

Charge effects in donor doped perovskite ferroelectrics

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Doping is a widely used method to tune physical properties of ferroelectric perovskites. Since doping can induce charges due to the substitution of certain elements, charge effects shall be considered in doped samples. To understand how charges can affect the system, we incorporate the dipole-charge interaction into our simulations, where the pinched hysteresis loops can well be reproduced. Two charge compensation models are proposed and numerically investigated to understand how lanthanum doping affect BaTiO₃'s ferroelectric phase transition temperature and hysteresis loop. The consequences of the two charge compensation models are compared and discussed.

I. INTRODUCTION

Barium titanate (BaTiO₃) is a prototype perovskite type crystal with good ferroelectric and dielectric properties. It is widely used in a variety of devices such as piezoelectric and ultrasonic actuators, pyroelectric detectors, posistors, multi-layer ceramic capacitors, temperature sensors and controllers, as well as tunable elements in microwave circuits^{1,2}. Doping BaTiO₃ with other chemical elements is an important way to further modifying their properties or improving their performances^{3,4}. As a matter of fact, trivalent rare earth (RE) elements are commonly used as dopants for ferroelectric perovskite BaTiO₃^{5,6}.

Depending on the valence state of the doped elements, doping can be divided into two categories: (i) Acceptor doping where the dopants own less ionic charge than the ion that they replace, and (ii) Donor doping where the dopants own more ionic charge. For the acceptor doping case, the charge balance is usually kept by oxygen vacancies, denoted by V_{O}^{\bullet} . These elements usually include large, monovalent ions substituting the A-sites, or small trivalent or divalent ions substituting the B-sites⁷⁻⁹. For the donor doping case, large trivalent cations substitutes some of the original A-site ions, or small pentavalent or hexavalent cations substituting some B-site ions. The charge balance is usually kept by A-vacancies, B-vacancies, or elements valance change.

Considering the intermediate size and charge of the RE³⁺ ions comparing to the Ba²⁺ and Ti⁴⁺ ions, several aliovalent doping mechanisms (ionic and electronic) are possible. In general, based on the size of the ions, RE ions could enter A-site (substituting Ba) or B-site (substituting Ti) in BaTiO₃: (i) Small RE³⁺ ions such as Yb³⁺ can exclusively enter the B-site with charge compensation by oxygen vacancies¹⁰; (ii) Intermediate size RE³⁺ ions, such as Dy, Ho, Er, can enter the A-site or B-site, forming systems like (Ba_{1-x}, Re_x)(Ti_{1-y}, Re_y)O₃, with charge balance fulfilled by the so-called self-compensation mechanism^{3,7,11}; (iii) Large RE³⁺ ions such as La, Sm dope exclusively on the

A-site^{12,13}. To make things even more complicated, the doping mechanism is also affected by the experimental process, such as the oxygen partial pressure (P_{O_2})¹⁴, sintering temperature/time and the overall A/B ratio in the raw materials before sintering^{8,9,15}.

Doping elements of nonequivalent valence state to a ferroelectric perovskite will inevitably induce effective charges in the system. It is therefore important to understand how the additional charges can affect the system, in particular their interaction with dipoles, and the subsequent influence on the phase transitions. In this work, we focus on the La-donor doping of BaTiO₃, which has attracted many theoretical and experimental studies^{6,7,16}. However, it is still one of the least understood aspects of the defect chemistry in solid state compounds^{13,16-18}. One important question is to determine the primary charge compensation mechanism. Due to its larger ion size, La ions (1.36 Å) can only occupy the A-sites (i.e., substituting Ba atoms) in the BaTiO₃ lattice. On the other hand, the charge compensation mechanism is still a controversial problem. When La³⁺ replaced Ba²⁺ on the A-site, the system must be compensated by either cation vacancies (A- or B-sites), free electrons, or the changed of valence state of Ti ions (i.e., Ti⁴⁺ to Ti³⁺). Since the way of charge compensation would influence the raw material ratio and physical properties of the resulting materials^{15,19}, understanding the compensation mechanism can help the material preparation.

