

Supporting Information

Intrinsic Compositional Inhomogeneities in Bulk Ti-doped BiFeO₃: Microstructure Development and Multiferroic Properties.

i) XAS analysis

The X-ray absorption measurements (X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS)) were performed at the Fe K-edge energy at room temperature in conventional transmission mode using ionization chambers as detectors. The experiments were carried out at the BM25 Spanish CRG Beamline (SpLine) of the ESRF (European Synchrotron Radiation Facility). Each powder sample was sandwiched between two pieces of kapton tape located on the beam path. The amount of material was calculated to optimize the expected signal-to-noise ratio. Several scans were taken, in order to obtain a good signal-to-noise ratio. Fe metal foil, FeO, α -Fe₂O₃, γ -Fe₂O₃, and Fe₃O₄ powders were chosen as bulk references. Data analysis was carried out using *Athena program* identifying the beginning of the absorption edge, E₀, the pre-edge and post-edge backgrounds. The spectra were subjected to a background subtraction and normalized by the edge jump.

Figure S1 show the XAS spectra at the Fe k-edge for both samples.

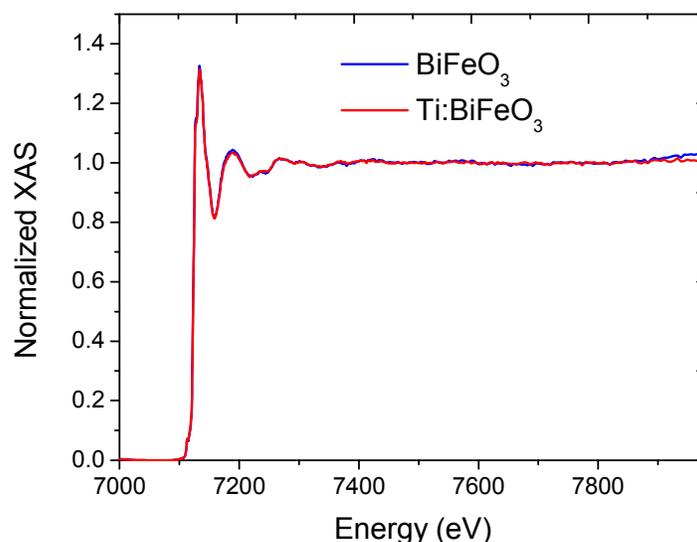


Figure S1. XANES spectra at the Fe k-edge for the BiFeO₃ and Ti:BiFeO₃ samples.

There are no clear differences pointing out that both samples exhibit very similar environment and oxidizing state for the iron atoms. Figure S2 show a detail of the edge region with the difference between both spectra.

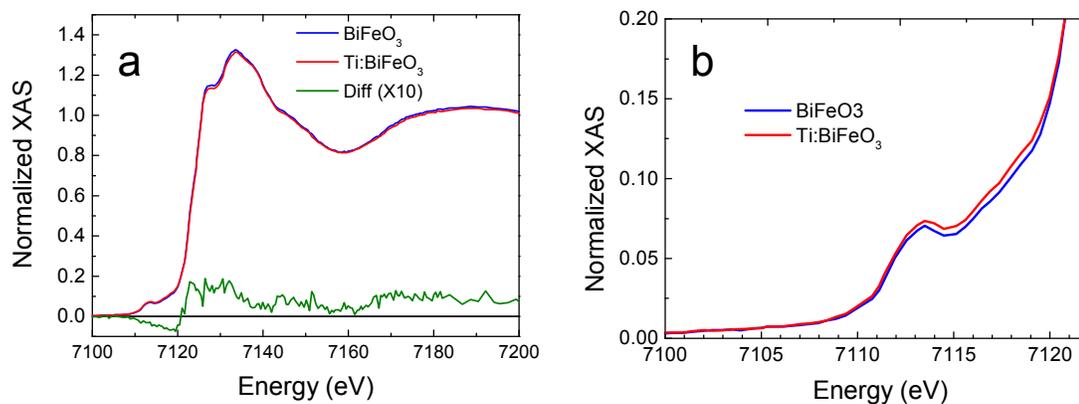


Figure S2. XANES spectra for the BiFeO₃ and Ti:BiFeO₃ samples and their difference and (b) detail of the pre-edge.

