Enhanced charge ordering transition in doped CaFeO$_3$ through steric templating

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Abstract

We report density functional theory (DFT) investigation of B-site doped CaFeO$_3$, a prototypical charge-ordered perovskite. At 290 K, CaFeO$_3$ undergoes a metal-insulator transition and a charge disproportionation reaction $2$Fe$^{4+} \rightarrow$Fe$^{5+}$+Fe$^{3+}$. We observe that when Zr dopants occupy a (001) layer, the band gap of the resulting solid solution increases to 0.93 eV due to a 2D Jahn-Teller type distortion, where FeO$_6$ cages on the $xy$ plane elongate along $x$ and $y$ alternately between neighboring Fe sites. Furthermore, we show that the rock-salt ordering of the Fe$^{5+}$ and Fe$^{3+}$ cations can be enhanced when the $B$-site dopants are arranged in a (111) plane due to a collective steric effect that facilitates the size discrepancy between the Fe$^{5+}$O$_6$ and Fe$^{3+}$O$_6$ octahedra and therefore gives rise to a larger band gap. The enhanced charge disproportionation in these solid solutions is verified by rigorously calculating the oxidation states of the Fe cations with different octahedral cage sizes. We therefore predict that the corresponding transition temperature will increase due to the enhanced charge ordering and larger band gap. The compositional, structural and electrical relationships exploited in this paper can be extended to a variety of perovskites and non-perovskite oxides providing guidance in structurally manipulating electrical properties of functional materials.

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I. INTRODUCTION

The perovskite (ABO$_3$) family of materials has been paid considerable attention both in experimental and theoretical studies due to their flexible and coupled compositional, structural, electrical and magnetic properties [1–3]. Such flexibility arises from the structural building blocks — the corner-connected BO$_6$ octahedra, where B is usually a transition metal. Typical structural variations from the cubic structure include rotation and tilting of the octahedra [4], off-centering of the A and/or B cations (pseudo Jahn-Teller effect) [5], and expansion/contraction of the BO$_6$ octahedral cages [6]. While the first two distortions are ubiquitous, the cooperative octahedral breathing distortion is rather rare in perovskites with a single B cation composition. Such breathing distortion, resulting from the alternation of elongation and contraction of the B-O bonds between neighboring BO$_6$ cages, is usually concomitant with the charge ordering of the B cations and a corresponding metal-insulator transition. CaFeO$_3$ is a typical perovskite material exhibiting such charge ordering transition [7]. At room temperature, the strong covalency in the Fe $e_g$ - O 2p interaction leads to a $\sigma^*$ band and electron delocalization which gives rise to metallic conductivity in CaFeO$_3$. Near 290 K, a second-order metal-insulator transition (MIT) occurs which reduces the conductivity dramatically [8]. The Mössbauer spectrum of low temperature CaFeO$_3$ has revealed the presence of two chemically distinct Fe sites (with different hyperfine fields) present in equal proportion [9]. This indicates that the Fe cations undergo charge disproportionation $2\text{Fe}^{4+} \rightarrow \text{Fe}^{5+} + \text{Fe}^{3+}$ below the transition temperature. The origin of the charge ordering transition is usually attributed to Mott insulator physics, where the carriers are localized by strong electron-lattice interactions [7, 9–11]. More recently, it has been debated whether the difference in charge state resides on the B cations or as holes in the oxygen 2p orbitals [12–14], and several computational studies showed that the magnetic configuration, in addition to structural changes, plays a vital role in stabilizing the charge ordered state in CaFeO$_3$ [15–17]. Nevertheless, the amplitude of the cooperative breathing mode is a key indicator of the magnitude of electron trapping and band gap opening in MIT. Conversely because the MIT is sensitive to lattice distortion, structural manipulation such as cation doping and epitaxial strain can be exploited to control the electrical properties of this family of oxide systems.

In this study, we examine the structural and electrical properties in B-cation doped
CaFeO$_3$ with density functional theory (DFT). Various dopant cations, concentrations, and arrangements have been tested. Dopants of different sizes are tested, and alignments of pairs of dopants along different crystallographic planes are examined. To confirm the presence of charge ordering in (111) doped CaFeO$_3$, we also carried out rigorous oxidation state calculations for Fe cations in different octahedral cages based on their wave function topologies [18]. Through examination of these model systems, we assess the extent to which the structure-coupled electronic transition in doped oxide materials like CaFeO$_3$ can be influenced via doping to enhance band gap tunability, which in turn controls the MIT temperature.

