Multisite occupation of divalent dopants in barium and strontium titanates

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A B S T R A C T

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 BaTiO₃ (BT) and SrTiO₃ (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 M²⁺ ions are studied, and their ionic radii are considered to have a coordination number of VI. We employ a six-fold coordination for each M²⁺ 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)):

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

$$U_{\text{LJ}}(r_{ij}) = 4\epsilon_0 \left[\left(\frac{\sigma_0}{r_{ij}}\right)^7 - \left(\frac{\sigma_0}{r_{ij}}\right)^6 \right], \quad (2)$$

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 TiO₂ bonds is also considered by using Eq. (2) and three-body potentials. Buckingham potentials are used for the Ba²⁺-O²⁻, Sr²⁺-O²⁻, O²⁻-O²⁻ and M²⁺-O²⁻ 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 M²⁺ 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):

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

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):

where oxygen vacancy formation is not required to neutralize the overall charge of the doped structure. This incorporation mechanism only involves the exchange of A²⁺ with M²⁺ at the twelve-fold coordinated A-site in the ATiO₃ perovskite structure. The other essential mechanism is referred to as the Ti-site substitution mechanism, which is described by:

where for each M²⁺ ion that occupies a Ti⁴⁺ 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:

where M²⁺ 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 M²⁺ ion is shown in Fig. 1.

In this state, multisite occupation is explicitly described by the partial occupation of the M²⁺ dopant in A- and Ti-sites in the ATiO₃ 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:

$$E_s = E_{\text{subs,A}}^{\text{M}^{2+}} + E_{\text{L}}^{\text{AO}} - E_{\text{L}}^{\text{MO}} \quad (7)$$

$$E_s = E_{\text{subs,Ti}}^{\text{M}^{2+}} + E_{\text{vac}}^{\text{O}^{2-}} + E_{\text{L}}^{\text{TiO}_2} - E_{\text{L}}^{\text{MO}} \quad (8)$$

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

Table 1

Substitution, vacancy, and lattice energies used in the calculations of the solution energies. The units for substitution and vacancy energies are eV for defect and eV/uc for lattice energies.

Species	E_L^{MO}	Ionic radii ^a	BT		ST	
			$E_{subs,A}^{M^{2+}}$	$E_{subs,Ti}^{M^{2+}}$	$E_{subs,A}^{M^{2+}}$	$E_{subs,Ti}^{M^{2+}}$
Co	−40.15	0.65	−5.25	71.37	−3.12	72.14
Ni	−40.68	0.69	−5.39	70.88	−3.27	71.57
Zn	−39.97	0.74	−5.20	71.54	−3.07	72.34
V	−41.87	0.79	−5.67	69.90	−3.55	70.45
Cd	−36.67	0.95	−3.70	75.63	−1.53	76.95
Ca	−36.12	1	−3.54	76.80	−1.37	78.34
Eu	−33.27	1.17	−0.53	81.25	1.70	83.09
$E_L^{BaO} = -32.58$			$E_L^{TiO_2} = -127.64$		$E_{vac}^{O^{2-}} = \begin{cases} 24.66 & b \\ 25.31 & c \end{cases}$	
$E_L^{SrO} = -34.47$						

^a Ionic radii taken from VI-coordination number in Ref. [34].

^b Generated in BaTiO₃ $E_L^{BaTiO_3} = -160.02$ eV/uc.

^c Generated in SrTiO₃ $E_L^{SrTiO_3} = -162.23$ eV/uc.

$$E_s = \frac{1}{2} (E_{subs,Ti}^{M^{2+}} + E_{subs,A}^{M^{2+}} + E_{vac}^{O^{2-}} + E_L^{AO} + E_L^{TiO_2} - 2E_L^{MO}), \quad (9)$$

for the A-site, Ti-site, and mixed incorporation mechanisms, respectively. The values of the individual terms in these mechanisms are listed in Table 1, i.e., the substitution ($E_{subs,Ti}^{M^{2+}}$ and $E_{subs,A}^{M^{2+}}$), lattice (E_L^{MO} , E_L^{AO} and $E_L^{TiO_2}$), and oxygen vacancy formation ($E_{vac}^{O^{2-}}$) energies.

The negative values of $E_{subs,A}^{M^{2+}}$ confirm that the substitution energy of M^{2+} dopants in the A-site is more favorable than that in the Ti-site for both ATiO₃ structures.

