

Figure S1. Bi and La arrangement on the A site in the rhombohedral system with $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$.

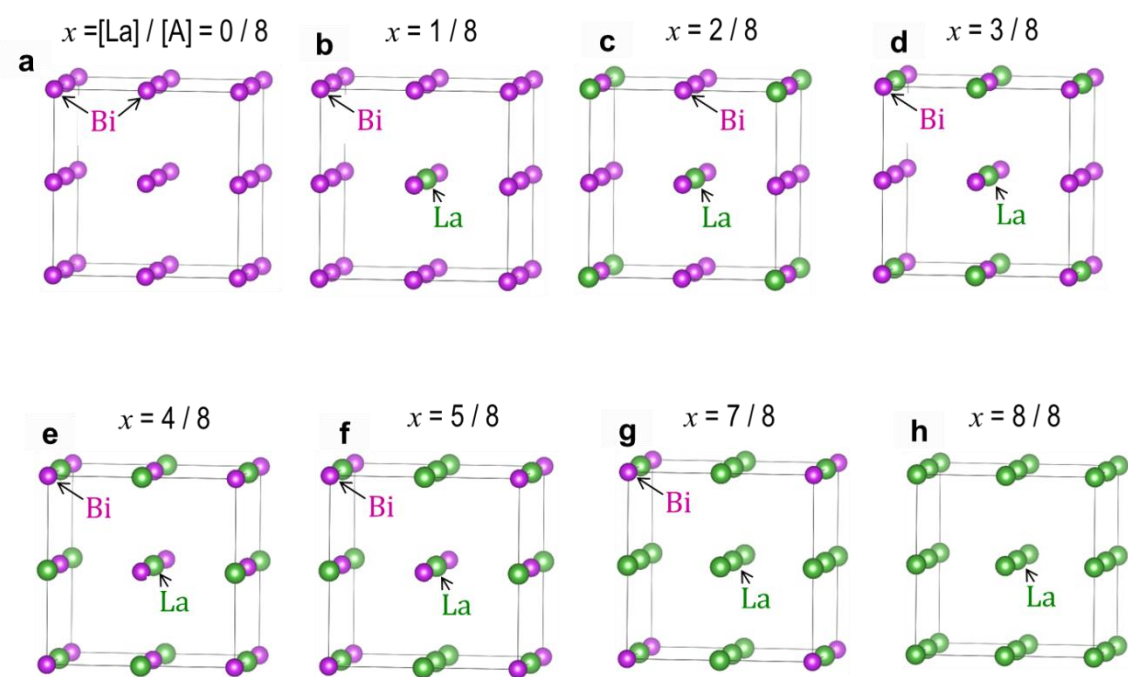


Figure S2. Bi and La arrangement on the A site in the tetragonal system with $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$.