II. METHODOLOGY

Our DFT calculations are performed using the norm-conserving nonlocal pseudopotential plane-wave method [19]. The pseudopotentials [20] are generated by the Opium package [21] with a 50 Ry plane-wave energy cutoff. Calculations are performed with the Quantum-Espresso package [22] using the local density approximation [23] with the rotationally invariant effective Hubbard $U$ correction [24] of 4 eV on the Fe $d$ orbitals [17, 25] for the exchange-correlation functional. In case of Ni and Ce doping, we applied $U = 4.6$ eV [26] and $U = 5$ eV [27] for Ni $d$ and Ce $f$, respectively. Calculations are performed on a $4 \times 4 \times 4$ Monkhorst-Pack $k$-point grid [28] with electronic energy convergence of $1 \times 10^{-8}$ Ry, force convergence threshold of $2 \times 10^{-4}$ Ry/Å, and pressure convergence threshold of 0.5 kbar. For polarization calculations a $4 \times 6 \times 12$ $k$-point grid is used, where the densely sampled direction is permuted in order to obtain all three polarization components. Different spin orderings for pure CaFeO$_3$ are tested to find the magnetic ground state, and subsequent solid solution calculations all start with that magnetic ground state.

III. RESULTS AND DISCUSSION

A. Ground state of CaFeO$_3$ and CaZrO$_3$

To identify the correct spin ordering in pure CaFeO$_3$, we performed relaxations on both high temperature metallic orthorhombic $Pbnm$ [7, 9, 11, 29] and low temperature semiconducting monoclinic $P2_1/n$ [30] structures with common magnetic orderings commensurate
with the $2 \times 2 \times 2$ supercells, as shown in Fig. 1 (note that diamagnetic (DM) ordering is not included in the figure).

![Diagram showing crystal structure and spin ordering]

FIG. 1. (a) Low temperature $P2_1/n$ structure of CaFeO$_3$ with two symmetry-distinct Fe cation sites color coded. The spin ordering of the Fe cations are (b) ferromagnetic (FM), (c) A-type anti-ferromagnetic (AFM), (d) C-type anti-ferromagnetic and (e) G-type anti-ferromagnetic.

TABLE I. Calculated total energy $E$, atomic magnetization $m_1$ and $m_2$ for the two Fe sites, total magnetization per five-atom formula unit $M$ and FeO$_6$ octahedral volume $V_1$ and $V_2$ for the two Fe sites of relaxed CaFeO$_3$ with different starting structures and magnetic orderings.

|       | $E$ (eV) | $m_1$ ($\mu_B$) | $m_2$ ($\mu_B$) | $M$ ($\mu_B$) | $V_1$ (Å$^3$) | $V_2$ (Å$^3$) |
|-------|---------|----------------|----------------|-------------|-------------|-------------|
| $Pbnm$ | DM      | 6.64           | N/A            | N/A         | 8.40        | 8.40        |
|       | FM      | 0.07           | 3.38           | 3.38        | 4.00        | 8.94        | 8.94        |
|       | A-AFM   | 0.43           | 3.29           | -3.29       | 0.00        | 9.00        | 9.00        |
|       | C-AFM   | 0.58           | 3.24           | -3.24       | 0.00        | 8.92        | 8.92        |
|       | G-AFM   | 0.96           | 3.44           | -3.51       | 0.06        | 9.52        | 8.47        |
| $P2_1/n$ | DM      | 6.64           | N/A            | N/A         | 8.40        | 8.40        |
|       | FM      | 0              | 3.13           | 3.60        | 4.00        | 9.16        | 8.75        |
|       | A-AFM   | 0.32           | 3.69           | -3.69       | 0.00        | 9.57        | 8.40        |
|       | C-AFM   | 0.58           | 3.24           | -3.24       | 0.00        | 8.92        | 8.92        |
|       | G-AFM   | 0.81           | 3.85           | -2.39       | 1.00        | 10.05       | 8.13        |