With the previous investigation on the positive temperature coefficient of resistance (PTCR) of La-doped BTO, it is widely accepted that ionic compensation ($4\text{Ba}_{\text{Ba}}^{\times} + \text{Ti}^{4+} \Rightarrow 4\text{La}_{\text{Ba}}^{3+} + V_{\text{Ti}}^{\prime\prime\prime}$) is the primary mechanism for high dopant concentration²¹. Meanwhile, lattice energy calculations and the ternary phase diagram of BaO-TiO₂-LaO_{1.5} also support the Ti-vacancy compensation mechanism^{13,16,21}. On the other hand, experimental studies indicate that the electronic compensation mechanism ($\text{Ba}_{\text{Ba}}^{\times} \Rightarrow \text{La}_{\text{Ba}}^{\bullet} + e'$) are also plausible and, in fact, preferred²² (Ref: Wei Paper). As these two mechanism corresponds to two stoichiometry formula, both of

which are valid, it seems hard to resolve this problem solely by experiments. Here, we propose two models to investigate the properties of La-doped BTO and determine if one compensation mechanism is more likely than the other. The goal of this work is providing us a comprehensive understanding charges and macroscopic ferroelectric properties under doping condition on the atomic scale.

This paper is organized as the follows. In Sec. II, we introduce the charge-dipole interaction to effective Hamiltonian method and our theoretical models used for numerical simulation. Meanwhile, we well reproduced pinched hysteresis loop of acceptor doping. In Sec. III and Sec. IV, we apply Monte Carlo (MC) calculation to BaTiO₃ and numerically obtain the results of dopant charges. A detailed comparison is discussed. Finally, in Sec. V, we present a brief conclusion.

II. MODEL AND METHOD

In this section, we will build two models for simulations, corresponding to the two possible charge compensation mechanisms. The charge effects of the two models are reflected in the new terms added to the effective Hamiltonian terms used to simulation the phase transitions of BaTiO₃²³.

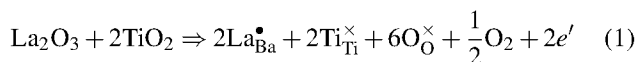
A. Models for dopant charges

In previous investigations, charge effects have been incorporated to understand heterovalent relaxors such as PbMg_{1/3}Nb_{2/3}O₃²⁴. Here, for doped BaTiO₃, we consider the long-range dipole-dipole and charge-dipole interactions, which can be conveniently computed using the Coulomb interaction matrix obtained using the Ewald method²⁵.

As we have mentioned in the introduction, different charge compensation mechanism had been proposed for La-doped BaTiO₃^{7,10,21,26–28}. It should be noted that, due to the large size of La³⁺ (1.36 Å), La³⁺ can only substitute the A-sites Ba²⁺ ions. Meanwhile, there is no direct experimental evidence of the Ba-vacancy and/or Ti-vacancy as the charge compensation mechanism¹³. Given such considerations, we will focus on two most likely charge compensation mechanisms: (i) the electron compensation ($\text{Ba}_{\text{Ba}}^{\times} \Rightarrow \text{La}_{\text{Ba}}^{\bullet} + e'$); (ii) Ti vacancy compensation ($4\text{Ba}_{\text{Ba}}^{\times} + \text{Ti}^{4+} \Rightarrow 4\text{La}_{\text{Ba}}^{3+} + V_{\text{Ti}}^{\prime\prime\prime}$)²¹, which will be called model A and model B hereafter.

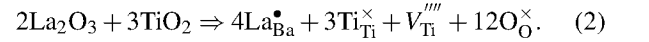
1. Dopant arrangement

In model A, the charge neutrality is maintained by electron compensation. This model are preferred by experiments in which the Ti concentration is believed not to be modified^{12,22,27,29}, i.e., the ratio of $(N_{\text{La}} + N_{\text{Ba}})/N_{\text{Ti}}$ is kept to 1. It can be represented as:



and leads to the general formula $(\text{Ba}_{1-x}\text{La}_x)\text{TiO}_3$ ³⁰. The above formula shows that, in the sintering process, La₂O₃ and TiO₂ react, producing La³⁺, which substitutes Ba and owns a positive charge. Production of Ti⁴⁺ ($\text{Ti}_{\text{Ti}}^{\times}$) and O²⁻ ($\text{O}_{\text{O}}^{\times}$) entered their usual positions without charge anomaly. Meanwhile, the process releases O₂, and due to the requirement of charge neutrality, extra negative charge of $2e^-$ is required. In Eq. (1), La_{Ba}[•] indicates that the La dopant substitutes a Ba²⁺ with $+e$ charge that is compensated by an electron. The electrons would be associated primarily with Ti⁴⁺, while final location of this electron is uncertain. Considering the minimization of Coulomb energy, one obvious choice for the electron is to stay in the same cell of the La dopant, in which the electron combines with the Ti⁴⁺ ($\text{Ti}^{4+} + e^- \Rightarrow \text{Ti}^{3+}$).

