Exploring the structural, electronic and magnetic properties of cation ordered 3d-5d double perovskite \( \text{Bi}_2\text{FeReO}_6 \) and \( \text{Bi}_2\text{FeIrO}_6 \) thin-films from first-principles

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We report a first-principles study of Bi-based 3d-5d ordered double perovskite oxides \((\text{A}_2\text{BB'}\text{O}_6)\) with a 3d atom (Fe) at the B-site and 5d atoms (Re,Ir) at the B’-site while keeping highly polarizible ions \((\text{Bi}^{3+})\) at the A-site. We find that, under coherent heteroepitaxy, \(\text{Bi}_2\text{FeReO}_6\) exhibits a strain-driven anti-ferromagnetic insulator to ferrimagnetic semi-metal transition, while \(\text{Bi}_2\text{FeIrO}_6\) shows correlation driven ferromagnetic insulator to ferrimagnetic half-metal transition with calculated magnetic moments of \(5 \mu_\text{B}/\text{f.u.}\) and \(3 \mu_\text{B}/\text{f.u.}\), respectively. These properties along with the low band gaps in the insulating phases make the compounds appealing for spintronic applications. Furthermore, in \(\text{Bi}_2\text{FeIrO}_6\), the conduction and valence states are localized on different transition metal sublattices implying more efficient electron-hole separation upon photoexcitation, a desirable feature for photovoltaic applications.

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INTRODUCTION

Transition metal (TM) double-perovskites (DP) \((\text{A}_2\text{BB'}\text{O}_6)\) have gained enormous attention recently due to their fascinating properties in the areas of magnetism, ferroelectrics, spintronics and multiferroics \(^{[1]}\) and long served as a platform for device applications. Particularly, multiferroic materials are quite promising due to their multipurpose technological implications \(^{[2,3]}\). These materials are characterized by coexistence of ferroic orders such as ferroelectricity, ferromagnetism and/or ferroelasticity along with a coupling of at least two of these orders which can, in turn, lead to magnetoelectric, magnetoelastic effects, etc. A prominent example of DP multiferroic is \(\text{Bi}_2\text{FeCrO}_6\) (BFCO), which was designed from the AFM parent multiferroic compound \(\text{BiFeO}_3\) (BFO) by replacing half the Fe ions by Cr with an aim to increase the magnetic moment through ferrimagnetic interaction of \(B\) and \(B'\) sites while retaining ferroelectricity and magneto-electric coupling intact \(^{[4]}\). Due to AFM ordering, the parent compound BFO shows \(\sim\) 0 magnetic moment, however, BFCO was predicted to show a magnetic moment of \(2 \mu_\text{B}/\text{f.u.}\) in its bulk form with a G-type AFM ordering.

In practice, multiferroics can be prepared as high quality epitaxial thin films on oxide substrates. The epitaxial strain (ES), which can be introduced by varying lattice mismatch between the thin-film and substrate, has the tendency to control the material properties and to stabilize other metastable magnetic structures \(^{[5,9]}\). The potential of multiferroic materials towards photovoltaic (PV) and photocatalytic (PC) application is currently being explored. The narrow band gap, which arises due to electron-electron interaction governing the magnetic ordering, makes multiferroics special candidates for PV application over the general perovskite materials \(^{[10]}\). Among multiferroics, BFO was considered to show appreciable PV effect due to the presence of a direct band gap, a fact latter corroborated by Chui et al. \(^{[11]}\). However, the power conversion efficiency (PCE) of BFO based thin film devices is still very low for practical application. Lowering the band gap of these oxides without affecting their FE properties is a promising conceptual route to obtain solar energy conversion devices with higher PCE. Recently, it was shown that the epitaxial multiferroic ordered BFCO thin-films possess a power conversion efficiency of 6.5% under the illumination of red light laser \(^{[12]}\) and 8.1% under AM1.5G illumination \(^{[13]}\). In both the works, it was pointed out that the Fe and Cr cation order and the narrow band gap play a crucial role in the PV performance of BFCO thin films. Kim et al. \(^{[14]}\) recently attributed the excellent performance of BFCO to the spatial separation of the photoexcited electron and hole states onto the Fe and Cr sites, respectively, with the extent of separation increasing with the disorder at the \(B\)-site.