From the results in Table. I, we can see that both high temperature and low temperature ferromagnetic CaFeO$_3$ relax to the ferromagnetic ground states. Note that an additional magnetic phase transition is experimentally observed for CaFeO$_3$ at 15 K, where it adopts
an incommensurate magnetic structure with a modulation vector \([\delta, 0, \delta]\) \((\delta \approx 0.32, \text{ and reciprocal lattice vectors as basis})\) \([7]\). Since DFT calculates 0 K internal energy, the ferromagnetic ground state represents a reasonable approximation of the spin-spin interactions within a unit cell given the relatively long spin wave length and low experimental crossover temperature to FM. The volumes of the two FeO\(_6\) cages are equivalent in the high temperature metallic phase, as expected. The low temperature ground state has a cage size difference \(\Delta V = 0.41\text{Å}^3\), indicating some degree of charge ordering. However, the projected density of states (PDOS) of the \(P2_1/n\) ground state \(\text{CaFeO}_3\) in Fig. 2a shows that although there are separate gaps in each spin channel, the valence band edge in the majority spin touches the conduction band edge in the minority spin, resulting in zero total gap. The absence of band gap and the weak charge ordering is a result of the underestimation of band gaps in DFT \([31]\) due to its unphysical electron delocalization, This result is common in Mott insulators with partially filled \(d\) orbitals and is in agreement with another DFT study of \(\text{CaFeO}_3\) \([12]\). Even though DFT does not predict the correct electronic ground state of \(\text{CaFeO}_3\), it is however indicative of the sensitive nature of the \(\text{CaFeO}_3\) band gap as it can be easily influenced when Fe \(d\) orbital filling is varied by structural or other perturbations. Moreover, the different \(\Delta V\) between high temperature and low temperature of FeO\(_6\) ground state suggests that the structural aspect of the MIT can be modeled reasonably well by DFT.

FIG. 2. Projected density of states of (a) \(\text{CaFeO}_3\) (left) and (b) \(\text{CaZrO}_3\).

For comparison, we calculated the PDOS of \(\text{CaZrO}_3\) relaxed from experimental \(Pbnm\)
structure [32], shown also in Fig. 2b. Because Zr\(^{4+}\) has empty \(4d\) orbitals, the fraction of Zr \(d\) states in the valence band is negligible compared to O \(p\) states, and a wide charge-transfer gap of 3.82 eV occurs. Since we expect to exploit the size effect of the dopants like Zr to influence the electronic property of CaFeO\(_3\), we expect that the nature of Fe spin-spin interaction is not greatly affected by doping. Therefore in the following study we continue to use FM as the starting magnetic configuration for relaxations of the doped materials.

**B. CaFeO\(_3\)-CaZrO\(_3\) solid solutions with \(2 \times 2 \times 2\) super cell**

To test how Zr doping influences the structural and electrical properties of CaFeO\(_3\), we performed relaxations and subsequent band gap calculations of CaFeO\(_3\)-CaZrO\(_3\) solid solutions. We employ a \(2 \times 2 \times 2\) super cell and explore all possible \(B\)-site cation combinations. All the solid solutions tested turn out to be metallic except one, which has a gap of 0.93 eV. The insulating solid solution has a cation arrangement with four Zr cations on the (001) plane, making it a layered structure along [001]. Interestingly, instead of a breathing-mode charge disproportionation, this structure has a 2D Jahn-Teller type distortion, and all four Fe cations are in the same chemical environment. As shown in Fig. 3, the Fe-O bond lengths in the \(xy\) plane are 2.16 Å and 1.83 Å in each FeO\(_6\), with the orientation alternating between neighbors. The shorter Fe-O bond length is essentially the same as that in high temperature CaFeO\(_3\). The consequence of the addition of larger Zr\(^{4+}\) cations (\(r = 0.72\) Å) compared to Fe\(^{4+}\) (\(r = 0.59\) Å) is that when Zr cations occupy an entire (001) plane the in-plane lattice is expanded from 3.70 Å to 3.88 Å, elongating the Fe-O bonds and enabling the 2D Jahn-Teller type distortion.

From the PDOS of the solid solution in Fig. 4a we can see that like pure CaFeO\(_3\) both the valence and the conduction edges are of Fe \(3d\) and O \(2p\) characters, with virtually no Zr contribution. In charge ordering MIT, the delocalized electrons on Fe\(^{4+}\) transfer to neighboring Fe\(^{4+}\), making Fe\(^{3+}\)/Fe\(^{5+}\) pairs with the valence and conduction bands located on different cations, concomitant with FeO\(_6\) cage size changes. The band gap in case of charge ordering therefore depends on the energy difference between the \(e_g\) orbitals in Fe\(^{3+}\) and Fe\(^{5+}\), which in turn is affected by the crystal field splitting energy caused by the oxygen ligands. On the other hand, as illustrated in Fig. 4b, the solid solution band gap is caused by the removal of degeneracy in the \(e_g\) orbitals and is controlled by the difference in energy
between the two $e_g$ orbitals on the same Fe$^{4+}$ cation. Since the $e_g$ gap splitting is a result of the Fe-O bond length difference, it is easier to tune by applying either chemical pressure or biaxial strain to change the in-plane lattice constant, whereas the charge ordering mechanism requires the control of individual FeO$_6$ octahedral sizes to change the relative energy of $e_g$ orbitals between two Fe sites. Nevertheless, this CaFeO$_3$-CaZrO$_3$ solid solution demonstrates that when arranged in a particular way, in this case on (001) plane, the size effect of the large Zr cation can cause a cooperative steric effect on the structure and affect the electrical properties of CaFeO$_3$, opening up the band gap via a completely different mechanism.