On the other hand, model B fulfills charge neutrality by introducing Ti vacancies^{13,21,30,31}, which can be represented as:



The above formula shows that, during the sintering, four Ba²⁺ are replaced by four La³⁺ ($4\text{La}_{\text{Ba}}^{\bullet}$) while a Ti vacancy ($V_{\text{Ti}}^{\prime\prime\prime}$) appears, which is needed for charge neutrality, giving the general formula $(\text{Ba}_{1-x}\text{La}_x)\text{Ti}_{1-x/4}\text{O}_3$ ³⁰. Again, with energy consideration, the Ti vacancy should be close to the four La ions.

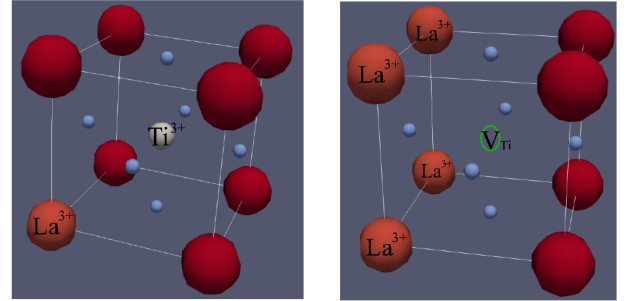


Figure 1. Atom configurations for the two models: (a) Electron compensation (model A); (b) Ti vacancy compensation (model B).

Figure 1 shows the atomic arrangements of these two models, which is used in later MC calculations. For model A, each La_{Ba}[•] is located on the 8 corners around a Ti³⁺ with equal probability [see Fig. (1)(a)]; for model B, four La³⁺ ions are randomly distributed among the 8 corners of a given Ti vacancy [Fig. (1)(b)], where different choices only have minor energy differences³¹. The dipoles on the Ti vacancies is set to null ($p_i = 0$), since the dipole is mostly related to Ti displacement in BaTiO₃³². For the samples used in MC simulations, the positions of Ti³⁺ and Ti vacancies are randomly distributed.

2. Effective charge

For numerical simulation with model A and B, we also need to know the effective charges on the La dopant and Ti

ions. Such extra charge will cause charge inhomogeneity in the system, and affect the dynamics of dipoles, which is the focus of this work. It is important to note that the effective charges of the relevant elements (or vacancies) could be different from their valence states as the Born effective charge has shown^{32–34}. To determine the values, we adopted a pragmatic approach by comparing simulation results to experimental observations that the three phase transition temperatures converge at the dopant concentration of $p \simeq 10\%$ ^{21,29,35}. With a vast number of numerical calculations (not shown here), in model A, the effective charge for La_{Ba} is set as $+2.1 |e|$, and Ti'_{Ti} is $-2.1 |e|$ respectively, which is larger than the initially expected $\pm |e|$. For model B, the effective charge of La_{Ba} remain the same ($2.1 |e|$) and, in order to achieve charge neutrality, V_{Ti}'''' owns a charge of $-8.4 |e|$. We note that, according to first principle phonon calculation described by Ref.³³, the Born effective charge of Ti is $7.492 |e|$, which is close to the value we adopt here.

B. Effective Hamiltonian

We use a first-principles-based effective Hamiltonian approach^{32,33,36,37} to obtain finite temperature properties of the doped system. A new energy item is introduced into total energy to account for the charge-dipole interaction. The new energy expression is given by :

$$\begin{aligned} E^{\text{tot}} = & E^{\text{self}}(\{u\}) + E^{\text{dpl}}(\{u\}) + E^{\text{short}}(\{u\}) \\ & + E^{\text{elas}}(\{\eta_l\}, \eta_H) + E^{\text{int}}(\{u\}, \{\eta_l\}, \eta_H) \\ & + E^{\text{chg-dpl}}(\{u\}, q) \end{aligned} \quad (3)$$