Fig. 2 shows the solution energy (E_s) for each dopant and the incorporation mechanism. The A-site mechanism is the preferred scheme from an energetics perspective for all the M^{2+} dopants considered in both structures with almost similar probability due to the small differences in the value of E_s . This finding agrees well with available results for divalent doped ATiO₃ structures. The substitution in the Ti-site is unfavorable in both structures, especially for ST, which has the highest value for E_s . In fact, for each M^{2+} dopant, incorporation generates one oxygen vacancy, which results in structural disorder

Fig. 2. Solution energy for each incorporation mechanism and perovskite structure.

according to the changes in the lattice parameters as well as other related properties of the doped samples. However, the Ti-site substitution appears to be more favorable in BT than ST because the corresponding E_s values are lower in BT than those of the ST structure.

In terms of the ionic radius, for the A-site mechanism, the E_s value generally decreases as the ionic radius increases, but the behavior is the opposite for the Ti-site scheme. The mixed scheme remains almost constant in both structures for all the dopants considered ranging between A- and Ti-site substitutions, thereby demonstrating that the mixed incorporation mechanism is more promising for BT compared with the ST structure.

3.2. Binding energy and final solution energy

In the previous section, we discuss the solution energy results, but the incorporation mechanism implies formation of defect clusters, it is therefore necessary to calculate the binding energy to further examine their formation. The solution energy can be interpreted as the energy required to take the atoms from “infinity” to their correct atomic positions in the lattice structure. In a real sample, “infinity” can be another defect type (two- or three-dimensional defect type), such as pores, grain boundaries in polycrystalline samples, and accidentally doped cases. The binding energy between oppositely charged defects is defined as the difference between the total energy of the isolated defects and the energy when they are simulated together to form a defect cluster. In this context, the binding energy is the energy required to maintain or cleave the cluster defects generated by the incorporation mechanism. The binding energy (E_{bind}) is explicitly calculated as the sum of the cluster and isolated defect energies, as follows:

$$E_{bind} = E_{cluster} - \sum E_{iso}, \quad (10)$$

where $E_{cluster}$ and E_{iso} are the cluster and isolated energies, respectively. The isolated energies considering the values of $E_{subs,A}^{M^{2+}}$, $E_{subs,Ti}^{M^{2+}}$, and $E_{vac}^{O^{2-}}$ are given in Table 1. A negative value for E_{bind} indicates that the host lattice favorably accepts the inclusion of these isolated defects and the formation of the resulting defect cluster.

The binding energies of the mixed and Ti-site substitution mechanisms for both ATiO₃ structures are shown in Fig. 3. In general, the highest (absolute values) binding energies are found for ST in the mixed mode. Strong binding energies are obtained in both perovskite

Fig. 3. Binding energy for Ti-substitution and the mixed incorporation mechanism of ST and BT perovskite structures.

structures, where E_{bind} is decreased as the ionic radius is increased. This behavior was also observed for trivalent dopants in our previous study [21–24].

The binding energies of the Ti-site and mixed schemes are smaller for BT compared with those for the ST structure, which can be attributed to electrostatic interactions. The cell parameter is greater for BT than ST, in such a way that Coulombic interactions in the resulting defect clusters are smaller than those in BT. The mixed scheme for BT has weaker binding as compared to that for ST, which can be attributed to the same electrostatic interactions, except for V^{2+} . Therefore, there is a crossover point for the binding energies of Ca^{2+} , Cd^{2+} , and Eu^{2+} for Ti-site substitution and the mixed mechanism in BT. Thus, the mixed schemes for these dopants can be masked by each other. In our previous study, we also found strong and similar binding energy values for the mixed and Ti-site substitution schemes determined for Ca^{2+} in the BT structure [24]. Further explanations of these result were not provided in a previous study [24], but we obtain the same behavior for the other dopants mentioned above in the present study. Thus, we confirm that the source of these crossover points in the binding energy for different incorporation schemes is the masking effect mentioned above. In order to refine the masking effect, a study based on full X-ray characterization (as reported in a previous study [25]) is required to demonstrate the multisite occupation of these dopants in real samples.

Due to the strong interactions between the components of the defect clusters, the solution energy must be modified by a fraction of the binding energy in order to establish the correct behavior and the main incorporation mechanism for each dopant and structure.