Recently, we have shown that epitaxially grown (001) BFCO thin-films are unstable to anti-site defects and prefer a C-type AFM (C-AFM) ordered ground state \(^{[15]}\), both features leading to loss of magnetization \(^{[16,18]}\). The anti-site defects (disordering) occur basically due to the similarity of charge and ionic radii of \(\text{Fe}^{3+}\) and \(\text{Cr}^{3+}\) ions. We have also recently shown that by manipulating both ES and aliovalent A-site doping in BFCO thin films \(^{[19]}\), one can not only mitigate the issues like cation disorder and low magnetism but also significantly reduce the band gap, a desirable feature for PV applications. An alternative approach to suppress B-site disorder and encode functionality in Bi-based DPs is to form 3d-5d oxides \(^{[20]}\). Doping with 5d TM ions can not only improve magnetisation but also prevent the formation of antisite defects like BFCO thin-films due to their larger sizes compared to the 3d ions. Apart from this, the mixture of 3d-5d ions would likely improve the transition temperature as seen in case of \(\text{Ca, Sr-based systems, due to the induced magnetic moment at the nonmagnetic sites}\) \(^{[21,22]}\).

In this work, we investigate the strain-dependent magnetic and electronic properties of two new double-perovskite 3d-5d systems: \(\text{Bi}_2\text{FeReO}_6\) (BFRO) and \(\text{Bi}_2\text{FeIrO}_6\) (BPIO) from first-principles DFT simulations. BFO was chosen as a starting point for the doping with 5d ions given its robust ferroelectric nature. We chose Fe atom as the 3d ion in the B-site as...
it usually occurs in high-spin 3+ oxidation state, which could lead to large magnetic moment in DPs, stronger magnetic interactions and hence larger transition temperatures.

Our calculations predict an anti-polar $P2_1/n$-like structure for both compounds if grown on cubic substrates. We find that a C-type AFM ordering is favored for BFRO, while BFIO becomes a ferromagnetic insulator through out the ES region. In the band gap and magnetic phase transition, which was completely ignored in the previous study [24]. Presence of very narrow band gap $\sim 1.1$ eV in both the compounds (considering correlation effect on both 3$d$-5$d$ ions) makes them suitable candidates for PV applications.

**METHOD OF CALCULATION**

Our calculations employed a spin-polarized GGA+$U$ [25–27] approach using the revised version Perdew-Burke-Ernzerhof (PBE) [28,29] for solids, PBEsol [30] as exchange-correlation functional within the framework of the Quantum-ESPRESSO code [31]. Ionic cores were modeled by ultrasoft pseudopotentials keeping the 4$f$ electrons of 5$d$ transition metals and Bi atoms as part of the core. Plane-wave cut-off energy of 85 Ry was used for representing wavefunctions, and 700 Ry for the augmentation charge. The Hubbard $U$ parameter can be calculated ab initio using the linear response formalism [26,27]. We found the $U$ values to be 6.4 eV (Fe) and 3.6 eV (Re) in BFRO system, whereas in BFIO case, the $U$ values were 6.38 (Fe) and 5.18 (Ir). We used a $10 \times 10 \times 8$ Monkhorst-Pack k-point mesh for Brillouin zone integration. For the density of states (DOS) calculations, a denser Monkhorst-Pack k-point grid of $16 \times 16 \times 16$ was employed. All the structures were relaxed until the Hellmann-Feynmann forces are less than 0.26 meV/Å.

