

First-principles Exploration of Ferromagnetic and Ferroelectric Double-perovskite Transition-metal Oxides

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Abstract

Possible ferromagnetic and ferroelectric phases are explored for bismuth transition-metal oxides with double-perovskite structure $A_2BB'O_6$ on the basis of first-principles calculations within the local spin-density approximation (LSDA) and generalized gradient approximation (GGA). It is found that a lattice instability of the cubic to a non-centrosymmetric phase always happens in the all cases of lead and bismuth perovskite oxides with the $3d$ transition-metal ions at the B site. Placing bismuth ion at the A site in the double-perovskite structure, several sets of the $3d$ transition-metal ions are selected according to their total valence sum and the Goodenough-Kanamori rule for the superexchange coupling. Ferromagnetic solutions are actually obtained both within LSDA and GGA for $\text{Bi}_2\text{CrFeO}_6$, $\text{Bi}_2\text{MnNiO}_6$ and $\text{Bi}_2\text{CrCuO}_6$. For non-centrosymmetric monoclinic $\text{Bi}_2\text{MnNiO}_6$, the ferromagnetic and ferroelectric phase has the spin magnetic moment of $5\mu_B$ and the electric polarization of $28\mu\text{C}/\text{cm}^2$.

Key words: multiferroics, first-principles calculation, ferromagnetic, ferroelectric, double-perovskite structure

Condensed matter systems show a macroscopic response, either magnetic, electric or elastic, to the corresponding external field. Each response originates in spin and orbital magnetic moments, electric dipole or lattice strain in the microscopic level. Some systems reveal a spontaneous response associated with a ferro-ordering of the relevant microscopic degree of freedom under certain circumstances. Multiferroic materials have more than one ferro-orderings simultaneously. Among them, ferromagnetic and ferroelectric materials are potentially important for applications to next-generation devices such as spin field-effect-

transistor or logic in memory and may involve many unsolved issues to be investigated in basic science. There are only a few known as ferromagnetic and ferroelectric materials, particularly with perovskite-type crystal structure. It is, therefore, quite important and valuable in materials science and engineering to explore possible ferromagnetic and ferroelectric materials.

Considering why they are so rare in nature might provide us a clue to the exploration. The reason may be because most of magnetic perovskite oxides (typically denoted as ABO_3) have an antiferromagnetic order due to a superexchange coupling between the magnetic ions. It is well known, according to the Goodenough-Kanamori rule for the

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superexchange coupling, [1,2] that certain combinations of the transition-metal ions B and B' ($d^3 - d^5$ and $d^3 - d^8$ electronic configurations) may possibly give a *ferromagnetic* coupling for the 180-degree superexchange mechanism. Note that the bond angle of $B-O-B'$ is nearly 180 degrees in the perovskite structure. Using this strategy, Ueda *et al.* have successfully fabricated a ferromagnetic superlattice stacking LaCrO_3 (d^3) and LaFeO_3 (d^5) layer-by-layer along the [111] direction. [3]

Ferroelectric materials should be insulating for preventing charge leakage and thus are likely ionic crystals. Furthermore, it is widely recognized that covalent bonds between the cation and anion orbitals are crucial to realize atomic displacements to a non-centrosymmetric structure. [4–7] The covalency leads to not only such a symmetry-breaking lattice instability (phonon softening) but also enhancement of the Born effective charge as a result of electronic response of the bond charge by the atomic displacements. [8] For example, in BaTiO_3 as a typical ferroelectric perovskite oxide, the $3d$ orbitals of Ti located at the B site hybridize with their neighboring O- $2p$ orbitals and have finite weights in the valence bands with sharing the bond charge, which gives rise to significant electronic response. As pointed out in the previous first-principles calculations of the Born effective charges for several perovskite oxides, the $6p$ orbitals of Pb located at the A site also participate the covalent bonds in lead perovskite oxides such as PbTiO_3 and PbZrO_3 .

In our previous studies, first-principles calculations have been carried out for the ferromagnetic and ferroelectric oxides BiMnO_3 and antiferromagnetic and ferroelectric oxides PbVO_3 and BiCoO_3 . [9,10] In BiMnO_3 , the coexistence of the ferromagnetic and ferroelectric orderings has been explained in terms of an antiferro-orbital ordering of the Mn $3d$ e_g orbitals and Jahn-Teller distortions around the Mn^{3+} ions with the d^4 configuration. [9] As for tetragonal PbVO_3 and BiCoO_3 , a ferro-orbital ordering of the V (Co) $3d$ xy orbitals associated with large tetragonal distortions and ionic displacements results in the stable antiferromagnetic ordering via a superexchange coupling between the neighboring xy orbitals along the ab directions, and giant electric polarizations

are predicted to be larger than $150\mu\text{C}/\text{cm}^2$. [10]

In this paper, following the guiding principles described above, possible coexistence of ferromagnetism and electric polarization is investigated from first principles, by focusing double-perovskite oxides $\text{Bi}_2\text{BB}'\text{O}_6$ ($B, B' = 3d$ transition-metal ion) as target materials. The reason why we choose a bismuth ion at the A site is based on the fact that a frozen phonon calculation for cubic perovskites BiBO_3 ($B = 3d$ transition-metal ion) shows a soft mode in which bismuth ions and BO_6 octahedra move in the opposite direction, leading to non-centrosymmetric structure. [9] The same type of the soft phonon mode is also found for PbBO_3 . This phonon softening is driven by the covalent bonds between the Bi (Pb) $6p$ and O $2p$ orbitals.

