of charge transfer on point defect size misfits.

We demonstrate a computationally efficient method to calculate the effective size misfits of point defects in aliovalently doped

SrTiO$_3$ by linearly combining the size misfits of charged single point defects, without the need for charge correction. The size misfit calculation of single point defects produces a smaller finite size effect compared to the multiple defective geometry. We calculate the size misfits for multiple defects in aliovalently doped SrTiO$_3$ and single point defects for different charge states. The sum of size misfits of single charged defects *without correction* matches well with the size misfits of neutral defect complexes, while the sum of size misfits of single neutral defects disagrees. In addition, electrons and holes have different sizes in Sr vacancies compared with substitutional sites. We attribute the disagreement in size misfits to differences in charge transfer for neutral point defects compared with defect complexes in aliovalently doped SrTiO$_3$.

2. Computational details

We perform DFT calculations using the Vienna ab initio simulation package (VASP) [17,18] based on plane wave basis sets. The projector-augmented wave (PAW) potentials generated by Kresse [19] describe the Sr ([Ni]$4s^2 4p^6 5s^2$), Ti ([Ne]$3p^6 3d^2 4s^2$), O ([He]$2s^2 2p^4$) and substitutional atoms (La, Ce, and Nd) with the same core electron configuration [Kr]. The Perdew–Burke–Ernzer hof (PBE) generalized gradient approximation (GGA) functional [20] accounts for electron exchange–correlation energy. A plane-wave energy cutoff of 850 eV is required for an energy convergence of less than 1 meV/atom. A $2 \times 2 \times 2$ Monkhorst–Pack [21] k-point grid samples the Brillouin zone of the $3 \times 3 \times 3$ SrTiO$_3$ supercells (135 atoms). Gaussian smearing is employed for integrating the density of states with a smearing width of 0.05 eV. All the atoms in the supercells are relaxed until the force on each atom is less than 5 meV/Å. The SrTiO$_3$ unit cell has a cubic structure with computed lattice constant $a = 3.94$ Å and bulk modulus $B = 171.8$ GPa, which agree well with the experimental values of $a = 3.905$ Å [9] and $B = 174$ GPa [22]. It is assumed that the presence of defect does not change the bulk modulus significantly, thus negligible. We applied strain on unit cell from $\pm 0.1\%$ to $\pm 0.4\%$ by 0.1% difference to appropriate directions and relaxed ions with fixed volume to calculate three independent elastic constants C_{11}, C_{12} and C_{44}, where the calculated values are 320.3, 99.0 and 109 GPa respectively. Then, the bulk modulus B is calculated by $1/B = (S_{11} + S_{22} + S_{33}) + 2^*(S_{12} + S_{13} + S_{23})$, where S_{ij} is the compliance tensor in Voigt notation which is the inverse of stiffness tensor. The calculated bulk modulus of SrTiO$_3$ using various exchange correlation functionals is compared [23], showing the range of bulk modulus from 159 to 222 GPa with different estimation of lattice constants. The electron density on each atomic site in the SrTiO$_3$ supercells is calculated using the Bader charge integration method [24].

The size misfit of a point defect is the fractional change of lattice constant a with respect to the concentration c of the defect. We compute size misfits ε_b by introducing point defects into a supercell and relaxing the atoms at fixed volume, which is found to be more suitable choice than the constant pressure method [10]. Point defects induce stress σ in the cell, which yields the size misfits as [25,10]

$$\varepsilon_b = \frac{1}{a} \frac{da}{dc}\bigg|_{c=0} \approx \frac{N\sigma}{3B}, \tag{2}$$

where N is the number of atoms in the supercell and B is the bulk modulus of undefective SrTiO$_3$. The size misfits of point defects in the aliovalently doped system are computed for $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells to estimate finite size effects. The absolute errors for size misfit values between $2 \times 2 \times 2$ supercells and $3 \times 3 \times 3$ supercell are 0.010 and 0.038 for La and Ce, respectively. However, the Nd $2 \times 2 \times 2$ supercell calculations suffered from

severe charge-sloshing exacerbated by finite size effects. All reported size misfits are from the $3 \times 3 \times 3$ supercells.

3. Effective size misfits

Fig. 1 shows the geometries used to calculate the size misfits of point defects in aliovalently doped systems using a direct method and an indirect method. The direct method calculates the size misfits using the SrTiO$_3$ structure containing two substitutional atoms and a Sr vacancy. In the direct method, the point defects are separated as far as possible from each other within the periodic geometry to minimize the effect of defect interactions on the size misfits. The absolute error of size misfits computed from two different atomic arrangements (i.e., different distances between point defects) using the $2 \times 2 \times 2$ supercell are 0.001 and 0.015 for La and Ce respectively, indicating that point defect interactions have a smaller effect than finite supercell size. The indirect method calculates the effective size misfits for the aliovalently doped systems by summing the size misfits of isolated neutral/charged point defects. This enables us to quantify the contribution of the point defect charge states to the effective size misfits.

Table 1 shows the strong dependence of size misfits on the charge state of single point defects in SrTiO$_3$. The negative size misfits for neutral Ce, Nd, and vacancy indicate that the cell volume contracts when these defects are present in SrTiO$_3$, while La causes
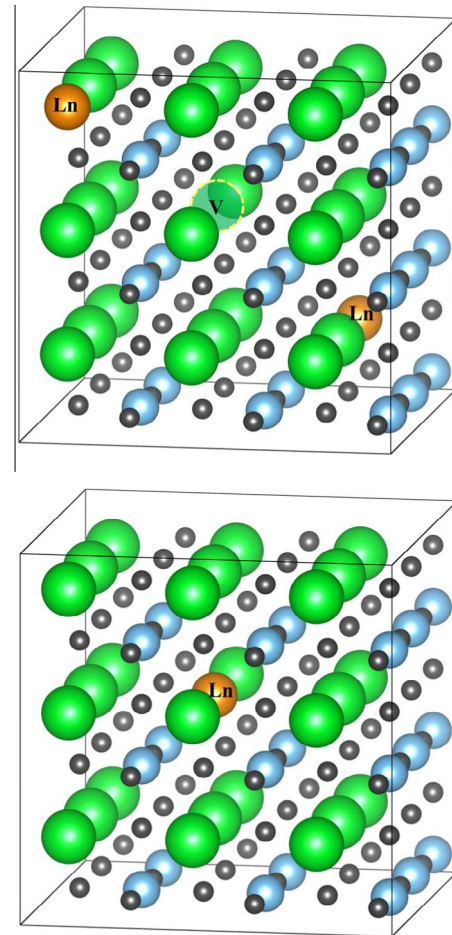

Fig. 1. Geometry of SrTiO$_3$ (top) with two substitutional atoms (Ln$_{Sr}$ = La, Ce, and Nd) and a Sr vacancy (V_{Sr}), and (bottom) with a single substitutional atom (Ln$_{Sr}$) or a Sr vacancy (V_{Sr}). The supercells without defects contain 27 Sr atoms (green), 27 Ti atoms (blue), and 81 O atoms (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)