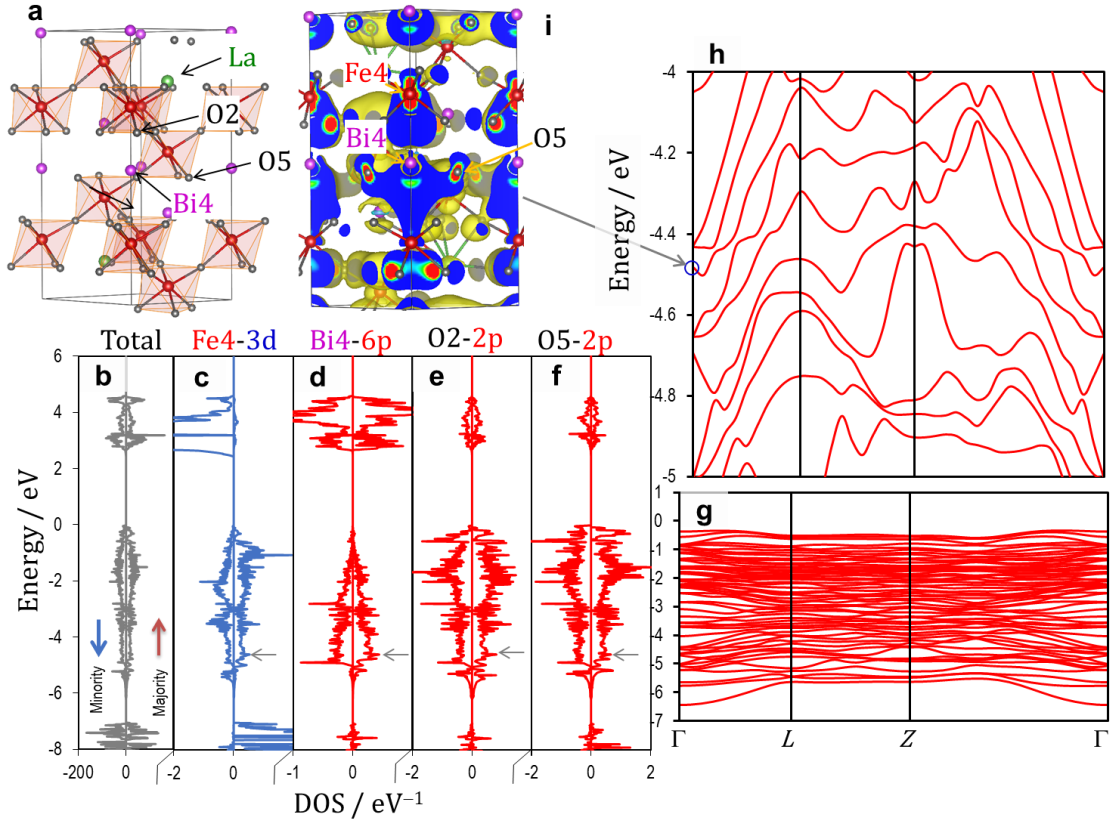


Figure S3. Crystal structures (a), electronic density of states (DOS) (b–f) and band structures (of the majority spin band) in the valence band (g, h) of the rhombohedral cell with $x = 2/6$. The wavefunction of the band shown in blue circle in h is displayed in i. The up (red) and down (blue) arrows in b denote the majority and minority spin bands, respectively, The horizontal arrows (gray) in c–f correspond to the energy level of the blue circle in h.

