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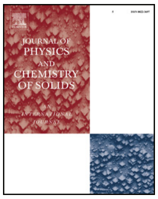

Multisite occupation of divalent dopants in barium and strontium titanates

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ABSTRACT

Based on recent experimental and theoretical proofs of calcium multisite occupation in barium titanate, we investigated a mixed incorporation mechanism for divalent dopants in barium and strontium titanates ($BaTiO_3$ and $SrTiO_3$). Our present theoretical results demonstrated the multisite occupation of divalent dopants in both perovskite structures. We determined the dependences of the solution, binding energies, and final solution energies with respect to the ionic radii of the dopants. Calculated results obtained based on classical simulations showed that the divalent dopants can occupy both A- and Ti- cation sites in $ATiO_3$ perovskite structures. Such a multisite occupation has direct implications for other experimental findings regarding $BaTiO_3$, such as non-stabilization of the tetragonal phase, shifts in the Curie temperature, intensification of the diffuse phase transition, and shifts in the absorption of ultraviolet light to the visible range in photocatalytic applications related to solar cells for producing energy.

1. Introduction

$ATiO_3$ perovskite compounds where A = Ba, Sr have valuable structural and electrical properties and direct technological applications such as that in the electroceramics industry. Some of known applications of these materials include multilayer ceramic capacitors, positive temperature coefficient of resistivity thermistors, random access memories, microwave devices, and thermoelectrics [1–10].

Both compounds have been employed in photocatalytic applications related to solar cells for producing renewable green energy due to their small band gap energies at room temperature [11]. In order to improve the performance of the compounds used in this field, foreign cations have often been used as dopants to modify the structural and electronic properties, and by shifting the absorption of ultraviolet light to the visible range [12–15].

Thus, divalent dopants (behaving as M^{2+}) have often been incorporated into both $ATiO_3$ perovskite structures to improve their thermoelectrical and conducting properties. The doping process depends on various factors such as the chemical environment where the dopant is incorporated in the $ATiO_3$ lattice structure, the tolerance factor as a function of the ionic radius of the dopant, and the oxygen partial pressure combined with electron doping [16–20]. Recently, the existence of two new incorporation mechanisms for rare-earth dopants was demonstrated on the basis of experimental investigations of Er-doped $BaTiO_3$ (BT) [21–23]. These mixed incorporation mechanisms generate cation and anion vacancies, and the dopants are incorporated into both host cation sites in the $ATiO_3$ lattice structure [21–23]. These mixed mechanisms induce slightly higher energies with respect to classical self-compensation and they can be active under certain experimental conditions [21–23]. Ca^{2+} multisite occupation was also demonstrated in BT [24–29]. An experimental and theoretical study based on atomistic simulations determined the implications of Ca^{2+} multisite occupation based on the defect energetics and transport properties of 5 mol% Ca^{2+}-doped BT [24]. A new mixed incorporation mechanism was also proposed considering Ca^{2+} multisite occupation [24]. The existence of this mixed scheme was supported by direct current (dc) conductivity and activation energy results obtained using molecular dynamics simulations, and also experiments using dielectric modulus measurements [24].

In this context, we use in the present study statics simulations to investigate the existence of the mixed incorporation mechanism, i.e., multisite occupation by divalent dopants in both $ATiO_3$ perovskite structures. We aim to provide an additional reliable toolbox for examining the implications of M^{2+} multisite occupation in both perovskite structures, as well as to understand the roles of divalent dopants and their defect energetics in solids.

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2. Methodology

The procedure employed for defect energy calculations using potential-based methods has been described previously [16,17,19–24,30], and thus we provide only a brief outline. The General Utility Lattice Program [31] (GULP) is used to perform all lattice statics calculations. All calculations are conducted for the cubic phases of $BaTiO_3$ (BT) and $SrTiO_3$ (ST), with lattice parameters of 4.01 Å and 3.96 Å, respectively. The lattice statics calculations are based on the Born model of ionic compounds, where each atom is modeled as a charged sphere with attractive and repulsive short-range interactions described by the potential model. Seven M^{2+} ions are studied, and their ionic radii are considered to have a coordination number of VI. We employ a six-fold coordination for each M^{2+} cation in order to infer the energetic behavior of the dopant in each incorporation mechanism considered.

Long-range interactions between pair-species are modeled using Coulombic long-range forces. The short-range interactions are modeled using Buckingham (Buck, Eq. (1)) and Lennard-Jones potentials (LJ, Eq. (2)):

$$U_{\mathrm{Buck}}(r_{ij}) = A\exp\left(\frac{-r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^{6}} \tag{1}$$

$$U_{\mathrm{LJ}}(r_{ij}) = 4\varepsilon_0\left[\left(\frac{\sigma_0}{r_{ij}}\right)^{7} - \left(\frac{\sigma_0}{r_{ij}}\right)^{6}\right], \tag{2}$$

where A, ρ, and C are fitted parameters for a pair of ions, i and j, and r_{ij} is the interatomic distance between them. The r^{-6} term considers the attractive dispersion or van der Waals interaction, and the exponential term of the Buckingham potential accounts for Pauli repulsion.

