

Ab initio prediction of a multiferroic with large polarization and magnetization

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We describe the design of a magnetic ferroelectric with large spontaneous magnetization and polarization using first-principles density functional theory. The usual difficulties associated with the production of robustly insulating ferromagnets are circumvented by incorporating the magnetism through *ferrimagnetic* behavior. We show that the ordered perovskite $\text{Bi}_2\text{FeCrO}_6$ will have a polarization of $\sim 80 \mu\text{C}/\text{cm}^2$, a piezoelectric coefficient of $283 \mu\text{C}/\text{cm}^2$, and a magnetization of $\sim 160 \text{emu}/\text{cm}^3$ ($2 \mu_B$ per formula unit), far exceeding the properties of any known multiferroic. [DOI: 10.1063/1.1843290]

Multifunctional materials that combine a spontaneous magnetization with a ferroelectric polarization are of tremendous fundamental and practical interest.^{1–4} For example, they have high dielectric permittivity and high magnetic permeability, and could therefore replace the inductor and capacitor in resonant circuits with a single component, further miniaturizing portable cellular technologies. Strong coupling between the polarization and magnetization would allow ferroelectric data storage combined with a magnetic read and the ability to tune or switch the magnetic properties with an electric field and vice versa could lead to as-yet-unanticipated developments in conventional devices such as transducers. However, a single phase material with large and robust magnetization and polarization has not been previously identified; known ferromagnetic ferroelectrics tend to have low magnetic Curie temperatures,⁵ are often weak ferromagnets,⁶ or are not strong enough insulators to sustain a ferroelectric polarization at room temperature.⁷

The coexistence of ferromagnetism and ferroelectricity is difficult to achieve for many reasons.^{8,9} First, and most fundamentally, the off-centering of transition metal ions which creates the electric polarization in conventional ferroelectrics is driven by a second-order Jahn–Teller distortion which requires a formally empty *d*-electron configuration.⁸ In contrast, ferromagnetism requires unpaired electrons, which in many materials are provided by *d* electrons on transition metal ions. Therefore the coexistence of the two phenomena, although not prohibited by any physical law or symmetry consideration, is discouraged by the local chemistry that favors one or the other but not both. In practice, alternative mechanisms for introducing off-centering on ions other than the magnetic transition metal ions, such as stereochemically active lone pairs¹⁰ or geometrically driven distortions,¹¹ can be used to circumvent this restriction. Second, and important from a practical point of view, is the fact that ferroelectrics must be robust insulators, so that an applied field can reorient the spontaneous polarization without causing conductivity. In practice, many ferromagnetic materials are metallic, and magnetic insulators tend to show antiferromagnetic coupling between the magnetic ions. Finally, magnetic transition metal ions tend to be fairly easy to oxi-

dize or reduce, and are associated with multiple valence states accompanied by anion nonstoichiometry. Those few ferromagnetic insulators that do exist often show hopping conductivity at room temperature.⁷

In this work we propose a class of robustly insulating magnetic ferroelectrics in which all three of these limitations are circumvented. We use the $6s^2$ lone pair on Bi^{3+} ions, well-established to be the source of the ferroelectricity in the multiferroics BiMnO_3 ¹⁰ and BiFeO_3 ,¹² to introduce the off-center distortion. To avoid the difficulty of finding insulating ferromagnetic behavior, we instead choose to introduce spontaneous magnetization via *ferrimagnetism*. In ferrimagnets, the coupling between neighboring magnetic moments is robustly antiferromagnetic, but two antiferromagnetic sublattices of different magnetizations are incorporated to provide a net magnetization. Because the antiferromagnetic superexchange is so strong, the magnetic Curie temperatures in ferrimagnets are usually far above room temperature. In addition, to promote strongly insulating behavior, we choose transition metal ions which are resistant to oxidation and reduction: $d^3 \text{Cr}^{3+}$, in which the up-spin t_{2g} -shell is filled, and high-spin $d^5 \text{Fe}^{3+}$, with its completely filled up-spin manifold.