This procedure was developed by Freeman et al. [19] and subsequently employed in other studies [19–24,30]. The modified energy mentioned above is referred to as the final solution energy, which is defined as:

$$E_f^{\text{Ti-site}} = E_S^{\text{Ti-site}} - |E_{\text{bind}}^{\text{Ti-site}}| \quad (11)$$

$$E_f^{\text{mixed}} = E_S^{\text{mixed}} - \frac{1}{2} |E_{\text{bind}}^{\text{mixed}}|, \quad (12)$$

for the Ti-site and mixed incorporation mechanisms, respectively. Fig. 4 shows the final solution energies computed with respect to the ionic radii of both structures and with the different mechanisms. The ionic radii are similar with the Ti-site scheme for both compounds, but the

values are lower for the BT structure, thereby confirming the preferential divalent doping in BT. The behavior is also similar with the mixed mechanism, but divalent doping is equally probable because of relatively small differences in E_f values for each dopant.

The mixed scheme is between the Ti-site and A-site substitution mechanisms for both compounds (except for V^{2+} , which exhibits the lowest E_f value in the mixed scheme with the BT structure). The E_f values determined for the mixed incorporation mechanism are higher than those determined for the mixed schemes with trivalent dopants in ST and BT [23] structures. However, the mixed mechanism for divalent dopants is more promising in the BT structure than ST [23].

The tolerance factor (t) determines the stability of perovskite type structures [35], including the preferential occupation site of the dopant on their host cations [16,17]. For the pure (non-doped) ST and BT samples, the tolerance factor for the ATiO_3 ($A = \text{Sr}, \text{Ba}$) structure is defined based on the ionic radii of the constituent ions as:

$$t = \frac{1}{\sqrt{2}} \frac{R_A + R_O}{R_{\text{Ti}} + R_O}, \quad (13)$$

where R_A , R_{Ti} , and R_O represent the ionic radii of the A-host cation, Ti, and oxygen ions, respectively. For a stable perovskite structure, the value of t should be close to unity [35]. With the VI coordination number [34], t reaches values of 1.06 and 0.91 for the non-doped BT and ST structures, respectively.

To further explore the multisite viability of divalent dopants, a modified version of Eq. (13) needs to be used to determine how the occupation site affects the stability and to establish the preferential occupation of the dopant. The tolerance factor can be redefined as [36]:

$$t_{A,\text{subs}} = \frac{1}{\sqrt{2}} \frac{(0.9R_A + 0.1R_M) + R_O}{R_{\text{Ti}} + R_O} \quad (14)$$

$$t_{\text{Ti},\text{subs}} = \frac{1}{\sqrt{2}} \frac{R_A + R_O}{(0.9R_{\text{Ti}} + 0.1R_M) + R_O}, \quad (15)$$

for the A-site and Ti-site mechanism, where R_M is the ionic radius of the M^{2+} dopant taken from the VI coordination number [34,36]. For the mixed incorporation mechanism, the tolerance factor is defined as follows:

$$t_{\text{mixed}} = \frac{t_{A,\text{subs}} + t_{\text{Ti},\text{subs}}}{2} \quad (16)$$

Fig. 5 shows the behavior of the tolerance factor obtained using the VI coordination number for the A-site, Ti-site, and mixed incorporation mechanisms of M^{2+} dopants in both the BT and ST structures. As the ionic radius is increased, the tolerance factor is decreased for Ti-site substitution in both compounds, whereas the results are found to be the opposite for the A-site scheme. For the BT structure, the results show that the divalent dopants are preferentially included at the Ti-site, except for Cd^{2+} , Ca^{2+} , and Eu^{2+} , because the differences in the tolerance factors are small as compared to the remaining dopants. In the latter cases, as mentioned above, the preferential sites are dependent on other external factors, such as the oxygen partial pressure and the A/Ti ratio.

It is well known that Ca^{2+} doped via an A-site substitution mechanism can stabilize the tetragonal phase of BT in the $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ composition [37]. Even Cd^{2+} has been proposed as a potential dopant for this purpose based on theoretical (density functional theory) results and machine learning predictions [38]. However, a subsequent experimental study using samples prepared with an A-site scheme to obtain a $\text{Ba}_{1-x}\text{Cd}_x\text{TiO}_3$ ($0 < x < 0.25$) composition demonstrated that the Cd^{2+} dopant did not stabilize the tetragonal phase [37].