Since the formal valency of bismuth is likely to be $3+$, the sum of the valence of B and B' ions in $\text{Bi}_2\text{BB}'\text{O}_6$ should be $6+$ to make the system neutral in an ionic picture. Considering the $d^3 - d^5$ electronic configuration, two combinations of transition-metal ions B and B' , $\text{Cr}^{3+} - \text{Fe}^{3+}$ and $\text{V}^{2+} - \text{Co}^{4+}$, can be proposed according to possible valence. The former is just the same combination as in the $\text{LaCrO}_3/\text{LaFeO}_3$ ferromagnetic superlattice. In the latter, Co^{4+} could be hardly realized. As for the $d^3 - d^8$ configuration, $\text{Mn}^{4+} - \text{Ni}^{2+}$ and $\text{Cr}^{3+} - \text{Cu}^{3+}$ may be candidates. Again, Cu^{3+} rarely happens as a purely ionic situation in nature.

Besides the charge neutrality, there should be some sort of mechanism which leads to energy gaps with non-zero d electrons. In the perovskite structure, the transition-metal ions are situated at the B site octahedrally coordinated by oxygen ions. Therefore, it may be plausible that d^3 and d^8 electronic configurations give energy gaps between e_g and t_{2g} bands opened by the crystal field (or by the orbital hybridization) in a high-spin magnetic phase, while d^5 may have exchange gaps.

First-principles electronic structure calculations are performed for all of the candidates proposed above, namely $\text{Bi}_2\text{CrFeO}_6$, Bi_2VCoO_6 , $\text{Bi}_2\text{MnNiO}_6$ and $\text{Bi}_2\text{CrCuO}_6$ in cubic double-perovskite crystal structure with lattice constant of 8.0\AA , where two kinds of transition-metal ions B and B' are arranged in a rock-salt manner so that the magnetic interaction between the neighboring

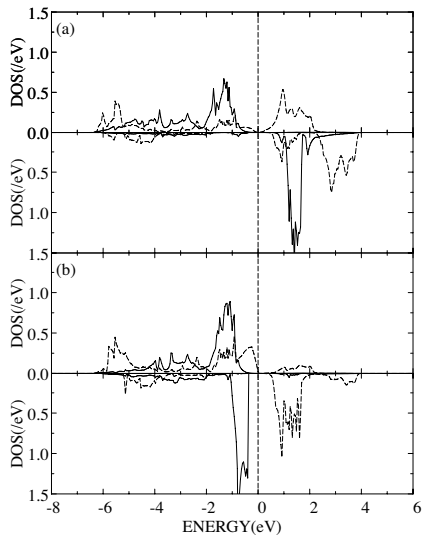


Fig. 1. Calculated partial density of d -states projected on the (a) Mn and (b) Ni sites of ferromagnetic $\text{Bi}_2\text{MnNiO}_6$ with NaCl-type arrangement of Mn and Ni in the cubic structure. Solid and dotted lines denote t_{2g} and e_g components, respectively. Upper (lower) panels represent the spin up (down) bands. The top of the valence band is taken at the origin.

B and B' is realized by the 180-degree superexchange couplings. Magnetic solutions are searched either ferromagnetic or ferrimagnetic by assuming the different initial magnetic structure in the self-consistent-field iterations. The theory is based on the local spin-density approximation (LSDA) or generalized gradient approximation (GGA) to the density-functional theory. Kohn-Sham equations are self-consistently solved in a scalar-relativistic fashion by using the full-potential linear augmented plane wave method.

Ferromagnetic solutions are actually obtained for $\text{Bi}_2\text{CrFeO}_6$, $\text{Bi}_2\text{MnNiO}_6$ and $\text{Bi}_2\text{CrCuO}_6$ within LSDA and GGA. Among them, the ferromagnetic state is clearly lower in energy than the ferrimagnetic one in $\text{Bi}_2\text{MnNiO}_6$ but both the magnetic states are nearly degenerate in $\text{Bi}_2\text{CrFeO}_6$ and $\text{Bi}_2\text{CrCuO}_6$. In case of $\text{Bi}_2\text{MnNiO}_6$, furthermore, the electronic structure is just gapped with Mn- d^3 and Ni- d^8 configurations, as shown in Fig. 1. Gap formation is realized between the t_{2g} and e_g sub-bands of both spins even in the cubic structure because of the crystal-field splittings.