Having selected our cationic composition ($\text{Bi}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}$), our next step is to choose a trial arrange-

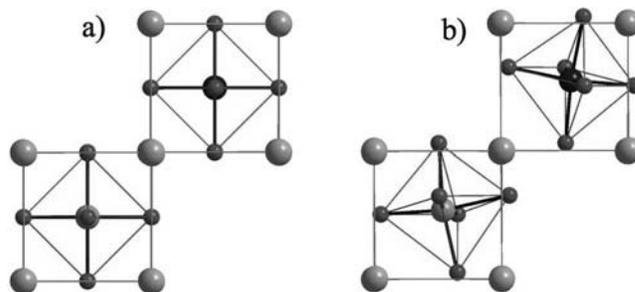


FIG. 1. Comparison of ideal cubic perovskite-structure $\text{Bi}_2\text{FeCrO}_6$ (a) with our calculated ground state structure (b), looking down the y axis of the ideal cubic unit cell. (111) planes of Fe ions (light gray) alternate with planes of Cr ions (dark gray) along the [111] direction. Each transition metal is surrounded by an octahedron of oxygen anions (black), and the Bi ions (medium gray) occupy the corners of the ideal cubic unit cells. The transition from the cubic to the ground state structure consists of two distortions: rigid rotations of adjacent oxygen octahedra in opposite directions around the [111] axis, and displacements of the anion cages relative to the cations in the [111] direction.

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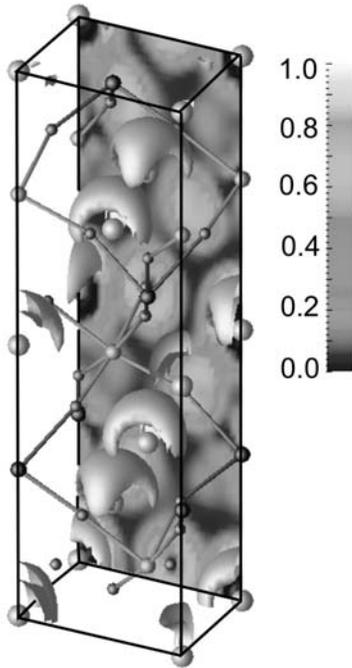


FIG. 2. Calculated electron localization function (ELF), at a value of 0.65, for $\text{Bi}_2\text{FeCrO}_6$. The polar [111] axis is oriented vertically (the Bi–Fe–Bi–Cr–Bi ordering can be seen clearly along the front right edge of the cell). The lobes are regions of high electron localization associated with the lone pairs of electrons on the Bi ions. A contour plot of the electron localization in a slice at the back of the cell is also shown. The ELF was generated using the STUTTGART TB-LMTO-ASA-code (Ref. 25) with the LSDA formalism.

ment of the ions, and to calculate the crystal structure and magnetic properties. Motivated by the report of the possibility of single-atomic-layer superlattice ordering in double perovskite $\text{La}_2\text{FeCrO}_6$,¹³ we choose as our trial compound the ordered perovskite $\text{Bi}_2\text{FeCrO}_6$, with planes of Fe and Cr ions alternating in the [111] direction; this corresponds to a rock-salt ordering of the Fe and Cr octahedra, as shown in Fig. 1(a). We use density functional theory within the LDA+ U method,¹⁴ as implemented in the VASP package,¹⁵ to determine the properties. This extension to the usual local spin density approximation (LSDA) is necessary, because the LSDA gives qualitatively incorrect results for systems with a strong local correlation. In our case, LSDA predicts that $\text{Bi}_2\text{FeCrO}_6$ should be a metal containing low-spin Fe ions, instead of the high-spin insulator obtained within the LDA+ U method. Technical details include a U value of 4 eV, a J value of 0.8 eV, a $6 \times 6 \times 6$ k -point grid for the two formula-unit rhombohedral unit cell, the projector-augmented plane wave (PAW) method with default pseudopotentials¹⁶ and an energy cutoff of 450 eV. $U=4$ eV is the smallest value that gives an insulating centrosymmetric structure; this represents a lower limit for U , which is not inconsistent with the experimental estimation for LaCrO_3 and LaFeO_3 .¹⁷

First we calculate the lowest-energy crystal structure using the standard method of adjusting the positions of the atoms to minimize their Hellmann–Feynmann forces. To ensure that our calculations explore all likely symmetries in a reasonable computational time, we use a range of starting structures for the optimization, which we obtain by freezing in combinations of the unstable phonon modes of BiCrO_3 .¹⁸ We find that the lowest energy structure has $R3$ symmetry (spacegroup 146) and exhibits alternating rotations of the oxygen octahedra along the [111] direction, combined with