Both Cd^{2+} and Ca^{2+} ions are electronically similar but multisite occupation is probably the main reason for this difference. Non-stabilization of the tetragonal phase can result in a trade-off effect between small variations in the ionic radii ($\sim 0.5 \text{ \AA}$ for Ca^{2+} and Cd^{2+} ions) and multisite occupation. The possibility of multisite occupation by Ni^{2+} was also suggested previously [39]. The effect of multisite occupation

Fig. 4. Final solution energy for each incorporation mechanism and perovskite structure.

Fig. 5. Tolerance factors for each incorporation mechanism and perovskite structure. The dashed horizontal lines (blue and green) denote the tolerance factor values for perfect ST and BT perovskite structures. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

can be used to explain the shift in the T_c , increases in the diffuse phase transition, and decreases in the dielectric constant [39].

An experimental impedance study of the V^{5+} -doped derivative showed that substitution on the A- and Ti- sites in the BT structure decreased the alternate current (AC) conductivity [36], and reductions in the conductivity are well known for divalent dopants [24,39]. In addition, the incorporation of V^{5+} into the BT or ST structure requires a cation vacancy for charge compensation instead of an oxygen vacancy, which is inconsistent with the conductivity analysis.

Inclusion of V^{5+} on the ST lattice structure increases the lattice parameters [14], but this is not reliable with the 5 + formal charge. The ionic radius of V^{5+} in a VI coordination number is 0.54 Å, which is smaller than that of the Ti^{4+} (0.61 Å) and Sr^{2+} (1.18 Å) ions. Thus, the inclusion of V^{5+} is expected to reduce the lattice parameters rather than increasing them. The only explanation for the expansion of the lattice parameters is that the formal charge of vanadium should be equal to 2 + with a large ionic radius (0.79 Å) and multisite occupation characteristics. According to the results obtained in terms of the solution, binding, and final solution energies, as well as the tolerance factor trends, it is clear that incorporation of small dopants in BT will affect all of the features mentioned above. A-site substitution is the most favorable mechanism for all dopants in both $ATiO_3$ structures, except for V^{2+} , which prefers the mixed scheme in the BT structure. From the perspective of the tolerance factor t , these effects are illustrated by their separation from the tolerance factor of the non-doped compound.

For the Ca^{2+} dopant, multisite occupation was demonstrated in a previous study [24] and confirmed in the present investigation given that the tolerance factors are coincided for the values obtained using three different incorporation schemes. In contrast to the binding energy results described in the previous section, our results agree well in terms of the binding energies of Cd^{2+} , Ca^{2+} , and Eu^{2+} with both the mixed and Ti-site substitution mechanisms (see Fig. 3) for the BT structure.

In summary, at the theoretical level considered, we can confirm that all the dopants can occupy both cationic sites, thereby leading to multisite occupation in both perovskite structures.

4. Concluding remarks

In the present theoretical study, we demonstrated the existence of multisite occupation by divalent dopants in BT and ST using classical simulations and determined the effects of doping on various properties. Classical divalent dopant incorporation mechanisms were studied, including a mixed scheme that leads to multisite occupation by divalent dopants in these perovskite structures.

Defect energetics calculations showed that the preferential incorporation mechanism is A-site substitution for all of the divalent dopants considered. Strong binding energies have been found and they are comparable to the values reported previously for Ca^{2+} doped BT. The mixed incorporation mechanism showed that multisite occupation is more likely to occur for BT compared with ST. We would suggest that appropriate experiments using X-ray or impedance techniques as well as other suitable methods could be conducted to investigate this electronic phenomenon.