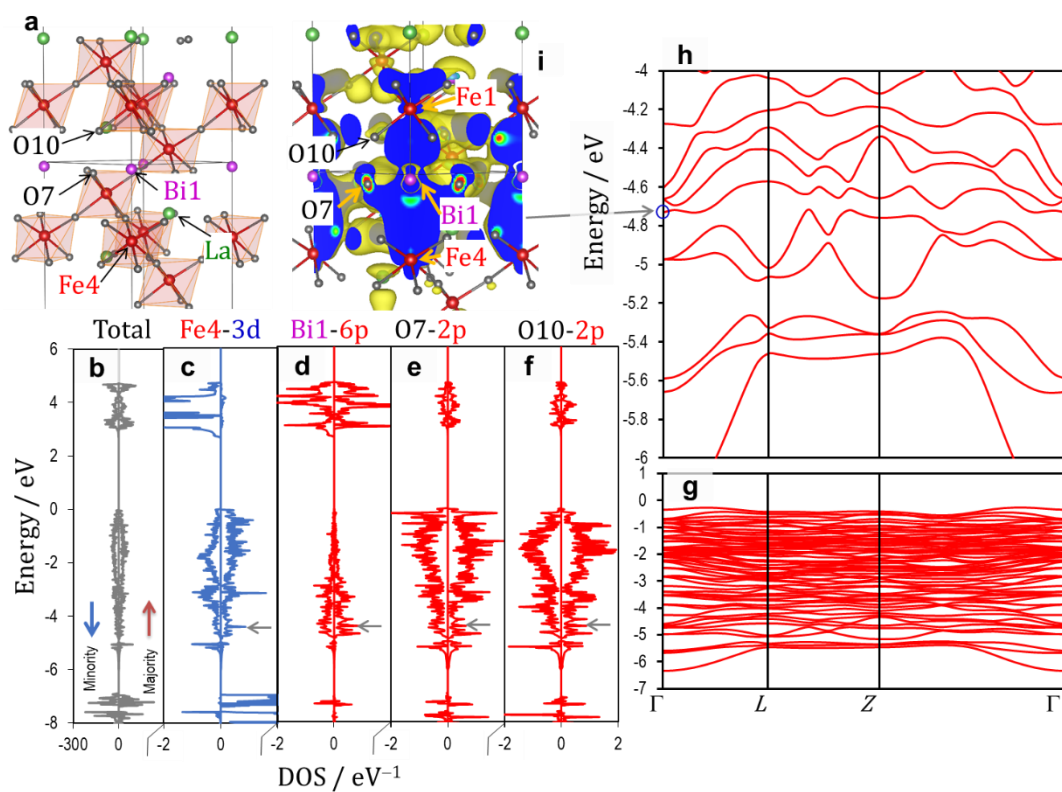


Figure S4. Crystal structures (a), electronic density of states (DOS) (b–f) and band structures (of the majority spin band) in the valence band (g, h) of the rhombohedral cell with $x = 4/6$. The wavefunction of the band shown in blue circle in h is displayed in i. The up (red) and down (blue) arrows in b denote the majority and minority spin bands, respectively, The horizontal arrows (gray) in c–f correspond to the energy level of the blue circle in h.

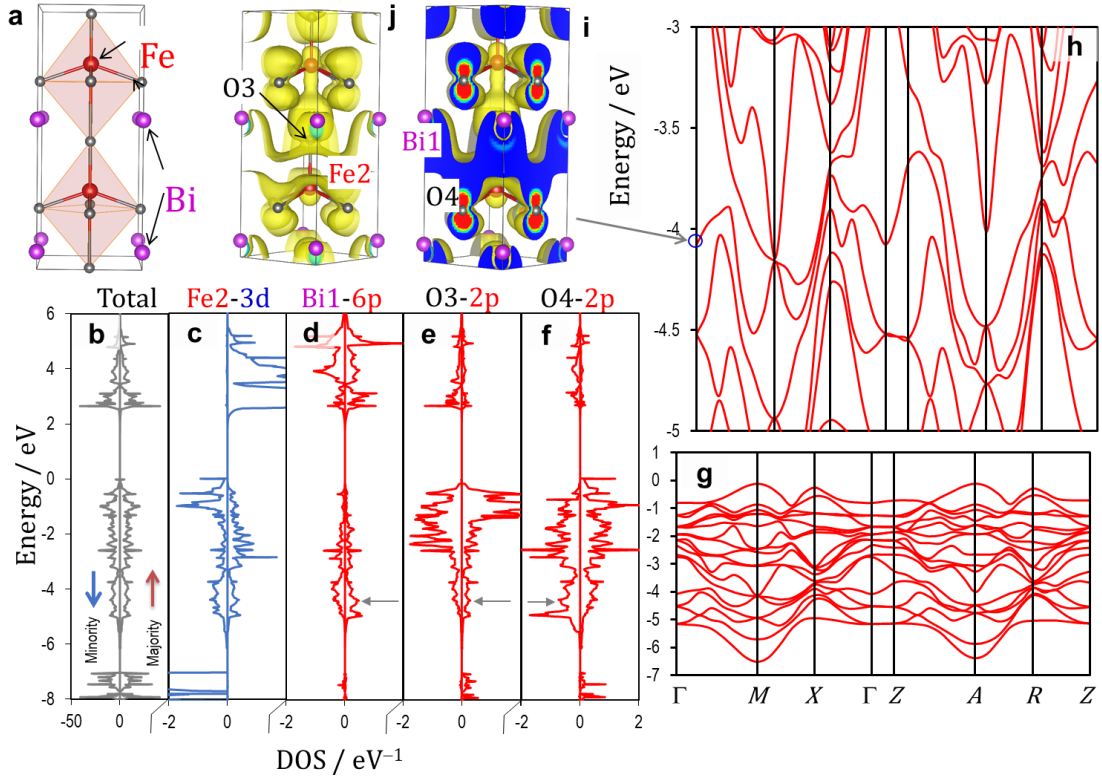


Figure S5. Crystal structures (a), electronic density of states (DOS) (b–f) and band structures (of the majority spin band) in the valence band (g, h) of the tetragonal BiFeO_3 cell with $x = 0$. The wavefunction of the band shown in blue circle in h is displayed in j and i. The up (red) and down (blue) arrows in b denote the majority and minority spin bands, respectively, The horizontal arrows (gray) in c–f correspond to the energy level of the blue circle in h.

