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Asymmetric covalence bonding between In 5s and O 2p states in ferroelectric $InFeO_3$

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The structural evolution, electronic and magnetic properties of the high-pressure nonpolar orthorhombic phase (orthorhombic, space group *Pnma*) and the $LiNbO_3$-type (rhombohedral, space group *R3c*) $InFeO_3$ have been explored via first-principles calculations. Furthermore, the ferroelectric properties of the $LiNbO_3$-type phase have been revisited thoroughly. First of all, the nonpolar orthorhombic phase crystallized within *Pnma* space group was theoretically recognized. Secondly, the results reasonably reproduced the pressure-induced *R3c* → *Pnma* structural phase transition, which is in fair agreement with the experimental observation that the $LiNbO_3$-type phase can be achieved from the decompression of the high pressure perovskite phase. In addition, the electric polarization for the non-centrosymmetric $LiNbO_3$-type within the G-type antiferromagnetic ground state is evaluated to be $86.5\ \mu C/cm^2$ by means of the Berry phase formula. More interestingly, in conjunction with the geometric factor, an additional mechanism behind the ferroelectric displacement is clarified as the strong chemical bonding between the In 5s and O *2p* orbitals, i.e., the hidden tendency to create space for the unoccupied antibonding states, independent of whether the cation is an s^0 or s^2 configuration, and is manifested in terms of the analysis of Born effective charges, potential energy surfaces, charge density isosurfaces.

1. Introduction

The $LiNbO_3$-type ABO_3 oxides containing extremely small A-site cations, within noncentrosymmetric polar space group *R3c*, have ignited widespread scientific and technological interest owing to the potential candidates for single phase magnetoelectric multiferroics [1]. This structure is characterized by relative ions displacements along the three-fold [111] direction, conjugated with out-of-phase tilting of BO_6 octahedra around it, driving a spontaneous polarization along the [111] direction. Furthermore, the flexibility of the framework allows incorporation of different magnetic transition metal ions in both the A- and B-sites, facilitating the design of polar magnetic materials [2–12]. Due to the small tolerance factors, high pressure and high temperature techniques are required to achieve the strongly tilted BO_6 octahedral framework in the $LiNbO_3$-type structure. On the other hand, the mechanism insight into the ferroelectric displacements is obscure and still under debate. N. A. Benedek et al. clarified the origin of ferroelectric distortion as the coordination preference of the small A-site cations, i.e., the geometric effect. The A-site acentric displacements play a significant role in optimizing the bonding environment for the extremely small ions [13]. However, the asymmetric covalent bonding effect has been highlighted in the $LiNbO_3$-type systems containing the cations with ns^0 electronic configuration [14–18]. Contrary to naive expectations, this ferroelectric mechanism can then be assimilated to the $BiFeO_3$ [19], in which the stereochemical activity of the $6s^2$ lone pair of the Bi^{3+} cation plays an imperative role. The role of the asymmetric covalent bonding between *ns* states and oxygen *2p* ones, however, seems less conspicuous and was disregarded in the systems embodying the cations with ns^0 electronic configuration.

Up to now, many polar magnetic materials [3–8] within the $LiNbO_3$-type structure have been synthesized under the high pressure and high temperature conditions. Unfortunately, the magnetic transition temperature drops mostly below the room temperature. Exceptionally, $ScFeO_3$ [10] and $InFeO_3$ [12] have been reported to exhibit the antiferromagnetic transition temperature T_N up to 545 K, generally owning to the strong magnetic interactions in the Fe^{3+} (S = 5/2) sublattice. Experimentally, it is challenging to stabilize the completely cation ordered $LiNbO_3$-type $InFeO_3$, realized through quenching from the nonpolar orthorhombic perovskite phase synthesized under 15 GPa at high temperature. Magnetic studies suggested the ground magnetic state of $InFeO_3$ is G-type antiferromagnetic arrangement, i.e., the antiferromagnetic coupling among the nearest neighbor Fe spins. The lack