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References

- [1] H. Kishi, Y. Mizuno, H. Chazono, Base-metal electrode-multilayer ceramic capacitors: past, present and future perspectives, *Jpn. J. Appl. Phys.* 42 (2003) 1–15.
- [2] M.J. Pan, C.A. Randall, A brief introduction to ceramic capacitors, *IEEE Electr. Insul. Mag.* (2010) 44–50.
- [3] J.F. Scott, C.A. de Araujo, Ferroelectric memories, *Science* 246 (1989) 1400–1405.
- [4] A.A. Sirenko, C. Bernhard, A. Golnik, A.M. Clark, J. Hao, W. Si, X.X. Xi, Soft-mode hardening in $SrTiO_3$ thin films, *Nature* 404 (2000) 373–376.
- [5] D.C. Sinclair, A.R. West, Effect of atmosphere on the PTCR properties of $BaTiO_3$ ceramics, *J. Mater. Sci.* 29 (1994) 6061–6068.
- [6] B. Huybrechts, K. Ishizaki, M. Takata, The positive temperature coefficient of resistivity in barium titanate, *J. Mater. Sci.* 30 (1995) 2463–2474.
- [7] H. Muta, K. Kurosaki, S. Yamanaka, Thermoelectric properties of rare earth doped $SrTiO_3$, *J. Alloy. Comp.* 350 (2003) 292–295.
- [8] S. Ohta, T. Nomura, H. Ohta, K. Koumoto, High-temperature Carrier transport and thermoelectric properties of heavily La- or Nb-Doped $SrTiO_3$ single crystals, *J. Appl. Phys.* 97 (2005) 34106.
- [9] A.K. Tagantsev, V.O. Sherman, K.F. Astafiev, J. Venkatesh, N. Setter, Ferroelectric materials for microwave tunable applications, *J. Electroceram.* 11 (2003) 5–66.
- [10] Y. Hao, X. Wang, L. Li, Highly dispersed $SrTiO_3$ nanocubes from a rapid sol-precipitation method, *Nanoscale* 6 (2014) 7940–7946.
- [11] I.A. Sluchinskaya, A.I. Lebedev, A. Erko, Structural position and charge state of nickel in $SrTiO_3$, *Phys. Solid State* 56 (3) (2014) 449–455.
- [12] S. Bisen, A. Mishra, K.M. Jarabana, Structural, optical and dielectric properties of nickel substituted barium titanate ceramics, *J. Phys. Conf.* 755 (2016) 012048.
- [13] S. Maletic, D. Maletic, I. Petronijevic, J. Dojilovic, D.M. Popovic, Dielectric and infrared properties of $SrTiO_3$ single crystal doped by 3d (V, Mn, Fe, Ni) and 4f (Nd, Sm, Er) ions, *Chin. Phys. B* 23 (2) (2014) 026102.
- [14] P. Jing, W. Lan, Q. Su, E. Xie, High photocatalytic activity of V-doped $SrTiO_3$ porous nanofibers produced from a combined electrospinning and thermal diffusion process, *Beilstein J. Nanotechnol.* 6 (2015) 1281–1286.
- [15] E. Echeverri, O. Arnache, Structural and impedance analysis of Co-doped $SrTiO_3$ perovskite, *J. Phys. Conf.* 687 (2016) 012040.
- [16] G.V. Lewis, C.R.A. Catlow, Defect studies of doped and undoped barium titanate using computer simulation techniques, *J. Phys. Chem. Solid.* 47 (1986) 89–97.
- [17] M.T. Buscaglia, V. Buscaglia, M. Viviani, P. Nanni, Atomistic simulation of dopant incorporation in barium titanate, *J. Am. Ceram. Soc.* 84 (2001) 376–384.
- [18] M. Schultz, L. Klein, Relaxation of transport properties in electron-doped $SrTiO_3$, *Appl. Phys. Lett.* 91 (2007) 151104.
- [19] C.L. Freeman, J.A. Dawson, H.-R. Chen, J.H. Harding, L.-B. Ben, D.C. Sinclair, A new potential model for barium titanate and its implications for rare-earth doping, *J. Mater. Chem.* 21 (2011) 4861–4868.
- [20] J.A. Dawson, J.H. Harding, H. Chen, D.C. Sinclair, First-principles study of intrinsic point defects in hexagonal barium titanate, *J. Appl. Phys.* 111 (2012) 94108.
- [21] Y.A. Zulueta, F. Guerrero, Y. Leyet, J. Anglada-Rivera, R.L. González-Romero, Juan J. Meléndez, Can erbium dopant occupy both cation sites in cubic barium titanate via a mechanism different than self-compensation? *Phys. Status Solidi B* 252 (3) (2015) 508–516.
- [22] Y.A. Zulueta, J.A. Dawson, Y. Leyet, F. Guerrero, J. Anglada-Rivera, M.T. Nguyen, The potential existence of mixed defect incorporation modes for rare-earth doped cubic $BaTiO_3$, *Phys. Status Solidi B* 253 (4) (2016) 733–737.
- [23] Y.A. Zulueta, J.A. Dawson, P.D. Mune, M. Froeyen, M.T. Nguyen, Oxygen vacancy generation in rare-earth-doped $SrTiO_3$, *Phys. Status Solidi B* 253 (11) (2016)