which consists of six parts: (i) the local-mode self-energy, $E^{\text{self}}(\{u\})$; (ii) the long-range dipole-dipole interaction, $E^{\text{dpl}}(\{u\})$; (iii) the short-range interaction between soft modes, $E^{\text{short}}(\{u\})$; (iv) the elastic energy, $E^{\text{elas}}(\{\eta_l\})$; (v) the interaction between the local modes and local strain, $E^{\text{int}}(\{u\}, \{\eta_l\})$; (vi) the long range charge-dipole interaction energy, $E^{\text{chg-dpl}}(\{u\}, q)$, where u is the local soft-mode amplitude vector (directly proportional to the local polarization), q is the charge induced by doped unequivalent-valence ions, and η_H (η_l) is the six-component homogeneous (inhomogeneous) strain tensor in Voigt notation³². The parameters appearing in the effective Hamiltonian have been reported in Ref. [33] with the effective charges being discussed in Sec. II A 2. We further assume that the charges are fixed in space, the long range charge-charge Coulomb interaction energy, $E^{\text{chg-chg}}(q)$ is not included in the effective Hamiltonian. The charge-dipole energy is treated with the Ewald method and the details can be found in Ref. ? .

With the above effective Hamiltonian, we perform MC simulations with a pseudo-cubic supercell of size $12 \times 12 \times 12$ (i.e., 1728 unit cells) with periodic boundary conditions. Among the supercell, the dopants and vacancies are placed according to the arrangement described in Sec. II A 1 and the dopant concentration is calculated with respect to by La ions,

which is from 0 % to 10 % with an step of 1 %. For each of the doped samples, we gradually cool down the system from high temperature (~ 550 K) to low (~ 30 K) with a step of 10 K using 320,000 MC sweeps for each temperature to obtain the equilibrium state and thus the local mode $\{u\}$, which is used to obtain the polarization of the system at the given temperature.

III. RESULTS

Having shown the models and the effective Hamiltonian, we proceed to use MC simulations to obtain basic properties of La donor doping BaTiO_3 , including hysteresis loops, polarization, as well as phase transition temperatures, with different charge concentration and configurations. Before showing such results, we firstly certify our numerical scheme, including the Ewald interaction matrix and the newly developed MC program with $E^{\text{chg-dpl}}(\{u\}, q)$, against the defect dipole model^{38–40}, which is known to gives rise to the pinched hysteresis loop.

A. Pinched hysteresis loop

It is generally accepted that the oxygen-vacancy plays an important rule in the formation of pinched and double hysteresis loops for acceptor doping³⁸. Ren proposed that the defect dipole is microscopically formed by oxygen vacancies and an impurity ions within one unit cell³⁸. Such intentionally oriented dipoles (defect dipoles) are employed to investigate electrocaloric effect of BaTiO_3 ⁴¹. Cohen *et al.* used oriented dipoles to investigate the aging process of ferroelectric ceramics^{39,40}, and the key is that some dipoles are fixed to one particular direction without fluctuation^{38–40}.

Instead of using defect dipoles, we can deal with oxygen vacancies and impurity ions directly using the Ewald method²⁵. For each unit cell with defects, we set a positive charge $+q$ on the oxygen vacancy ($\text{V}_{\text{O}}^{\bullet\bullet}$) in a certain direction (e.g. the [001] direction) from the Ti ion, and a negative charge, $-q$, on the B site if it is an impurity ion^{25,32} [see Fig. 2(a)]. The electric field generated by the charges on dipoles are incorporated in the charge-dipole interaction matrix²⁵. The model used here is similar to Model A, except that in model A, the positive charge ($\text{La}_{\text{Ba}}^{\bullet}$) is randomly distributed on the 8 corners of the unit cell.

Figure 2(b) shows the result of the calculated hysteresis loop at 300 K with a sample of 1.2 % doping concentration. The shape of the hysteresis loop starts to show pinched effect at $q = 1.5 |e|$, which become pronounced when $q = 1.8 |e|$, consistent with the results of Liu *et al* (see Fig. 2 in Ref.⁴⁰). However, dealing with charges directly provide us more freedom in dealing with doping effects.

It is worth noting that defect dipoles are usually assumed to be fixed along some fixed directions (e.g., the [001] direction), making other dipoles easier to align and the ferroelectric phase transition temperature higher, which is inconsistent with many experimental result^{41,42}. This challenge and its possible solution will be discussed in more detail elsewhere.