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of the inversion center allows the canted of the magnetic moments through the Dzyaloshinsky-Moriya (DM) interaction, resulting into weak ferromagnetic trait. The saturation moment of the ferromagnetic component at 5 K is $\sim 0.03\ \mu_B$/Fe, revealing a canting angle of $\sim 0.2^\circ$ of ordered Fe^{3+} spins, oriented in directions perpendicular to the *c*-axis [12]. Moreover, the electric polarization of the $LiNbO_3$-type $InFeO_3$ is predicted to be 96 μC/cm^2, as the A-site driven geometric ferroelectrics, the emergence of polar displacement was ascribed to electrostatic interactions, i.e., geometric effect [12]. The experimental results mentioned above, therefore, put forward the $LiNbO_3$-type $InFeO_3$ as a promising candidate for magnetoelectric material above the room temperature. The mechanism behind the ferroelectric distortion in $InFeO_3$ is ascribed to the underbonded feature of the In ions [12], similar to $ScFeO_3$ [10]. If the geometric effect takes effect in $InFeO_3$ exclusively, the interoctahedral distortion parameter of InO_6 octahedra should be smaller than that of ScO_6, since the ionic radius of In^{3+} (with 6 coordination, 80 p.m.) is slightly larger than that of Sc^{3+} (with 6 coordination, 75 p.m.) [41]. However, the experimental observations ($\Delta = 18.8 \times 10^{-4}$ for InO_6 [12] versus$\Delta = 6.1 \times 10^{-4}$ for ScO_6^{10}) patently contradict with the geometric argument. The paradox suggested an additional contribution for the large ferroelectric distortion in $InFeO_3$, aside from the geometric effect. Hence, the origin of the ferroelectric distortion in the $LiNbO_3$-type phase deserves to be deliberated. Furthermore, the phase transformation and electronic, magnetic properties of both the $InFeO_3$ polymorphs (nonpolar orthorhombic and $LiNbO_3$-type) remain unclear from the theoretical perspective.

In this study, we present the results of first-principle calculations on structural, electronic and magnetic properties for the nonpolar orthorhombic and $LiNbO_3$-type phase of $InFeO_3$ via standard DFT + U scheme. We confirmed the stability of the $LiNbO_3$-type phase as well as the G-type antiferromagnetic alignment of the Fe spins. The pressure induced phase transition from the $LiNbO_3$-type phase to nonpolar orthorhombic phase has been recognized, which is in nice agreement with the experimental fact that the $LiNbO_3$-type phase is conquered by decompressing the nonpolar pervoskite phase. Furthermore, the results indicate that the asymmetric hybridization interaction between In 5s and O 2p orbitals acts as a supplemental impelling cause of the atomic polar displacement along the [111] direction, other than the geometric effect, leading to a considerable large spontaneous polarization of 86.5 μC/cm^2.

2. Computational details

We conducted first-principles density-functional spin-polarized calculations within the generalized gradient approximation (GGA) [20] according to the Perdew-Burke-Ernzerhof (PBE) parametrization scheme as constructed in Vienna ab initio simulation package (VASP) [21,22]. The effect of electron correlation in the Fe 3 d shell is taken into account by compensating the on-site Coulomb interactions with the Hubbard method [23]. We have chosen the effective value of the U_{eff} parameter to be 4.0 eV for the Fe atoms, the value adopted for $ScFeO_3$ [24,25]. Projector-augmented plane wave (PAW) potential limited by a cutoff energy of 500 eV were employed, including 13 valence electrons for In($4d^{10}5s^25p^1$), 8 for Fe ($3d^64s^2$), and 6 for ($2s^22p^4$), respectively. An integration of the Brillouin zone was sampled using $6 \times 4 \times 6$ and $6 \times 6 \times 6$ Γ-centered grid in *k* space, generated by Monkhorst-Pack scheme [26,27] for the nonpolar orthorhombic and $LiNbO_3$-type phase, respectively. Each self-consistent electronic calculation is converged to 10^{-5} eV, and the tolerance force is set to be 0.01 eV/Å for ionic relaxation.