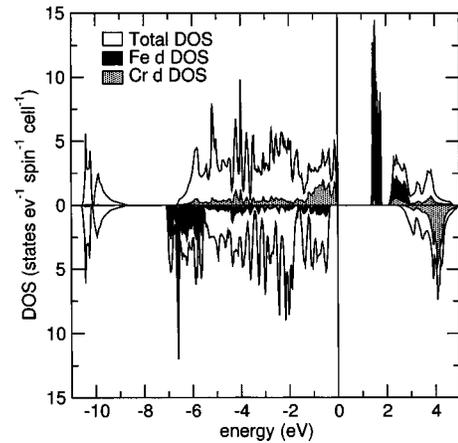


FIG. 3. Calculated density of states (DOS) of $\text{Bi}_2\text{FeCrO}_6$. The top of the valence band is set to 0 eV. The black line shows the total density of states, and the dark and light shading the contributions from the Fe 3d and Cr 3d states, respectively. The states at ~ -10 eV are the Bi 6s states, and the unshaded states in the broad band below the Fermi energy have largely O 2p character.

relative displacements of the anions and cations along [111] (see Fig. 1). This symmetry permits the existence of ferroelectricity, and indeed we calculate a ferroelectric polarization (using the Berry phase formalism^{19–21}) of $79.6 \mu\text{C}/\text{cm}^2$. The ferroelectric distortion is driven by the well-established stereochemical activity on the Bi lone pair¹⁰ as can be seen clearly in the calculated electron localization function²² (Fig. 2). We calculate a piezoelectric coefficient along [111] of $283 \mu\text{C}/\text{cm}^2$, comparable to that of PbTiO_3 ,²³ in which the piezoelectric coefficient along the polar z axis, e_{33} , is $323 \mu\text{C}/\text{cm}^2$.

Next, we determine the magnetic ordering. We test all the likely possibilities that are accessible in our computations: ferromagnetic and antiferromagnetic ordering of the Fe planes and Cr planes, coupled both ferromagnetically and antiferromagnetically to each other. (Note, that our supercell technique does not allow us to study less likely long-wavelength magnetic orderings, and so we have not explored more obscure magnetic arrangements, or noncollinear spin structures). Here we find that the most favorable magnetic ordering consists of ferromagnetic planes of Fe and Cr, that are antiferromagnetically coupled to each other. Since the magnetic moments of Fe and Cr are different ($5 \mu_B$ for Fe^{3+} and $3 \mu_B$ for Cr^{3+}) this arrangement results in a net magnetic ordering of $2 \mu_B$ per Fe–Cr pair, which corresponds to $160.53 \text{ emu}/\text{cm}^3$.

Thus we predict that the properties of $\text{Bi}_2\text{FeCrO}_6$ will surpass all previous reports for coexisting magnetism and ferroelectricity. The ferroelectric polarization is comparable to the best known ferroelectrics (the value for PbTiO_3 , for example,²⁴ is $\sim 75 \mu\text{C}/\text{cm}^2$), the piezoelectric response is substantial, and the large atomic displacements and polarization reflect a high ferroelectric Curie temperature. The material is insulating; we have chosen transition metal ionic configurations that are the most robust to oxidation and reduction and the spontaneous magnetization is comparable to that of the cubic ferrites (for example, the magnetization of nickel ferrite is $\sim 270 \text{ emu}/\text{cm}^3$). Finally we mention that, although we deliberately designed our system to be a robust insulator, if carriers are introduced either by doping or by optical excitation, the transport and optical properties could

be useful for spintronic applications. The calculated density of states, shown in Fig. 3, indicates that both the top of the valence band and the bottom of the conduction band are 100% spin polarized, with electrons confined to narrow, up-spin Fe 3*d* bands, and holes in broader, up-spin Cr 3*d*-O 2*p* hybrids.

Our work illustrates the viability of electronic structure methods in the design of new and multifunctional materials and offers a synthetic challenge which we hope will stimulate further research on this emerging class of multiferroic materials.

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