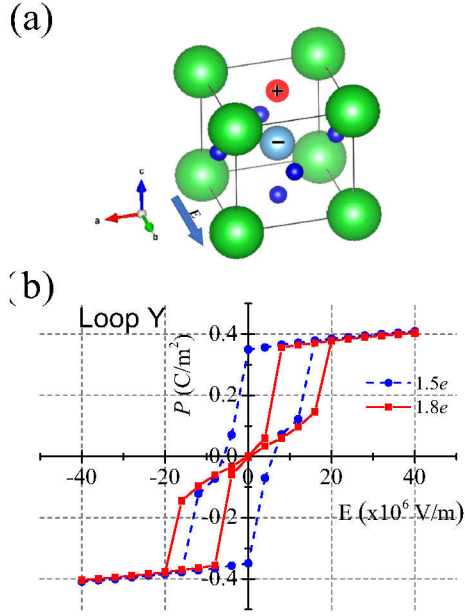


Figure 2. (a) Schematic drawing of defect dipole models ([001]) for acceptor doping. (b) Simulated hysteresis loops for BaTiO₃ with effective charge $q = 1.5 |e|$ and $q = 1.8 |e|$, at the dopant concentration $p = 1.2\%$, $T = 300$ K.

B. Energy

Energy (Hartree)	Model A	Model B	BaTiO ₃
Self energy	17.7758	19.0218	20.1890
Short range	-3.2441	-3.2003	-4.0979
Elastic	2.8230	2.8547	3.3897
Dipole-elastic	-1.9692	-2.0801	-2.9728
Dipole-dipole	-9.7998	-10.9265	-13.6581
Charge-dipole	0.2181	-0.0403	-
Total energy	5.8038	5.6293	2.8499

Table I. Constituent energy of the effective Hamiltonian for 3% doped samples relaxed at 300 K for model A and model B.

Table I shows the constituent energies from the effective Hamiltonian for the 3% doped sample. These samples are firstly relaxed at 300 K (resulting in the tetragonal phase) and then their energies calculated. For model A and B, the energies are close to each other, except the obvious difference in the charge-dipole interaction energy. Both doped samples show that the doping increases the energy of the system comparing to the pure BaTiO₃.

C. P_s and P_r

P_s and P_r are two important parameters to characterize a ferroelectric material. P_s is the saturation polarization under a large electric field, and P_r represents the remnant polarization under zero electric field when the electric field is gradually lowered. Larger P_s usually indicates larger dielectric con-

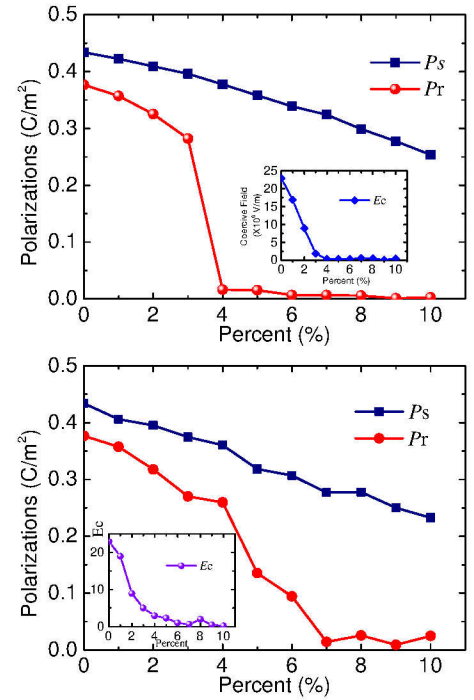


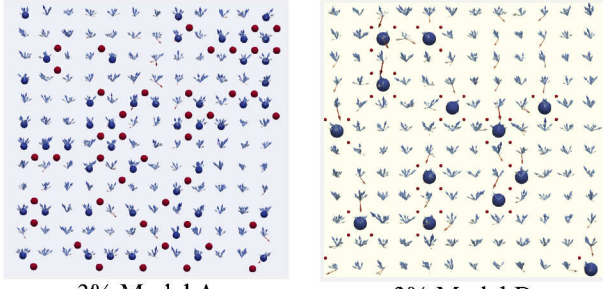
Figure 3. The saturation polarization (obtained at $E = 5.0 \times 10^7$ V/m), the remnant polarization and the coercive field obtained at 300 K with (a) model A; (b) model B.

stant, which are useful for capacitors, energy storage devices and insulators^{2,43}. P_r is often associated with pyroelectric and piezoelectric properties^{41,42}.

Using model A and B, we have numerically calculated a series of hysteresis loop for various doping concentrations (0 ~ 10%) and summarized the results in Figure 3. Pure BTO owns largest saturation polarization (P_s), remnant polarization (P_r), coercive field (E_c)^{5,11,12}. The hysteresis loops of the doped systems become much narrower with lower P_s , P_r , and E_c . It is attributed to the internal electric field associated with the dopants that disrupt the long range dipole-dipole interactions^{23,41}.

