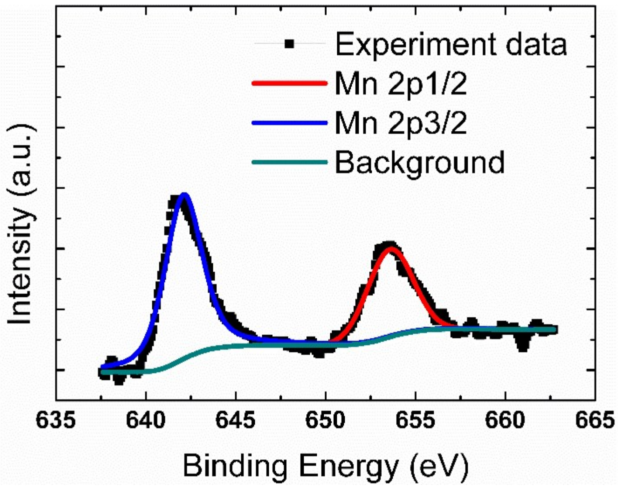
Fig. S1 XPS spectra of Mn and Ti. The Mn 2*p* core-level spectrum(a), the spin-orbit split $2p_{1/2}$ and $2p_{3/2}$ are located in 653.58 and 642.09 eV, respectively. These values are very close to the binding energy of Mn $2p_{1/2}$ (654 eV) and Mn $2p_{3/2}$ (642 eV) in $K_2TiF_6:Mn^{4+}$, this states explicitly that the valence state of Mn is +4 in BTMO. The Ti *2p* peak (b) , it can be decomposed into two peaks centered at 463.45 eV and 457.78 eV, which correspond to the binding energy of Ti $2p_{1/2}$ and Ti $2p_{3/2}$ in pure rutile TiO_2, indicating that the valence state of Ti is +4 in BTMO.

(a)



(b)

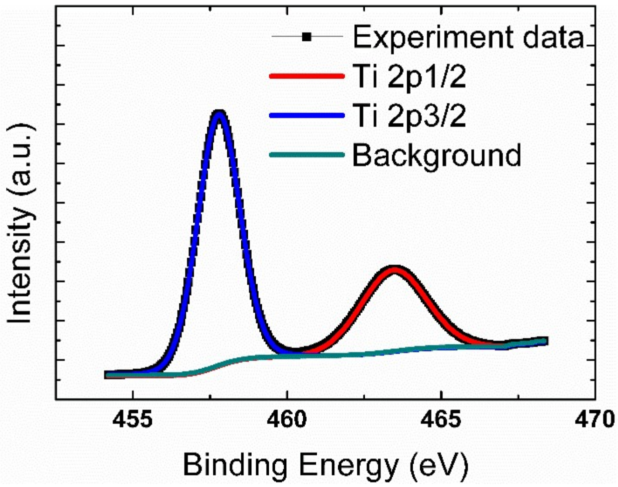


Fig. S2 MT curve of both BTMO and Mn_3O_4. The transition temperatures of the system and Mn3O4 have a tiny different. The system shows a transition at ~45 K, while the magnetic transition occurs at 42 K. In fact, if we attribute the magnetism to the Mn_3O_4 impurity, by choosing an appropriate proportion, the magnetic contribution of Mn_3O_4 shall be deducted. However, the proportion does not exist as the difference of transition temperature, and a " λ " like residual shall always exist.

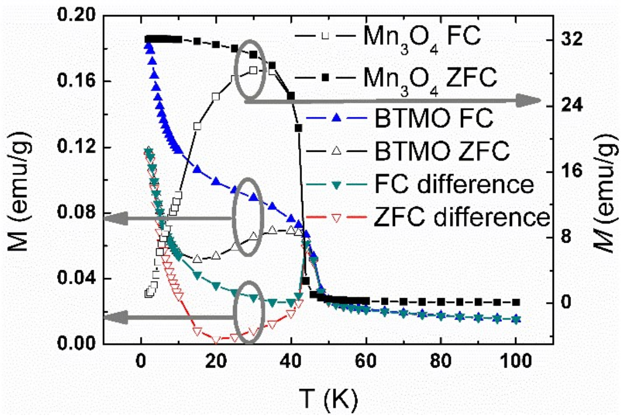


Fig. S3 Pyroelectric signal of BTMO. A large extrinsic thermally stimulated depolarization current (TSDC) signal is noticed which masked the intrinsic depolarization signal, making it difficult to determine the electrical polarization by pyroelectric measurement.

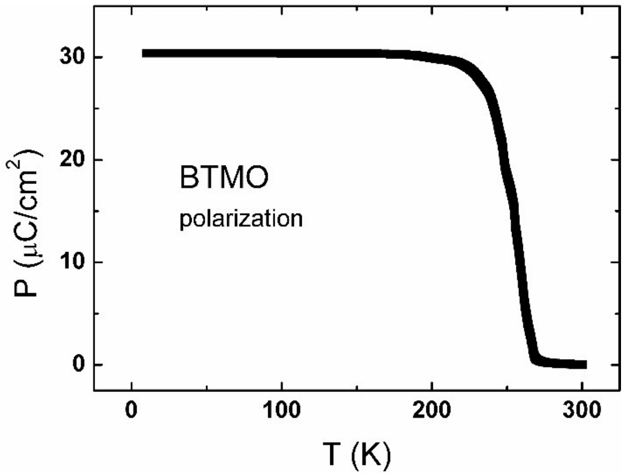


Fig. S4 PE loops of BTMO. The loops are affected by leakage and the polarization is overestimated.