No clear structure is observed in the difference that could be ascribed to structural modifications of the material. However, the Ti doped sample exhibits a slightly enhanced pre-edge feature (see figure S2b). This pre-peak is associated with the Fe cations in non-centrosymmetric positions. The incorporation of Ti in the BiFeO₃ lattice induces distortion that could account for the observed differences.

The derivative of these XANES spectra are presented in figure S3.

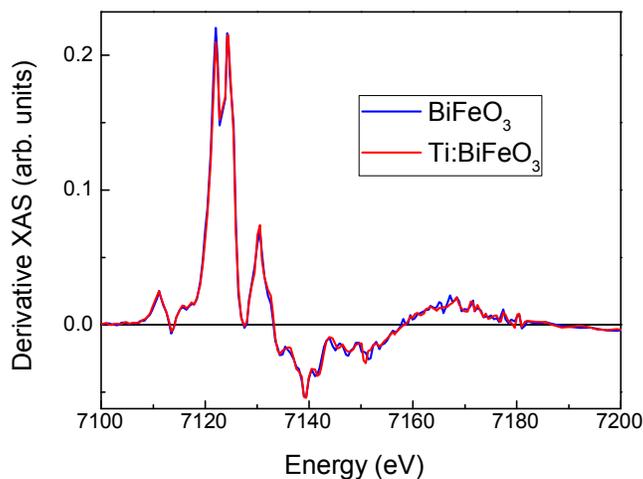


Figure S3. Derivative of the XANES for the BiFeO₃ and Ti:BiFeO₃ samples.

No shift in the position absorption edge (defined as the position where the derivative is maximum) is observed within the experimental resolution of the spectrum (0.2 eV).

Figure S4 show the XANES spectra of the analyzed samples with those of reference compound measured in the same conditions.

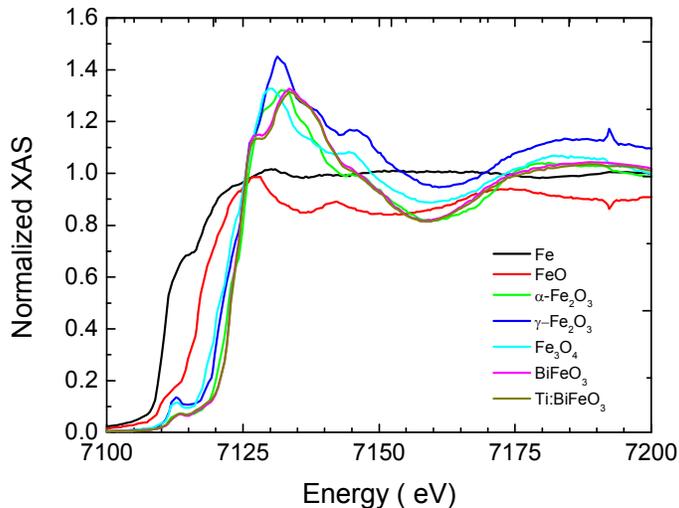


Figure S4 . XANES spectra for the BiFeO₃ and Ti:BiFeO₃ samples and the reference compounds

The position of the edge matches that of the hematite confirming that the oxidizing state of the iron cation is Fe⁺³ in both samples. From these results and considering the noise level of the spectra we may estimate that differences in the oxidizing state between both samples are smaller than 1%.

Figure S5 present the EXAFS spectra obtained using k2 weight.