For model A, Fig. 3 (a) shows that both P_r and E_c have a sudden change at $p \simeq 4\%$, indicating a transition from a ferroelectric to a paraelectric state and the hysteresis loop vanishes. For model B, Fig. 3 (b) shows that P_r and E_c gradually decreases and vanishes at $p \simeq 6\%$. We note that the P_s of model B [$P_s(B)$] is always smaller than model A for all the dopant concentration, which can be attributed to the difference in magnitude of active dipoles and the number of defective dipoles in the doped samples²³, which is shown in Tab. II.

Table II also shows other difference between model A and model B. At 300 K, for the $p = 3\%$ doped samples, the averaged local mode of the induced active dipoles in model B is $\langle \mathbf{u}_z \rangle \simeq -0.021$ (in opposite direction to the overall polarization), which is twice as larger as Model A. The number of active dipoles (N_{AD}) for model A and B are 59 and 87, respectively. In addition, there are 13 defective dipoles ($p_i = 0$) in model B, which are caused by the missing of Ti ions. There-



3% Model A		3% Model B		
		N_{AD}	\bar{u}_z	$N_{V_{Ti}}(u_i = 0)$
3% 300K	Model A	59	-0.011	0
	Model B	87	-0.021	13
5% 250K	Model A	107	-0.014	0
	Model B	152	-0.023	22

Table II. Dipole configuration information of doped samples. Red arrow: Active dipole; Red ball: positive charge; Blue ball: negative charge; N_{AD} : number of active dipoles in z -axis; \bar{u}_z : averaged z -axis local mode value of active dipoles; $N_{V_{Ti}}$: number of Ti vacancies.

fore, two factors explain why $P_s(B)$ is much smaller than $P_s(A)$ even for higher dopant concentrations: (i) The number and magnitude of active dipoles in model B are larger than that in model A; (ii) In model A, we do not assume that dipoles are missing on the dopant sites as in model B, where the dipole is ruined when V_{Ti}''' is present while fewer dipoles usually means weaker ferroelectricity. The observation that $P_r(A)$ shows a faster decrease is likely due to the wider spread of the dopants in model A. Such dopants distribution may effectively creates polar nanoregions that introduces relaxor behaviors into the system.

D. Ferroelectric phase transition

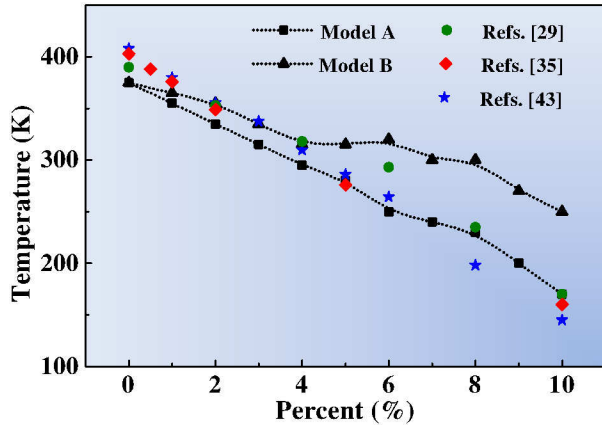


Figure 4. Numerically obtained ferroelectric phase transition temperature T_C versus dopant concentration using model A and model B are shown along with experimental values.

Pure BTO has the ferroelectric to paraelectric phase transition at $T = 375$ K³³. When La is doped into BTO, the phase

transition temperature T_C changes with dopant concentration p . Figure 4 shows the how the phase transition temperature change with dopant concentration for model A and B, and their comparison to experimental results. The results show that for both model A and model B T_C decreases rapidly with the dopant concentration. Model A has a faster decrease from 375 K (at $p = 0\%$) to 170 K (at $p = 10\%$), which agrees with the trend shown in experiments²⁹. Model B shows the same tendency for $p < 4\%$. However, the decrease with model B becomes stagnant for $p > 4\%$. We note that model B, which use Ti vacancy as the assumption, cannot produce either of the experimental results shown in Fig. 4, even for the experiment that claims the existence of Ti vacancies⁴³. Possible reasons will be discussed in Sec. IV

IV. DISCUSSION

Despite extensive experimental studies, charge compensation induced effects in La doped BaTiO₃ (and more generally rare-earth elements doped ferroelectrics) is still an open question. This lack of understanding is in part due to the various experimental results (with similar samples) that demonstrate significant differences. Most experiments with La doped BaTiO₃ assumes stoichiometry formula $(Ba_{1-x}La_x)TiO_3$ to effectively understand (or explain) properties arising from doping^{12,22,44,45}. Ganguly *et al.* prepared a variety of compositions in order to justify A-site vacancy is possible in La doped BaTiO₃²⁹. Morrision *et al.* considers the use of less Ti (in order to induce possible Ti vacancies) and obtained the experimental T_C (see Fig. 4).