In Eq. (2), the seven exponent (7) index for the repulsive element of the potential generates a shape most similar to the Buckingham potential, which attains good agreement with the atomic separations [19,30]. The covalent character of TiO_2 bonds is also considered by using Eq. (2) and three-body potentials. Buckingham potentials are used for the Ba^{2+}-O^{2-}, Sr^{2+}-O^{2-}, O^{2-}-O^{2-} and M^{2+}-O^{2-} interactions. Further details of this potential model can be found in previous studies [16,19,30]. In addition to the pair potential model, a shell approach is used to describe ionic interactions. The shell model provides a description of the polarization of ions [32]. In this model, each ion is represented in terms of a core and a shell, which are related harmonically via a spring with elastic constant k. The sum of the core and shell charges is equal to the formal charge of the ion [32]. All M^{2+} cations are considered non-polarizable species.

The two-region strategy [33] is the most promising approach for calculating defect energetics in classical simulations [19–24]. In this method, the crystal lattice is partitioned into two spherical regions, where ions in the inner spherical region (region 1) adjacent to the defect (or cluster defect) are relaxed. The remainder of the crystal is treated using an approximate quasi-continuum method. Thus, the local relaxation can be modeled, and the crystal is not treated as a rigid lattice through which ion species diffuse. In this study, we set the distances of regions 1 and 2 to 14 and 27 Å, respectively. The same defect energies were observed for larger regions, thereby suggesting that convergence is achieved with this choice for the radius of the spheres. The total defect energy, E_T, is described by Eq. (3):

$$E_T = E_1(x) + E_{12}(x, \mu) + E_2(\mu), \tag{3}$$

where the interatomic displacements in the inner region are denoted by x and the external displacements by μ, E_1 and E_2 represent the energies of regions 1 and 2, respectively, and E_{12} is the interchange energy between them.

The procedures used in this study were employed in previous studies, where a good agreement between the experimental and simulation results was attained, thereby reconciling our understanding of defect formation and experimental findings [21–24].

3. Results and discussion

3.1. Solution energy

Three incorporation mechanisms were considered for comparison. The first written in Kröger–Vink notation is described as follows (referred to as the A-site substitution mechanism):

$$MO + A_A \rightarrow M_A^{\times} + AO, \tag{4}$$

where oxygen vacancy formation is not required to neutralize the overall charge of the doped structure. This incorporation mechanism only involves the exchange of A^{2+} with M^{2+} at the twelve-fold coordinated A-site in the $ATiO_3$ perovskite structure. The other essential mechanism is referred to as the Ti-site substitution mechanism, which is described by:

$$MO + Ti_{Ti} + O_O \rightarrow M_{Ti}^{''} + V_O^{\cdot\cdot} + TiO_2, \tag{5}$$

where for each M^{2+} ion that occupies a Ti^{4+} site, the formation of one oxygen vacancy is required for charge neutralization.

We also consider the possible existence of a combined incorporation mechanism, i.e., the mixed mode [24], which is defined by the following reaction:

$$2MO + Ti_{Ti} + A_A + O_O \rightarrow M_{Ti}^{''} + M_A^{\times} + V_O^{\cdot\cdot} + AO + TiO_2, \tag{6}$$

where M^{2+} ions occupy both host-cation sites and create an oxygen vacancy. This mechanism has some similarities with the standard self-compensation scheme used for rare-earth doped perovskites where the dopants simultaneously occupy the A- and Ti-sites. A representation of the mixed incorporation mechanism for the M^{2+} ion is shown in Fig. 1.

In this state, multisite occupation is explicitly described by the partial occupation of the M^{2+} dopant in A- and Ti- sites in the $ATiO_3$ perovskite structure, thereby leading to the formation of one oxygen vacancy for charge neutralization. The effects of the mixed scheme on the properties of these perovskite structures are discussed and compared with the available experimental results in the following paragraph.

The solution energies related to the three aforementioned incorporation mechanisms are defined as:

$$E_s = E_{\mathrm{subs,A}}^{M^{2+}} + E_L^{AO} - E_L^{MO} \tag{7}$$

$$E_s = E_{\mathrm{subs,Ti}}^{M^{2+}} + E_{\mathrm{vac}}^{O^{2-}} + E_L^{TiO_2} - E_L^{MO} \tag{8}$$

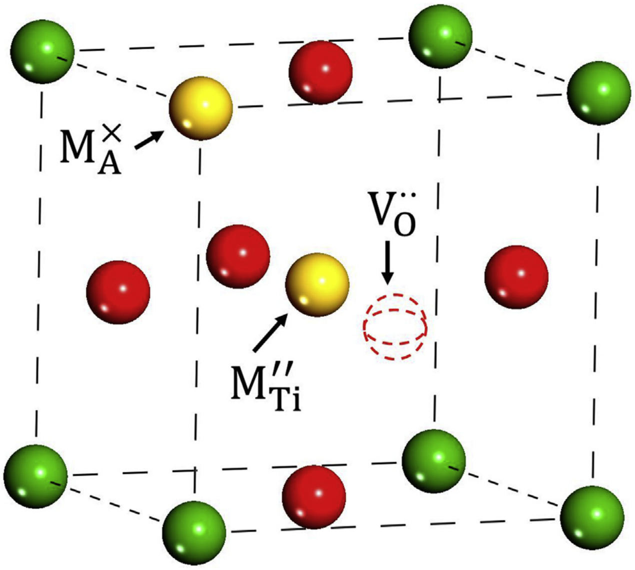

Fig. 1. Schematic representation of the mixed incorporation mechanism.