For both the compounds, we have constructed 20-atom $\sqrt{2} \times \sqrt{2} \times 2$ tetragonal supercells (shown in Figure 1), starting from a simple cubic double-perovskite structure, to allow for appropriate magnetic ordering of ions along (111) direction. The structures were chosen to conform to $P2_1/n$ (antipolar) and $R3$ (polar) space groups, respectively, given their compatibility with cubic substrates [16,18]. These essentially differ by the sense and relative magnitudes of oxygen octahedral rotations as indicated by the Glazer notations $a^-a^-c^+$ and $a^-a^-c^-$, respectively [32,33]. Using the substrate SrTiO$_3$ pseudo-cubic lattice parameter $a_{\text{cube}} = 3.90\AA$ [34] as a reference, we generated structures mimicking the epitaxially strained films by varying the in-plane lattice parameters over a range of realistic substrate strains corresponding to (001) epitaxial growth. The in-plane lattice parameters of supercell are set to $\bar{a} = \bar{b} = \sqrt{2} \times a_{\text{cube}}$ while the c parameters have been relaxed for each in-plane strain. The ES can be defined as

$$\epsilon = (\bar{a} - \bar{a}_{\text{ref}})/\bar{a}_{\text{ref}} \quad (1)$$

where $\bar{a}_{\text{ref}}$ is the unstrained lattice parameter. The selection of Re and Ir structures is based on the adapted tolerance factor $t$ of the double-perovskites [35]. The tolerance factor for DPs $A_2BB'\text{O}_6$, can be written as:

$$t = \frac{r_A + r_O}{\sqrt{2} \times (r_B' + r_{O})} \quad (2)$$

where $r_A$, $r_B$ and $r_{B}'$ are the ionic radii of the respective ions and $r_O$ is the ionic radius of oxygen. It is known that, for
double-perovskite family, if $t < 0.97$ the compound becomes either monoclinic ($P2_1/n$) or orthorhombic [56]. In case of $\text{Bi}_2\text{FeReO}_6$, the calculated average tolerance factor is 0.93 while for $\text{Bi}_2\text{FeIrO}_6$, it is 0.95. Hence, both structures are expected to take perovskite form.

RESULTS AND DISCUSSIONS

Strain-dependence ground-state structure of $\text{Bi}_2\text{FeReO}_6$

We first investigated the effect of ES on the ground-state structure of BFRO compound. We considered three types of AFM (A, C, G-type) and the FM orders for the calculations [13]. We have considered the two lowest energy phases $P2_1/n$ and $R3$ phase, which were also previously found to be stable for similar systems under various strains [24]. The ES is introduced in thin-film by constraining the two in-plane lattice vectors to be equal in length and enforce the angle between them to be 90°. We first obtained the optimized geometries in the $P2_1/n$ and $R3$ phases for different magnetic orderings at all the considered ES. A crossover between G-AFM and C-AFM ordering occurs at -2.7% strain.

![FIG. 2. Energy vs strain for the two lowest energy magnetic orderings of $P2_1/n$ structure. The energy of $R3$ structure indicated by magenta upper triangle are plotted at at higher compressive and tensile strain region. All the energies are positioned with respect to the lowest energy of C-AFM ordering in $P2_1/n$ symmetry. A crossover between G-AFM and C-AFM ordering occurs at -2.7% strain.](image)

TABLE I. Structural information for both C-AFM and G-AFM magnetic ordering at -2.7% strain.

| Type    | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$ (°) | $\beta$ (°) | $\gamma$ (°) |
|---------|---------|---------|---------|--------------|-------------|--------------|
| C-AFM   | 5.364   | 5.364   | 8.652   | 90.00        | 90.28       | 90.00        |
| G-AFM   | 5.364   | 5.364   | 9.094   | 90.00        | 84.75       | 90.00        |

FIG. 3. (a) Out-of-plane (top) view of G-AFM $\text{Bi}_2\text{FeReO}_6$ structure, (b) Out-of-plane (top) view of C-AFM $\text{Bi}_2\text{FeReO}_6$ structures at -2.7% strain.