For the structural evolution, we discerned the phase transition by matching the enthalpy as a function of pressure. The energy-volume (E-V) curves at various volumes were fitted to the third-order Birch-Murnaghan equation of state (EOS) [28]:

$$E(V) = E_0 + \frac{9V_0B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^3 B_0' + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2\left[6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\}$$

Where B_0 is the bulk modulus at zero pressure, B_0' its first derivative, E_0 the minimum energy, and V_0 the volume at the minimum energy. The pressure was obtained by numerical differentiation of the EOS, $P = -\partial E/\partial V$. Since the calculations were done at 0 K, the Gibbs free energy is equal to the enthalpy H, expressed as $H = E + PV$.

3. Results and discussion

3.1. Equilibrium structures and phase stability

Experimentally, the nonpolar orthorhombic perovskite $InFeO_3$ within space group of either *Pnma* or *Pn2₁a* has been proposed [12]. However, the absence of unambiguous information for lattice parameters and internal atomic positions has been an enigma for a deeper understanding of the structural transition under decompression. Hypothetically, the initial lattice and atomic positions of the *Pnma* and $Pn2_1a$ models referred to $CdTiO_3$ [29] reported were employed to optimize the structures. The non-centrosymmetric $Pn2_1a$ model converges to the centrosymmetric *Pnma* one after the optimization, suggesting the diffraction pattern of the high pressure perovskite phase should be indexed in *Pnma* space group rather than the $Pn2_1a$ model. The computed lattice constants, internal atomic positions for nonpolar orthorhombic $InFeO_3$ within *Pnma* space group are listed in Table 1, the corresponding crystal structure is depicted in Fig. 1. Notice that, the most typical structural feature of the orthorhombic *Pnma* phase is the presence of non-polar distortion induced by the tilting of the oxygen octahedra described by $a^-b^+a^-$ in terms of Glazer notation. The evident difference between In-O and Fe-O bond lengths engenders considerable cooperative rotation of the FeO_6 octahedra, manifested by the substantial derivation of the Fe-O-Fe bond angle (ca. 140°) from the ideal value 180°. Since there is no experimental data available in the literature for comparison, we do not comment further on this issue, but rather provide them as a guide for further experiments.

The $LiNbO_3$-type phase $InFeO_3$ can be envisaged as a highly distorted perovskite within an acentric space group R3c (No. 161). The primitive unit cell shown in Fig. 1, holds two formula units (10 atoms). It is shaped from the ideal cubic structure by appending two displacements: counter-rotations of adjacent oxygen octahedra around the cubic [111] axis, and polar movements of the anion and cation sublattices relative to each other along the [111] direction. The optimized lattice constants, internal atomic positions, and bond lengths obtained within GGA and GGA + U schemes are also collected in Table 1, compared to the experimental values. As expected, the pure GGA method overrates the experimental lattice constants by roughly 1.6%. After taking the Hubbard U_{eff} term into account, the rectification is negligible. The aberration is attributed to intrinsic approximations of theoretical methods and/or the absence of the temperature effect. Overall, the consistence of theoretical results with experimental ones provided greater assurance that the theoretical investigation presented is straight and trustworthy.

In the energy-volume curves depicted in Fig. 2(a), we compared the energy per formula unit for $LiNbO_3$-type and nonpolar orthorhombic phase. The structural sequence '$LiNbO_3$-type to nonpolar orthorhombic' is identified as a function of the compression. The bulk modulus was extracted by fitting the energy-volume curves to the third-order Brich-Murnaghan EOS [28], B = 157.1 GPa and 171.0 GPa for the $LiNbO_3$-type and nonpolar orthorhombic phase, respectively. In the enthalpy-pressure relationship illustrated in Fig. 2(b), we plotted the enthalpy of nonpolar orthorhombic phase with respect to that of $LiNbO_3$-type one as a function of the pressure. It is evident that the critical transition pressure predicted via GGA + U method is about 4.3 GPa, which is comparable to that of $ScFeO_3$ (3.7 GPa) [25], slightly