### C. CaFeO$_3$ with dopants on the (111) plane

As discussed in the previous section, simply doping Zr into $2 \times 2 \times 2$ CaFeO$_3$ does not increase the band gap except for one case where 2D Jahn-Teller instead of breathing mode serves to make the system insulating. In a perovskite system with rock-salt ordered alternating $B$ cations, such as CaFeO$_3$, one $B$ cation type occupies entire (111) planes and the other type occupies its neighbors in all directions. Since Zr cation is larger than Fe cation, to fully utilize its steric effect to distinguish Fe$^{3+}$ from Fe$^{5+}$, it follows that Zr should replace...
Energy
Fe\(^{3+}\) (d\(^5\))
Fe\(^{5+}\) (d\(^3\))
Fe\(^{4+}\) (d\(^4\))

\(t_2g\)
\(e_g\)

FIG. 4. (a) PDOS of of Ca(Fe\(_{1/2}\)Zr\(_{1/2}\))O\(_3\) and (b) illustration of band gap formation in CaFeO\(_3\) (left) and Ca(Fe\(_{1/2}\)Zr\(_{1/2}\))O\(_3\) (right).

a full Fe\(^{3+}\) plane to increase the BO\(_6\) size on the plane, maximizing its utility by enhancing the cage size difference. A schematic of the (111) doping strategy and the influence of the dopants on their neighboring planes is shown in Fig. 5b.

FIG. 5. (a) Crystal structure of \(\sqrt{2} \times \sqrt{6} \times 2\sqrt{3}\) CaFeO\(_3\) supercell doped with one layer of Zr on the (111) plane. The average BO\(_6\) octahedron size is listed on the side. (b) Schematic of how a layer of dopants with larger ionic radius exerts a cooperative size effect on the neighboring layers and enhances the existing charge ordering.
Following this logic, we perform calculations with $\sqrt{2} \times \sqrt{6} \times 2\sqrt{3}$ CaFeO$_3$ super cell, which has six (111) FeO$_2$ layers stacked perpendicularly, as the parent material. One layer of Fe’s is replaced with Zr’s and the structural is relaxed. The final structure is shown in Fig. 5a, as well as the average BO$_6$ cage size of each layer. Clearly the introduction of a (111) Zr layer drives the charge disproportionation of Fe$^{4+}$ by exerting chemical pressure on both sides of the layer and favoring the FeO$_6$ on the two adjacent planes to be smaller and become Fe$^{5+}$. The second next neighboring layers in turn have more room to expand and favor larger Fe$^{3+}$. The size difference between the largest and the smallest FeO$_6$ cages ($\Delta V = 0.58\text{Å}^3$) in this structure is an enhancement compared to pure CaFeO$_3$ $\Delta(V = 0.41\text{Å}^3)$, which suggests the presence of a stronger charge ordering and a wider band gap. However electronic structure calculation shows that this solid material is metallic as well. The reason that the seemingly more charge ordered system still does not possess a gap can be attributed to the supercell employed. By using a unit cell with six (111) layers and replacing only one layer of Fe with Zr, structurally the remaining five Fe layers are disturbed by the large Zr layer as expected. However the charge disproportionation reaction $2\text{Fe}^{4+} \rightarrow \text{Fe}^{5+} + \text{Fe}^{3+}$ cannot proceed to completion, because it requires an even number of Fe layers. Therefore with one layer of dopants there will always be Fe$^{4+}$ “leftovers” that render the whole system metallic.