also be achieved in $\text{Bi}_2\text{FeReO}_6$ thin-films through compressive strain. We ascribe the magnetic phase transition to the oxygen octahedra reorientation induced monoclinic to monoclinic structural transition. The structures of both C and G-AFM BFRO are shown in Figure [3] and the corresponding structural information for both the magnetic ordered structure at -2.7% strain are provided in Table [1]. The monoclinic angle (angle between $a$ and $c$ lattice parameters) changes from being obtuse in the C-AFM to be acute in the G-AFM structure. This transformation results from a sudden oxygen octahedra reorientation at -2.7% strain (see Figure [3]). So, beyond -2.7% strain, magnetic ground-state for BFRO can be achieved with a magnetic moment of $1\mu_B$/f.u.. The polar $R3$ phase, however, remains higher in energy in this strain region. One unusual finding in case of BFRO thin-film is the oxygen octahedral distortion around the Fe atom. It was observed that the Fe atom undergoes a Jahn-Teller-like distortion, leading to three different types of Fe-O bond length whereas the Re atom remains undisturbed. The three unequal bonds at reference (0% strain) are axial Fe-O$_{ax}$ long bond (2.28 Å), equatorial Fe-O$_{eq}$ medium bond (2.14 Å) and apical Fe-O$_{ap}$ short bond (2.05 Å). This octahedral distortion pattern is also seen in other strain regions.

Electronic and magnetic properties of $\text{Bi}_2\text{FeReO}_6$

In this section, we analyze the electronic structure of $\text{Bi}_2\text{FeReO}_6$ thin-films in the antipolar $P2_1/n$ structure. We
also briefly discuss about the magnetic properties of the corresponding structure.

We find that the BFRO structure prefers to adopt C-AFM ordering, where the spins on Fe (3d) and Re (5d) transition metal ions anti-aligned in the plane of epitaxy (in-plane) but align parallelly perpendicular to this plane (out-of-plane). However, the structure undergoes a magnetic phase transition beyond -2.7% strain leading to a G-AFM ordered phase where the spins are anti-aligned both in-plane and out-of-plane. The total density of states (DOS) and the contributions to it from the d and p states of Fe (Re) and O, respectively, for both the spin channels, calculated within GGA+U (only on Fe) at reference strain (0%) are shown in Figure 4(a). In BFRO, Re prefers 4+ oxidation state (high spin) and Fe prefers to stay in high spin 2+ oxidation state. The thick black line represents the total DOS for both the spin channels (spin up and down). The up and down channels contribute equally to the DOS indicating an AFM ground state. The orange solid line represents the local density of states (LDOS) for Fe (3d) orbitals and the solid blue lines LDOS for 5d (Re) states. The LDOS which arise from oxygen p orbitals, denoted by magenta color, contribute predominantly to the total density of states (see Figure 4(a)). The structure is insulating, with a small gap of 0.4 eV in the GGA+U calculations. However, this gap is significantly enhanced up to 1.2 eV after incorporating onsite Coulomb repulsion \( U = 3.6 \) eV on Re-sites as shown in Figure 4(b). This suggests that the correlation effects arising from Re atoms would be important in this system. The band near the Fermi energy arises predominantly from Re 5d \( (t_{2g}) \) states with strong oxygen 2p orbital hybridization. The bands just above the Fermi level have a predominantly Re 5d \( (e_g) \) character in both spin channels. The Fe \( t_{2g} \) bands lie between -8.5 to -5 eV for both the spin channels while the \( e_g \) bands extend from -5 to about -1.8 eV below the Fermi energy. There are two in-plane and one out-of-plane Fe-O-Re angles measuring 141°, 149° and 148°, respectively. The two in-plane angles are different due to oxygen octahedral distortion around the Fe atom. With these angular orientations, the magnetic moments on Fe and Re are coupled through antiferromagnetic superexchange mechanism along the in-plane direction and coupled ferromagnetically along out-of-plane.

Similarly, the DOS for G-AFM at -2.7% strain is also shown in Figure 4(a). Here, the correlation effect on both Fe and Re-sites are taken into account for the DOS calculations. Unlike the C-AFM phase, in this case, neither the total DOS nor the LDOS are identical in both the spin channels. The difference in the DOS indicates the ferrimagnetic (FiM) nature of the compound. The \( t_{2g} \) bands of Fe are sharply localized within -8.5 to -6.0 eV energy window, while the \( t_{2g} \) states of Re-sites are localized in the minority spin channel immediately below the Fermi energy. Interestingly, the valence and conduction band edges correspond to different spin channels and there is no gap in between. Hence, there is an insulator (C-AFM) to semi-metal (G-AFM) transition at -2.7% strain. The half-metallic (or semi-metallic) state (see Figure 5) results despite using \( U \) on both the TM sites, making it less likely to be an artifact of the DFT method employed. This is indeed one of our important findings in this compound under ES.

