

First-Principles Calculations of Ferroelectric Inosilicate Bi_2SiO_5

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Ferroelectric oxide materials have been widely studied for electronic and optical utilization. Ferroelectric materials exhibit spontaneous polar displacements in their crystal structures, and the direction of the polar displacement can be readily reversed by an external electric field. Therefore, ferroelectricity is strongly related to the crystal structure and symmetry. Perovskite-type oxides, as typified by BaTiO_3 , BiFeO_3 and PbZrO_3 - PbTiO_3 (PZT) solid solutions, are well-known ferroelectric oxides. Ferroelectricity in ABO_3 perovskite structures is characterized by distortion of the octahedrally coordinated BO_6 polyhedra, and driven by a soft-mode phonon at the center of the Brillouin zone. An enormous amount of research into these materials has been carried out over the past several decades. However, attempts to find more functional ferroelectric oxides seem to have reached a ceiling. In this paper, we present a new concept for producing ferroelectric effects in materials other than those containing octahedrally coordinated polyhedra.

Recently, Taniguchi *et al.* [1] reported a new class of ferroelectric oxides based on Bi_2SiO_5 , which is a type of inosilicate. The monoclinic structure of Bi_2SiO_5 is shown in Fig. 1. This compound has a stacking structure with alternating layers of $[\text{Bi}_4\text{O}_4]^{4+}$ and $[\text{Si}_2\text{O}_6]^{4-}$, and is characterized by periodic 1D-chain structures of $[\text{Si}_2\text{O}_6]^{4-}$ in the c direction. Each SiO_4 tetrahedron shares a corner with a neighboring SiO_4 unit. At higher temperatures, Bi_2SiO_5 becomes orthorhombic with space group symmetry $Cmcm$ and is paraelectric. As temperature is decreased, a displacive transformation occurs and the crystal structure becomes monoclinic with space group symmetry Cc (Fig. 1). From first-principles lattice dynamics calculations, it is found that this transformation is triggered by a zone-centered soft mode involving twisting of the $[\text{Si}_2\text{O}_6]^{4-}$ chains [1]. The ferroelectricity of Bi_2SiO_5 thus originates from displacement of tetrahedral, and represents a different mechanism to that of perovskites. This material thus opens up new possibilities in the search for ferroelectric materials. In this paper, we report the electronic structures of monoclinic Bi_2SiO_5 obtained from first-principles calculations.

The first-principles calculations of Bi_2SiO_5 were based on the projector augmented wave method implemented in the VASP code [2,3]. The local density approximation [4] was used for the exchange-correlation potentials. The cut-off energy of plane wave basis sets was set to 500 eV. The primitive cell of monoclinic Bi_2SiO_5 was optimized with a $4 \times 4 \times 4$ k-point sampling mesh until all residual Hellmann-Feynman forces acting on the ions were less than 0.02 eV/Å.

Figure 2 shows the calculated band structure of monoclinic Bi_2SiO_5 . Both the valence band top and conduction band bottom are located at the Γ point. The band gap of monoclinic Bi_2SiO_5 is thus a direct transition type with a magnitude of 2.78 eV. Figure 3 shows the projected partial density of states (PDOS) of each ion. PDOS profiles of O2 and O5 sites are similar to those of O3 and O4 sites, respectively.

Consequently, for clarity, O2 and O5 PDOS components are not shown in Fig. 3. The valence band top is mainly composed of Bi 6s and 6p bands and O3 and O4 2p bands. Bi and O4 are situated in the $[\text{Bi}_4\text{O}_4]^{4+}$ layer. O3 ions are located in the $[\text{Si}_2\text{O}_6]^{4-}$ chain and neighbor the $[\text{Bi}_4\text{O}_4]^{4+}$ layer. Hybridized orbitals between Bi and O4 ions additionally overlap with O3 2p orbitals. Almost all occupied 2p states of O3 are distributed at energies higher than -5 eV. In contrast, the O1 2p orbitals have deeper valence band state components below -5 eV. Each O1 atom is located at the corner of a polyhedron and is shared by two Si^{4+} . Coulomb interactions from two Si^{4+} lower the energy states of O1 2p bands.