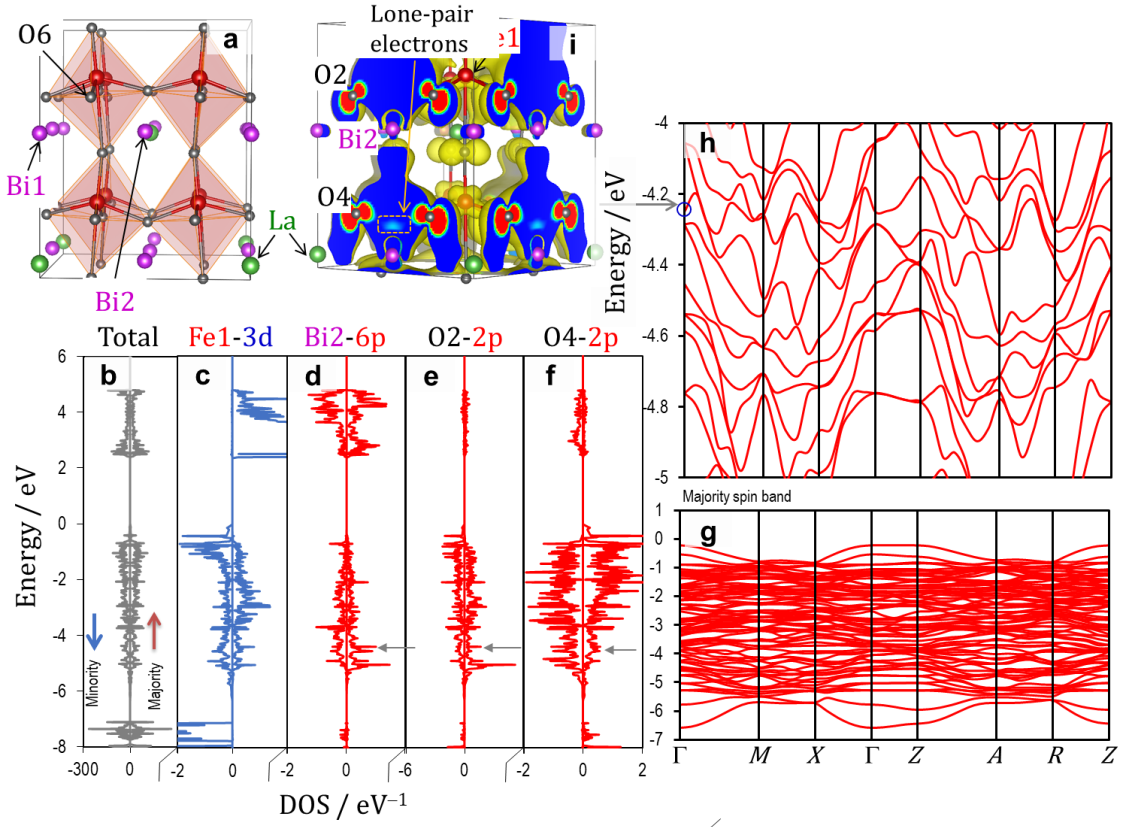
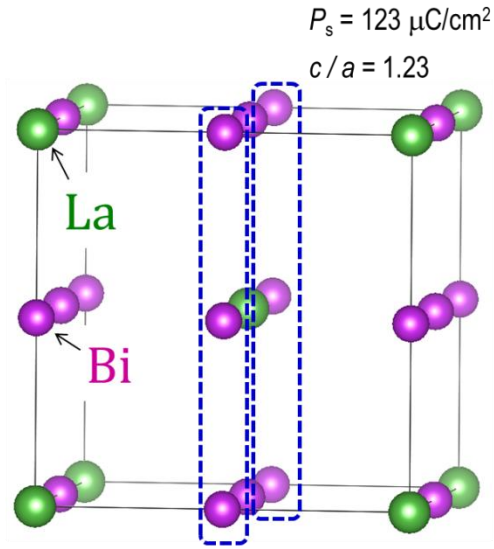