### Strain-dependence ground-state structure of Bi\(_2\)FeIrO\(_6\)

In this section, we have studied the influence of ES on Bi\(_2\)FeIrO\(_6\) thin-films. The ionic positions and the corresponding c-axis at each strain are optimized by using GGA+U (used \( U \) only on Fe) approach in \( P2_1/\bar{n} \) symmetry. We also studied the effect of \( U \) on Ir (5d) sites as it plays a very crucial role in predicting the electronic properties as seen in the previous section. The optimized energies are plotted against the ES as shown in Figure 6 which shows the lowest energy magnetic states with large magnetic moments due to the existence of different oxidation numbers in the TM ions. As can be seen in Figure 6(a) the G-AFM emerged as the lowest energy state throughout the epitaxial strain. The FiM ground-state (solid black pointed circle line) possesses a 2+ (Fe) and 4+ (Ir) oxidation state which contributes to a net magnetic moment of 3 \( \mu_B/\text{f.u.} \), while the solid square pointed line represents the higher energy ferrimagnetic structure with 3+ (Fe) and 3+ (Ir) oxidation states. In both the cases, the Fe-site assumes a high-spin configuration while Ir prefers low-spin. Note that the energy vs strain (Figure 6(a)) obtained by using the GGA+U approach, where the on-site Coulomb repulsion only included for Fe-site. However, keeping the necessity of \( U \) values on 5d-sites in mind, when we added \( U \) (5.18 eV) on Ir sites, we observed a sudden change in the ground state. Moreover, adding \( U \) on Ir sites the FiM (2+, 4+) state no longer remains as the lowest energy state. Instead, the ferrimagnetic (3+, 3+) state get stabilized under strain (see Figure ). The FiM (2+, 4+) state denoted by solid black line is shifted up in energy while the energy of the (3+, 3+) state, represented by the solid red line, is brought down significantly as compared to Figure 6(a). The ferrimagnetic ground-state leads to a total magnetic moment of 5 \( \mu_B/\text{f.u.} \), which comes predominantly from the Fe sites, while the Ir ion undergoes a low spin \( d^6 \) configuration. In the Bi-based 3d-5d compounds, this is a first observation of a 3+ (3d), 3+ (5d) states. In this compound, the magnetic moments of Fe atoms are aligned ferromagnetically and the induced moments on Ir sites are almost zero due to the low spin configuration as a result of which the total system becomes ferrimagnetic.

The high \( U \) value calculated for Ir is contrary to the usual expectation of lowered correlations in the more diffuse 5d levels. Hence, we tested the robustness of the (3+,3+) state by scanning the \( U \) (Ir) keeping the \( U \) (Fe) fixed at 6.38 eV. The results are summarized in Figure 7. We observed that, even at a lower \( U \) value of 1.0 eV, the system already undergoes a transition from ferrimagnetic (Fe\(^{2+}\), Ir\(^{4+}\)) to ferromagnetic (Fe\(^{3+}\), Ir\(^{3+}\)) state. The energy of ferromagnetic states lowers further as we increase \( U \) (Ir) towards our calculated value (\( U = 5.18 \) eV). This result indicates that, correlation effects at Ir play an important role in BFIO making the FiM to FM tran-
Electronic and magnetic properties of Bi$_2$FeIrO$_6$