To resolve the issue of odd number of Fe layers we introduce another layer of +4 dopants with smaller ionic radius than Fe. For simplicity we denote a solid solution in this case by listing the B cations in each of its six (111) layers, with dopant elements in bold. For example, the previously discussed one layer Zr-doped solid solution would be denoted as ZrFeFeFeFeFe. The presence of two dopant layers provides both positive and negative chemical pressure to expand Fe$^{3+}$ and contract Fe$^{5+}$. These two dopant layers are separated by an even number of Fe layers so that the FeO$_6$ size alternation is enhanced. An odd number of Fe layers in between the dopant layers would disrupt and impede the size modulation period. Relaxations are performed on ZrNiFeFeFeFe and ZrFeFeNiFeFe, as well as CeNiFeFeFeFe and CeFeFeNiFeFe. The average FeO$_6$ cage size per layer is listed in Table II, along with the maximum cage size difference $\Delta V$ and the corresponding band gap of each solid solution. It can be seen that with only Zr as dopant, the $\Delta V$ is significantly smaller than those with two layers of dopants, and $\Delta V$ correlates with the band gap. The Ce-containing solid solutions have a larger $\Delta V$ compared to the Zr-containing ones, due to the larger size of Ce. It also shows that when the larger dopant and the smaller dopant
layers are adjacent, the resulting $\Delta V$ is larger than when they are two Fe layers apart, this is due to the lack of symmetry of the former configuration where the absence of a mirror plane perpendicular to the $z$ axis allows for the FeO$_6$ close to the dopant layers to further expand or contract compared to the ones that are not neighbors of the dopant layers. In the latter configuration, symmetry guarantees that octahedra on either side of the dopant layer are deformed equally.

TABLE II. Properties of CaFeO$_3$ doped on the (111) plane. $V_1$ through $V_6$ are average FeO$_6$ volumes in Å$^3$, where the largest and the smallest cages in each solid solution are in bold. $\Delta V$ is the size difference between the largest and smallest volumes and $E_g$ is the band gap of the corresponding material in eV.

| (111) Layers | $V_1$ | $V_2$ | $V_3$ | $V_4$ | $V_5$ | $V_6$ | $\Delta V$ | $E_g$ |
|--------------|-------|-------|-------|-------|-------|-------|-----------|------|
| ZrFeFeFeFeFe | Zr    | 8.81  | **9.33** | 8.75  | 9.29  | 8.83  | 0.58      | 0    |
| ZrNiFeFeFeFe | Zr    | Ni    | 9.52  | 8.53  | **9.59** | 8.27  | 1.32      | 0.49 |
| ZrFeFeNiFeFe | Zr    | 8.32  | 9.43  | Ni    | **9.45** | 8.28  | 1.17      | 0.11 |
| CeNiFeFeFeFe | Ce    | Ni    | **9.77** | 8.61  | 9.69  | **8.29** | 1.48      | 0.83 |
| CeFeFeNiFeFe | Ce    | **8.39** | **9.75** | 8.73  | 8.41  | 1.36  | 0.53      |      |

From Fig. 6 we can see that with increasing difference in FeO$_6$ size, the band gap of the corresponding solid solutions increases accordingly. This relationship demonstrates the coupling between structural and electrical properties as larger FeO$_6$ size discrepancy indicates stronger and more complete charge disproportionation. As illustrated in Fig. 4b, when charge ordering is the band gap opening mechanism, the gap size depends on the crystal field splitting energy difference between Fe$^{3+}$ and Fe$^{5+}$. A larger FeO$_6$ cage size difference means that the O 2$p$ - Fe 3$d$ repulsion difference is also larger between the two Fe sites. This causes the energy difference of the $e_g$ orbitals in the two sites to increase and the band gap to increase as well. Using linear regression we estimate that the chemical pressure exerted on the band gap by the volume difference in this type of solid solutions is quite large at about 370 GPa, in accordance with the effective band gap tuning. Since the transition to metal occurs when thermally activated electrons have enough energy to cross the band gap and flow between the two Fe sites to make them indistinguishable, we believe that by (111) doping the MIT temperature of CaFeO$_3$ can be increased, making devices based on it more
operable at room temperature.

$$E_g = 2.30\Delta V - 2.58$$

FIG. 6. Band gap $E_g$ of the (111) doped CaFeO$_3$ solid solutions increases with the corresponding maximum FeO$_6$ size difference $\Delta V$. This gives an effective chemical pressure on the band gap of 2.30 eV/Å$^3$ or 370 GPa.