References

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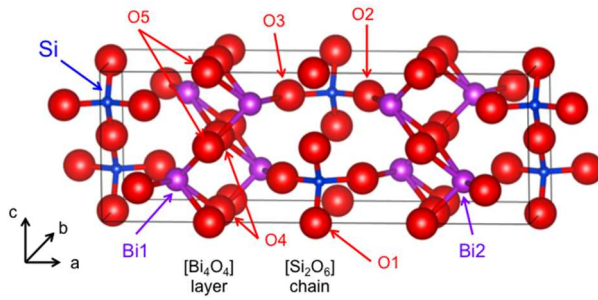


FIG. 1. Crystal structure of monoclinic Bi_2SiO_5 .

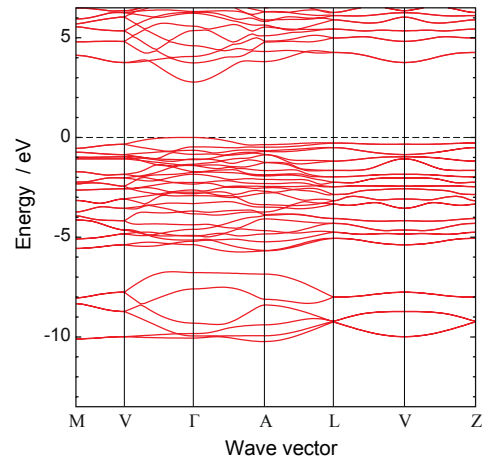


FIG. 2. Calculated band structure of monoclinic Bi_2SiO_5 .

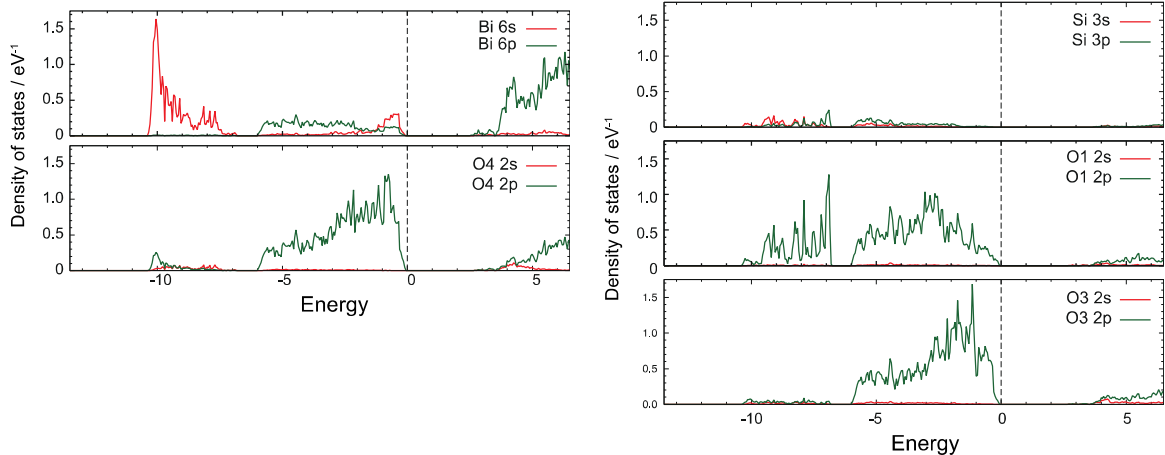


FIG. 3. Projected partial density of states (PDOS) of Bi_2SiO_5 . Left: $[\text{Bi}_4\text{O}_4]^{4+}$ layer; Right: $[\text{Si}_2\text{O}_6]^{4-}$ chain.