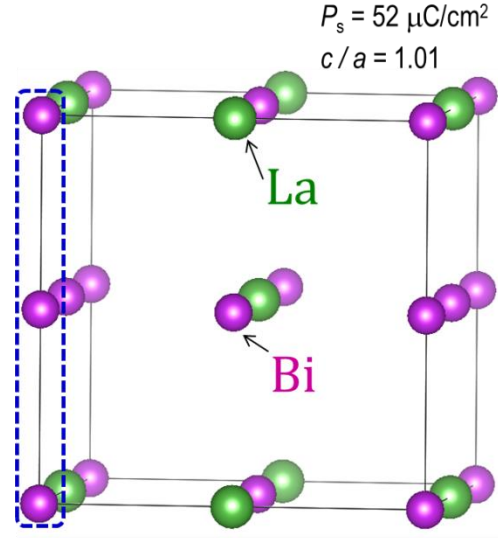
Figure S6. Crystal structures (**a**), electronic density of states (DOS) (**b–f**) and band structures (of the majority spin band) in the valence band (**g, h**) of the tetragonal cell with $x = 2/8$. The wavefunction of the band shown in blue circle in **h** is displayed in **i**. The up (red) and down (blue) arrows in **b** denote the majority and minority spin bands, respectively. The horizontal arrows (gray) in **c–f** correspond to the energy level of the blue circle in **h**.

a $x = [\text{La}] / [\text{A}] = 2 / 8$



Bi-O-Bi pillar: Two

b $x = 3 / 8$



Bi-O-Bi pillar: One

Figure S7. Bi and La arrangement along with Bi pillars along the polar c axis of the tetragonal cells with **a** $x = 2/8$ and **b** $3/8$. In the tetragonal cell with $x = 2/8$, two Bi pillars remains and thereby a large P_s of $123 \mu\text{C cm}^{-2}$ associated with a high tetragonality (c/a) of 1.23 appear. An increase in La content (x) to $3/8$ leads to a decrease in the Bi pillar to one, resulting in a marked decrease in P_s to $52 \mu\text{C cm}^{-2}$. Its c/a is markedly reduced to 1.01 at $x = 3/8$.