In this section, we analyze the magnetic and electronic properties of DP Bi$_2$FeIrO$_6$ thin-films in detail. The DOS of both the possible (FM and FiM) phases are studied and are shown in Figure 8 and Figure 10, respectively. As is evidenced from Figure 8 the states close to Fermi level ($E_F$) are dominated by Ir $d$-states strongly hybridized with O $p$-states. The dominating part of O $p$-states separated from Fe and Ir $d$-states are located below Fermi level within the range from -7.8 eV to -2.4 eV. In the majority spin channel, the Fe $t_{2g}$, as well as $e_g$ states, remain filled while in Ir-sites the $t_{2g}$ states are completely filled and the $e_g$ states remain empty. In the minority spin channel, the Fe $t_{2g}$ and $e_g$ states remain completely empty while in Ir-sites the $t_{2g}$ states remain filled and the $e_g$ states stay completely empty, thus give rise to an insulating character in both the spin channels. This rare FM insulating nature of BFIO makes it very special.

Figure 10 depicts the DOS of FiM metallic phase when the on-site Coulomb repulsion is switched off on $5d$ (Ir)-sites. The metallic character of this state comes from the Ir major-
FIG. 6. (a) Strain dependence structural stability of Bi₂FeIrO₆ thin films. Optimized energies are positioned as a function of biaxial with respect to the G-type ferrimagnetic structure at +2% strain. All the energies were optimized using GGA+U (Fe) approach. The solid black line denotes the ferrimagnetic metallic structure and the solid red line represents the ferromagnetic insulator. (b) Illustrates the energy vs biaxial strain where the energies are positioned with respect to the ferrimagnetic structure at +2% strain. The energies were obtained using the GGA+U method with $U_{eff} = 6.38, 5.18$ eV for Fe and Ir, respectively. Like Figure 6(a) the solid black line denotes the ferrimagnetic metallic state and that of the solid red line denotes the ferromagnetic insulator, as the lowest energy state.

FIG. 7. Phase diagram of monoclinic $P2_1/n$ structure on energy (E)-correlation ($U$) plane. There are two phases, the plane just above the dotted horizontal line is ferrimagnetic metallic and one just below it is a ferromagnetic insulator. The solid black line represents the change in energy by varying $U$ on Ir-sites keeping the $U$ on Fe-site fixed. Similarly, the red line shows the change in energy by varying $U$ on Fe-sites fixing $U = 0$ on Ir-sites.

FIG. 8. The density of states (DOS) of FM Bi₂FeIrO₆, calculated using the GGA+$U$ method with $U_{eff} = 6.38, 5.18$ eV for Fe and Ir, respectively. The dashed vertical zero line is set to the Fermi energy. The local magnetic moments on Ir site are antialigned with equal magnitude leading to zero magnetic moment, while on Fe site the up spin channel is completely filled and the down spin channel is completely empty, hence results in a net magnetic moment in the system. The solid black line, total DOS; orange solid line, Fe-d states; blue line, Ir-d states and solid magenta line, O-p states.

magnetic moment of 1 $\mu_B$/f.u. Like the FM insulating state, the metallic AFM states are also very special due to their rare existence.

As we know, 5$d$ transition metals have an intrinsically strong spin-orbit coupling (SOC). Particularly, iridates are known to display SOC effect [40] in perovskites and DPs. Motivated by this, we extended our calculation to consider the SOC effect on top of GGA as well as GGA+$U$ functionals. We observed that adding SOC to GGA, lowered the band gap, while the insulating behavior was recovered by adding $U$. However, there is no major change in the magnetic properties of the system. Once again the system preferred to stay in the Fe$^{3+}$, Ir$^{3+}$ oxidation state even with SOC. The low spin 3+ oxidation state of Ir ($d^5$) ion, weakens the role of SOC in BFIO.

As can be seen in Fig. 8 the conduction band is made up almost entirely by Fe states whereas valence band results from Ir-O hybridised states. In principle, this implies that the photoexcitation can lead to electron-hole separation in the sublat-
FIG. 9. Schematic level diagrams of 3d-5d orbitals. (a) Schematic representation of the 3d-5d electrons of d orbitals in Fe$^{3+}$, Ir$^{3+}$ oxidation state. The interaction between the two transition metals via O p orbitals leads to ferromagnetism. (b) Representation of the 3d-5d electrons of d orbitals in Fe$^{2+}$, Ir$^{4+}$ oxidation state. For case (b) the interaction between the atom leads to an AFM. The antiferromagnetic and ferromagnetic interaction basically depends on the occupations of the $e_g$ orbitals.