Quite recently, $\text{Bi}_2\text{MnNiO}_6$ has been successfully synthesized by the high-pressure technique. [11] The crystal structure of $\text{Bi}_2\text{MnNiO}_6$ is monoclinic (space group $C2$) analogous to the multiferroic oxide BiMnO_3 and can be regarded as a highly-distorted double-perovskite type with Mn^{4+} and Ni^{2+} ions ordered in a rock-salt configuration. They actually found that $\text{Bi}_2\text{MnNiO}_6$ is ferromagnetic with Curie temperature 140K, which is slightly higher than that in BiMnO_3 ($\sim 100\text{K}$). Magnetic moment at 5K is $4.1\mu_B$ by a magnetization measurement, which is smaller than $5\mu_B$ expected for the $d^3 - d^8$ high-spin configuration. This is attributed to the existence of antisite disorder of Mn^{4+} and Ni^{2+} ions. A ferroelectric transition is found to be at 485K by a dielectric-constant measurement and associated with a structural phase transition to non-centrosymmetric monoclinic structure. Determined crystal structure in the ferroelectric phase gives rise to the electric polarization of $18\mu\text{C}/\text{cm}^2$ with a point-charge model. Expected direction of the polarization should be along the b axis by the $C2$ symmetry.

First-principles calculations are carried out for monoclinic $\text{Bi}_2\text{MnNiO}_6$ by assuming a ferromagnetic or ferrimagnetic phase. Stable solutions are found to both magnetic phases while the ferromagnetic phase is lower in energy than the ferrimagnetic one by 56 and 67meV within LSDA and GGA, respectively. Calculated total and partial densities of states in ferromagnetic $\text{Bi}_2\text{MnNiO}_6$ are depicted in Figs. 2 and 3. The ferromagnetic and ferrimagnetic phases are found to be insulating with small energy gaps of 0.2eV. The energy gaps are located between the t_{2g} and e_g spin-up sub-bands of Mn and between the the t_{2g} and e_g spin-down sub-bands of Ni as shown in Fig. 3, though orbital separation is not so clear due to monoclinic symmetry as shown in the cubic phase (Fig. 1). The $d^3 - d^8$ high-spin electronic configuration is actually realized. Calculated spin magnetic moments are thus $5\mu_B$ and $1\mu_B$ per formula unit in the ferromagnetic and ferrimagnetic phases, respectively.

By using the Berry-phase approach,[12] the electric polarization can be evaluated in the present first-principles calculations. Rigorously speaking for bulk materials, one can calculate the variation

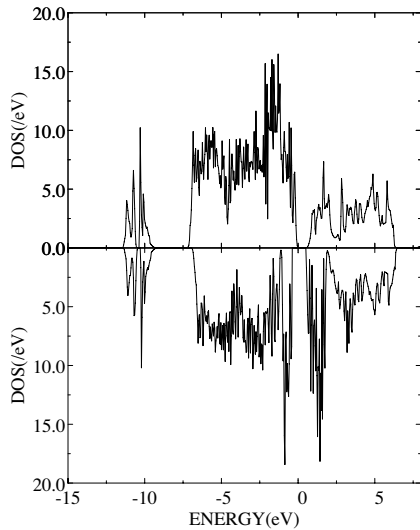


Fig. 2. Calculated total density of states of ferromagnetic $\text{Bi}_2\text{MnNiO}_6$. The top of the valence band is taken at the origin.

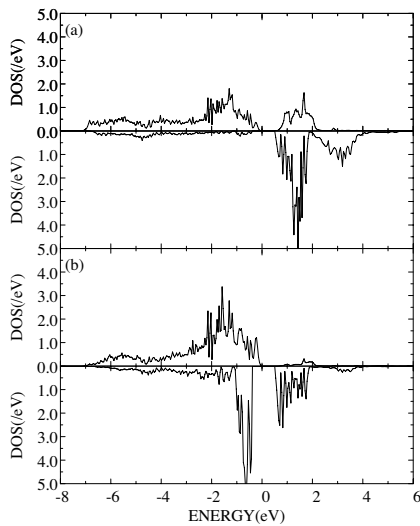


Fig. 3. Calculated partial density of d -states projected on the (a) Mn and (b) Ni sites of ferromagnetic $\text{Bi}_2\text{MnNiO}_6$ in the observed monoclinic structure. The top of the valence band is taken at the origin.

in the electric polarization along an adiabatic process, which is the proper measurable quantity. In this study, we reverse the crystal along the b axis and make one-to-one correspondence of the equivalent nearest neighbor ions between the original and reversed crystals. An adiabatic path can be con-

structed by connecting the corresponding ions with linearly-scaled ionic displacements. With this path and the Berry-phase method, the spontaneous polarization is evaluated to be $28\mu\text{C}/\text{cm}^2$, which is remarkably greater than that expected by the point-charge model ($18\mu\text{C}/\text{cm}^2$). Such an enhancement of the polarization is often seen in the ferroelectric materials due to the electronic response of the bond charge formed by hybridization of the cation and anion orbitals.

In conclusion, we have explored possible ferromagnetic and ferroelectric double perovskites of the form $\text{Bi}_2\text{BB}'\text{O}_6$. Our first-principles calculations show that a few combinations of transition-metal ions are feasible, including $\text{Bi}_2\text{MnNiO}_6$ that is actually synthesized and found to be multiferroic. Its polarization is predicted to be $28\mu\text{C}/\text{cm}^2$.

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