To investigate the layered nature of the solid solutions, we use ZrNiFeFeFeFe as an example and plot the projected density of states of it in Fig. 7 in a layer resolved fashion. Each of the six panels in Fig. 7 represents a layer of CaBO$_3$, and the relative position of the panels corresponds to the that of the six layers in the crystal. It can be seen clearly that for the four layers containing Fe ions, the first and the third layers have more majority spin Fe $d$ in the valence band, while the second and fourth layers have more majority spin Fe $d$ in the valence band. This difference is consistent with the fact that Fe$^{3+}$ has more filled $d$ orbitals than Fe$^{5+}$ and supports our prediction that the doubly doped (111) layered CaFeO$_3$ has an enhanced charge ordering due to the strong modulation of the FeO$_6$ cage volume.
FIG. 7. Layer resolved projected density of states of ZrNiFeFeFeFe. Each of the six panels represents a layer of CaBO$_3$, and the relative position of the panels corresponds to the that of the six layers in the crystal.

To further verify the charge disproportionation mechanism, we performed oxidation state calculations of the Fe cations in ZrNiFeFeFeFe. We employed an unambiguous oxidation state definition [18] based on wave function topology, whereby moving a target ion to its image site in an adjacent cell through an insulating path and calculating the polarization change during the process, the number of electrons that accompany the moving nucleus can be calculated. The oxidation state obtained this way is guaranteed to be an integer and is unique for an atom in a given chemical environment, not dependent on other factors such as charge partitioning or the choice of orbital basis. In Fig. 8 we show how the quantity $N = \Delta \vec{P} \cdot \vec{R} / \vec{R}^2$ changes as each Fe cation is moved along an insulating path to the next cell, which is equivalent to the oxidation state of the cation. The two Fe ions with larger cages
are confirmed to be Fe\(^{3+}\) and the ones with smaller cages are Fe\(^{5+}\). This proves that charge ordering occurs in this material and causes band gap opening. Note that the oxidation states calculated are not directly related to the charges localized around the Fe sites, which has been shown to change insignificantly upon oxidation reaction in some cases [33]. In fact the Bader charge [34] of the Fe cations are 1.76 and 1.73 for the smaller and larger FeO\(_6\) cages, respectively, which shows minuscule differences between Fe sites that are in significantly different chemical environments in terms of oxygen ligand attraction.

The (111) doping strategy shows that the size difference between Fe\(^{3+}\) and Fe\(^{5+}\) can be exploited and reinforced by selectively replacing layers of Fe\(^{3+}\) with Fe\(^{5+}\) with atoms of even larger or smaller size, respectively, to enhance charge ordering and the insulating character of the CaFeO\(_3\) system.

IV. CONCLUSIONS

We have demonstrated that for prototypical charge ordering perovskite CaFeO\(_3\), the band gap of the insulating state can be engineered by \(B\)-site cation doping and structural manipulation. For the dopant atoms to exert significant influence on the parent material, it is favorable to arrange them in a way that their size effects are cooperative and synergistic, producing a collective steric effect and greatly altering the structural and electrical properties. When doped on the (001) plane with larger Zr cations, the in-plane lattice constant expands and supports a 2D Jahn-Teller type distortion, where each FeO\(_6\) has two distinct Fe-O bond length in the \(xy\) plane. Such distortion removes the degeneracy of the two \(e_g\) orbitals on each Fe\(^{4+}\) and opens up a band gap (not caused by charge ordering) of 0.93 eV. On the other hand, to enhance the weak charge ordering in pure CaFeO\(_3\), we discovered that including two types of dopants on the (111) plane can increase the FeO\(_6\) cage size difference and enhance the charge ordering. Using Zr or Ce to replace the larger Fe\(^{3+}\) and Ni to replace the smaller Fe\(^{5+}\) increases the band gap up to 0.83 eV. The degree of charge ordering is closely related to the magnitude of FeO\(_6\) cage size difference. We used the rigorous definition of oxidation state to verify that in the latter case the band gap opening mechanism is indeed charge disproportionation, as the oxidation states of the larger and smaller Fe cations are calculated to be +3 and +5, respectively. Our results show that the structural and electrical properties of CaFeO\(_3\) are coupled, and simple steric effects can enhance charge ordering.
FIG. 8. Oxidation state $N$ of the four Fe cations. $\lambda$ denotes the reaction coordinate of moving the Fe ion sublattice to the neighboring cell and the change in $N = \frac{\Delta \vec{P} \cdot \vec{R}}{R^2}$ from $\lambda = 0$ to $\lambda = 1$ corresponds to the oxidation state of that Fe ion.

transition and alter the band gap of the material greatly when the dopant atoms are placed to act cooperatively. Lastly by enhancing the charge ordering via doping, we predict that the MIT temperature of CaFeO$_3$ can also be increased to a temperature more suitable for practical device operation.

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