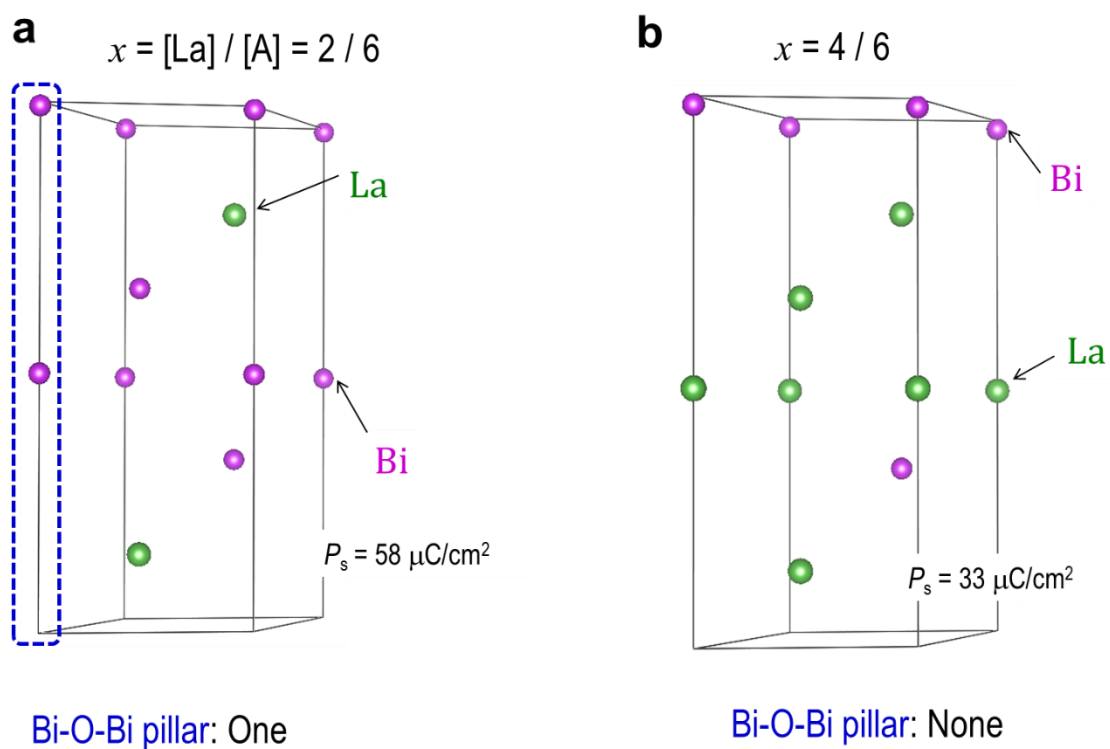


Figure S8. Bi and La arrangement along with Bi pillars along the polar c axis of the rhombohedral cells at **a** $x = 2/6$ and **b** $4/6$. In the rhombohedral cell with $x = 2/6$, one Bi pillar is present and a relatively large P_s of $58 \mu\text{C cm}^{-2}$ appears. An increase in the La content (x) to $4/6$ leads to a decrease in the Bi pillar to zero. The P_s monotonically decreases with increasing x : the rhombohedral cell $x = 4/6$ has a relatively large P_s of $33 \mu\text{C cm}^{-2}$ in spite of the absence of the Bi pillar.

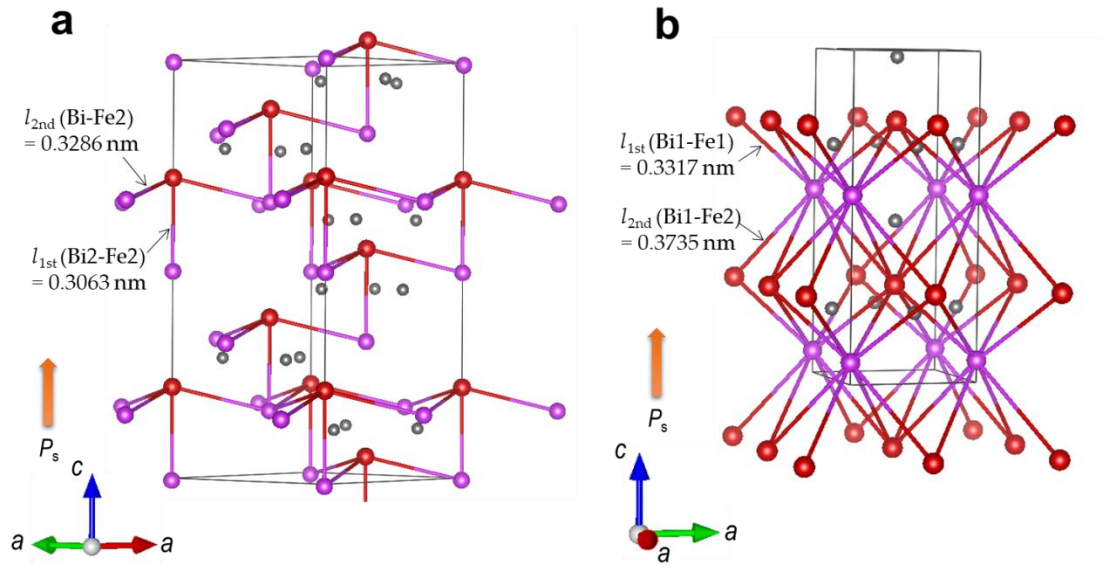


Figure S9. Bi-Fe bond lengths of BiFeO₃ in **a** rhombohedral and **b** tetragonal symmetries. Due to the distinct structural distortions, the 1st shortest Bi-Fe length (l_{1st}) and the 2nd shortest one (l_{2st}) are formed in the different directions with respect to their P_s vectors.