Makovec *et al.* prepared different samples (according to the two different formula) by the conventional mixed-oxide method and studied their microstructure change during their reduction/reoxidation process¹⁷. They have shown that when $(Ba_{1-x}La_x)(Ti_{1-x}^{4+}, Ti_x^{3+})O_3$ was exposed to oxidizing environment, electron diffraction pattern revealed that the Ti-rich phase ($Ba_6Ti_{17}O_{40}$) is expelled from the solid solution, and the donor charge compensation changed from electronic compensation to Ti vacancy compensation^{9,17}. Lanculescu *et al.* prepared the two different samples (assuming the two different compensation mechanism) at 0.5% dopant concentration²². They showed that the phase transition temperature T_C decrease remarkably with all their hysteresis loops disappear, which is not expected²². Meanwhile, Ti^{3+} is believed to be responsible for the dark color of the doped samples, which had been in experiments¹⁷.

On the theory side, Lewis *et al.* considered the ternary phase diagram proposed by Jonker *et al.*⁹ and the calculated binding energy of $[LaBaV_{Ti}''']$ ¹⁶, proposed that in La doped BTO the charge compensation is predominantly by electron, but with high dopant concentration, Ti vacancy appears^{9,16}. However, Freeman *et al.* keep the view that electron compensation mechanism is never the primary one, irrespective of the donor dopant concentration^{13,30}.

Based on our findings, the electron transfer model (model A) is the more likely compensation mechanism. Summariz-

ing the available results (including our simulation here), we have some insights regarding how doping works. The key that dopants work is disrupting the long range dipole-dipole interactions, which work through three ways: (i) Doping induces extra charges in the system, producing additional internal electric field than a pure dipole system, therefore disturbing the dipole-dipole order of pure BTO; (ii) Precipitated compounds. Under oxidation condition, Ba_2TiO_4 and/or $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ may arise and embed in the system^{16–18,46}, which can disrupt the long-range order as well; (iii) Local strain that may be induced by the change of the valence state from Ti^{4+} to Ti^{3+} since the ionic radius of Ti^{3+} is larger than Ti^{4+} . However, since Ti ions are inside the oxygen octahedron, it is hard to estimate how large the local strain shall be. While the model here have not included all the factors, the simulation results indicate that factor (i) is probably most important that can account for the T_C decrease and reproduce their properties and displays the dipoles configurations for samples with different dopant concentration.

Our simulation results have that model A is a better model to understand La-doped BaTiO_3 , supporting the idea that electronic compensation is the underlying mechanism. However, it should be noted that there are limitations to our models and simulations. In model B, since Ti vacancies exist, it may be better if the strain associated with them is included at higher dopant concentration. This factor could be the reason that model B cannot well reproduce the trend of T_C for $p > 5\%$. To reveal how important such an effect can be, we further tested a modified model B with charge and strain effects included.

However, we were not able to see a clear improvement.

V. CONCLUSION

In this work, we have considered the charge effects in ferroelectric materials, taking into account the long range charge-dipole interaction²⁵. We first verified our approach producing the pinched hysteresis loops of acceptor doping as known from defect dipole model. We have applied this scheme to La doped BaTiO_3 and proposed two theoretical calculation models. With these two models, saturation polarization, remnant polarization and coercive field are obtained, which decrease with increasing dopant concentration. Focusing on the paraelectric to ferroelectric phase transition temperature T_C , we find that the disruption of long range dipolar interaction due to the doped dopants can strongly influence the phase transition temperature. Our results indicate that the electron compensation mechanism (model A) is a more plausible model to understand the doping effects. We note that our approach is also applicable to other doped situations where the effective charge for the doped chemical element is known. We hope this work will inspire more investigation to understand the doping effects, which is important and interesting.

ACKNOWLEDGMENTS

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