Fig. S1 XPS spectra of Mn and Ti. The Mn 2p 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$_2$TiF$_6$: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.

Fig. S2 MT curve of both BTMO and Mn$_3$O$_4$. The transition temperatures of the system and Mn$_3$O$_4$ 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$_3$O$_4$ impurity, by choosing an appropriate proportion, the magnetic contribution of Mn$_3$O$_4$ 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.