FIG. 10. The density of states (DOS) of G-type AFM Bi$_2$FeReO$_6$, calculated using GGA+U method with $U_{c/f}$=6.38, 0.0 eV for Fe and Ir, respectively. The dashed vertical zero line is set to the Fermi energy. The local magnetic moments on Fe and Ir are antialigned with unequal magnitude leading to a net magnetic moment on the system. The solid black line, total DOS; green solid line, Fe-d states; blue line, Ir-d states and solid magenta line, O-p states.

SUMMARY

In summary, we have designed two Bi-based double-perovskites Bi$_2$FeReO$_6$ and Bi$_2$FeIrO$_6$ mimicking the thin-film geometry grown along [001] direction. These two structures were constructed by keeping the Fe atom fixed at B-site and substituting Re and Ir (5d) atoms in B$^2$-sites of ordered DP $A_2BB'O_6$ structure. The calculated tolerance factors indicate that both the compounds will adopt perovskite (orthorhombic-monoclinic) crystal structure. The Bi$_2$FeReO$_6$ thin-film becomes stable adopting a monoclinic $P2_1/n$ phase under a wide range of ES. By incorporating various types of magnetic ordering we show that the thin-film Bi$_2$FeReO$_6$ prefers a C-AFM spin ordering in its ground-state with zero magnetic moments. However, at -2.7% strain the structure adopts G-AFM ordering through a monoclinic to monoclinic structural transition. The G-AFM phase of BFRO provides a magnetic moment of 1 $\mu_B$/f.u. which is comparable to the previously reported Bi-based 3d-5d compounds [24]. Our DOS calculations indicate that the Bi$_2$FeReO$_6$ is an insulator with a band gap of around 1.2 eV in thin film form. We find the correlation effect on Re (5d)-site to be very important, as on-site Coulomb repulsion ($U$) widens the band gap significantly. In this compound, Fe takes a high spin 2$^+$ oxidation state, whereas Re adopts its formal high spin 4$^+$ state. One important finding of our calculations is that the oxygen octahedra around Fe atoms undergo a distortion leading to long-short Fe-O bonds in the octahedra, which is not observed in the BFIO thin-film.

In Bi$_2$FeIrO$_6$ the $P2_1/n$ symmetry structure emerged as the ground state. Both the transition metals (Fe, Ir) takes 3$^+$ oxidation state, where Fe acquires high spin configuration and Ir prefers to stay in a low spin. This configuration of Bi$_2$FeIrO$_6$ leads to a huge ferromagnetic ground state with a magnetic moment of 5 $\mu_B$/f.u. throughout the considered ES. However, when the onsite Coulomb repulsion term on Ir-site is switched off, the system stabilizes in FiM ground state with a magnetic moment of 3 $\mu_B$/f.u. over the ES. The DOS calculations show that the FM state is an insulator while the FiM state is a half-metal. Our calculations show that even a small value of $U$ on Ir site could, in principle, switch the (2+, 4+) oxidation state to (3+, 3+) state. So, there is a correlation driven metal to insulator transition in BFIO thin-film under ES. Given that ferromagnetic insulators and antiferromagnetic metals are very rare, the ab initio designed BFIO could prove to be quite technologically significant.

Both the compounds can be used in spintronic applications due to their magnetic and half-metallic nature. Apart from this, their narrow band-gaps ($\sim$ 1.2 and 1.3, respectively) make them a suitable candidate for PV applications. Although these materials are not ferroelectric, an appropriate doping strategy can make them ferroelectric [19][16]. Apart from PV applications, these materials can also be used for the photocatalytic activity, such as solar water splitting and water purification. Like the parent BFO compound, the narrow band gap nature of these 3d-5d compounds could allow them to harvest parts of the visible light of the solar spectrum. We hope that our observations will initiate further experimental efforts to verify the interesting predictions made in this work.

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