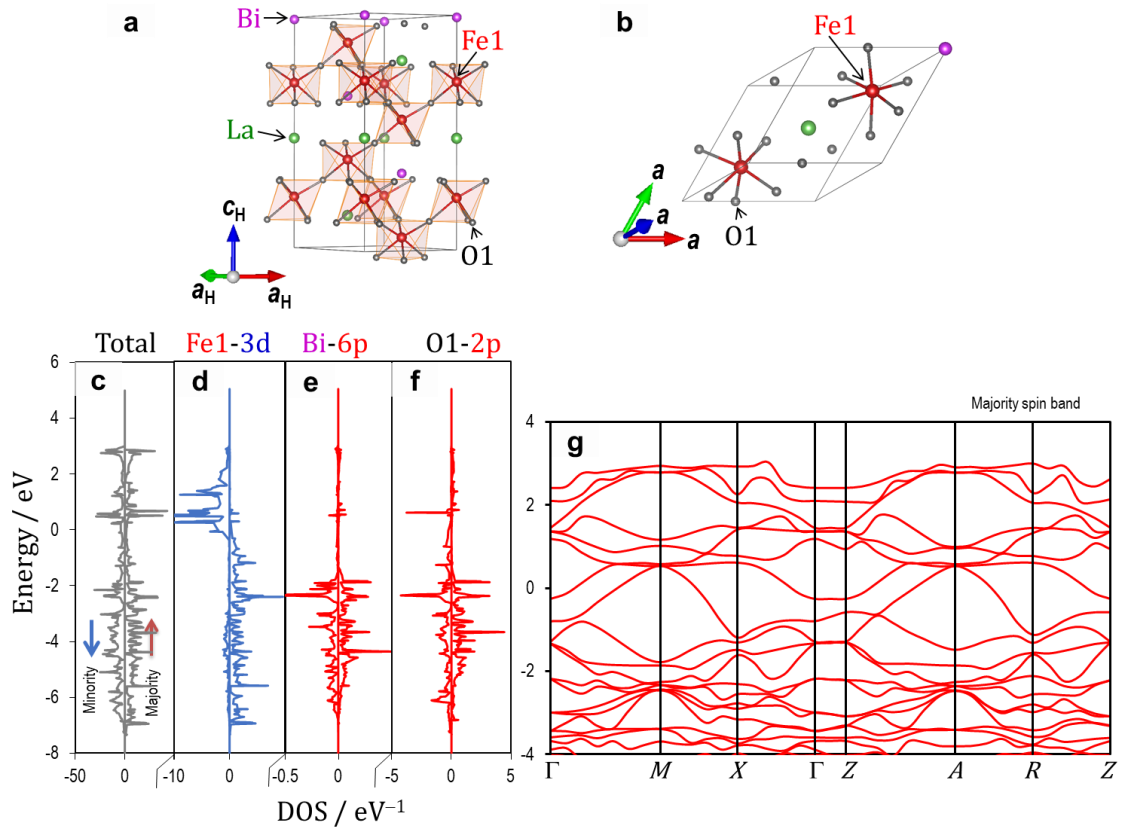


Figure S10. Crystal structures in the (a) hexagonal and (b) primitive settings, electronic density of states (DOS) (c–f) and band structure (of the majority spin band) in the valence band (g) of the rhombohedral ($x = 1/2$) with an ordered Bi-La arrangement along the polar c axis. The up (red) and down (blue) arrows in c denote the majority and minority spin bands, respectively. Note that the Fermi level is present inside the Fe-3d derived band and thereby this cell displays a metallic behavior. This is inconsistent with the experimental fact that these solid solutions exhibit an insulating nature. These results clearly show that not an ordered arrangement but a rock-salt one of Bi and La is preferred for our DFT calculations.