- 2197–2203.
- [24] Y.A. Zulueta, J.A. Dawson, Y. Leyet, J. Anglada-Rivera, F. Guerrero, R.S. Silva, M.T. Nguyen, Consequences of Ca multisite occupation for the conducting properties of BaTiO₃, *J. Solid State Chem.* 243 (2016) 77–82.
- [25] J.S. Park, Y.H. Lee, K.B. Kim, Yong-il. Kim, structural study of Ca doped barium titanate, *Nucl. Instrum. Meth. Phys. Res. B* 284 (2012) 44–48.
- [26] M.R. Panigrahi, S. Panigrahi, Diffuse phase transition and dielectric study in Ba_{0.95}Ca_{0.05}TiO₃ ceramic, *Phys. B Condens. Matter* 405 (11) (2010) 2556–2559.
- [27] S. Lee, C.A. Randall, A modified Vegard's law for multisite occupancy of Ca in BaTiO₃–CaTiO₃ solid solutions, *Appl. Phys. Lett.* 92 (2008) 111904.
- [28] D.Y. Lu, L.F. Yuan, W.N. Liang, Z.B. Zhu, Characterization of oxygen vacancy defects in Ba_{1-x}Ca_xTiO₃ insulating ceramics using electron paramagnetic resonance technique, *Jpn. J. Appl. Phys.* 55 (1) (2016) 011501.
- [29] R.S. Silva, M.L.B. Bernardi, A.C. Hernandez, Synthesis of non-agglomerated Ba_{0.77}Ca_{0.23}TiO₃ nanopowders by a modified polymeric precursor method, *J. Sol. Gel Sci. Technol.* 42 (2007) 173–179.
- [30] J.A. Dawson, X. Li, C.L. Freeman, J.H. Harding, D.C. Sinclair, The application of a new potential model to the rare-earth doping of SrTiO₃ and CaTiO₃, *J. Mater. Chem. C* 1 (2013) 1574–1582.
- [31] J.D. Gale, A.L. Rohl, The general utility lattice Program (GULP), *Mol. Simulat.* 29 (2003) 291–341.
- [32] B.G. Dick, A.W. Overhauser, Theory of the dielectric constants of alkali halide crystals, *Phys. Rev.* 112 (1958) 90–103.
- [33] N.F. Mott, M.J. Littleton, Conduction in polar crystals. I. Electrolytic conduction in solid salts, *Trans. Faraday Soc.* 34 (1938) 485–499.
- [34] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr.* 32 (1976) 751–767.
- [35] T.D. Dunbar, W.L. Warren, B.A. Tuttle, C.A. Randall, Y. Tsur, Electron paramagnetic resonance investigations of lanthanide-doped barium Titanate: dopant site occupancy, *J. Phys. Chem. B* 108 (2004) 908–917.
- [36] A. Jain, N. Maikhuri, R. Saroha, M. Pastor, A.K. Jha, A.K. Panwar, Microstructural and Dielectric Investigations Of vanadium substituted barium titanate ceramics, *Adv. Mater. Lett.* 7 (7) (2016) 567–572.
- [37] R. Yuan, P.V. Balachandran, D. Xue, Y. Zhou, X. Ding, J. Sun, T. Lookman, D. Xue, Role of cadmium on the phase transitions and electrical properties of BaTiO₃ ceramics, *Ceram. Int.* 43 (2017) 1114–1120.
- [38] P.V. Balachandran, D. Xue, T. Lookman, Structure-curie temperature relationships in BaTiO₃-based ferroelectric perovskites anomalous behavior of (Ba,Cd)TiO₃ from DFT, statistical inference, and experiments, *Phys. Rev. B* 93 (2016) 144111.
- [39] Y. Kumar, M.A. Mohiddon, A. Srivastava, K.L. Yadav, Effect of Ni doping on structural and dielectric properties of BaTiO₃, *Indian journal of eng. Math. Sci.* 16 (2009) 390–394.