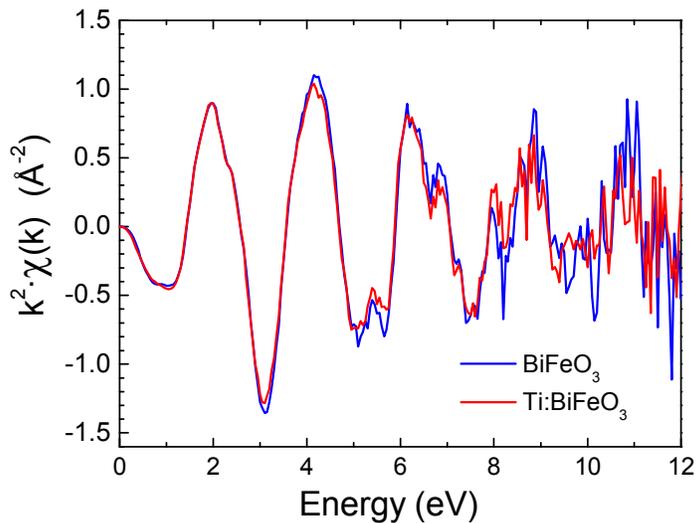


Figure S5. EXAFS spectra obtained using k2 weight for the BiFeO₃ and Ti:BiFeO₃ samples

Neither in this case have we found any variation in the structure of the Fe within the resolution of the experimental data.

In summary, we do not find significant differences neither in the Fe oxidizing state nor in its environment due to the incorporation of the Ti in the BiFeO_3 .

ii) Prolonged thermal treatments (48 h) in $\text{Bi}(\text{Fe},\text{Ti})\text{O}_3$:

$\text{Bi}(\text{Fe},\text{Ti})\text{O}_3$ ceramics were also obtained by sintering with prolonged thermal treatments, 1098 K during 48 h. As it is shown in Figure S6, under these conditions samples show similar structure as those sintered during shorter time (i.e., 2 h) so no appreciable grain growth is produced.

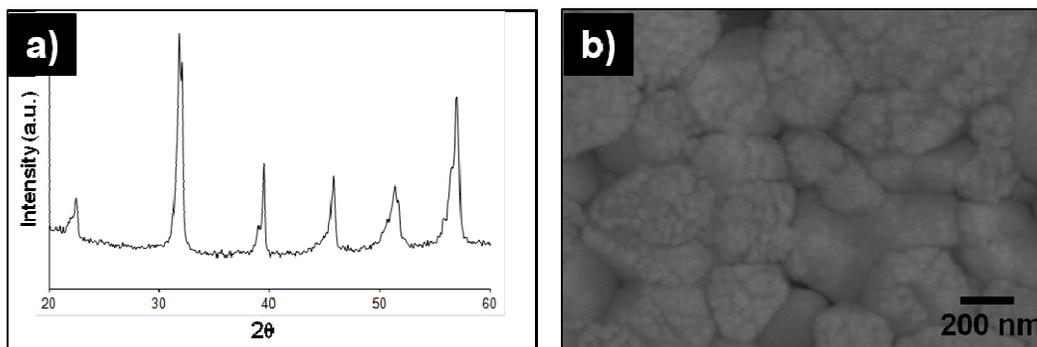


Figure S6. a) XRD diffractogram of the $\text{Ti}:\text{BiFeO}_3$ material sintered at 1098 K during 48 h. b) FESEM micrograph on the polished and etched surface of the $\text{Ti}:\text{BiFeO}_3$ material sintered at 1098 K/48h.

iii) Higher temperature treatments (1173 K) in $\text{Bi}(\text{Fe},\text{Ti})\text{O}_3$:

In the same way $\text{Bi}(\text{Fe},\text{Ti})\text{O}_3$ ceramics were also obtained by sintering at higher temperature, 1173 K during 8 h. Figure S7 shows again a similar microstructure, with no appreciable grain growth when compared to the samples treated at (1098 K).

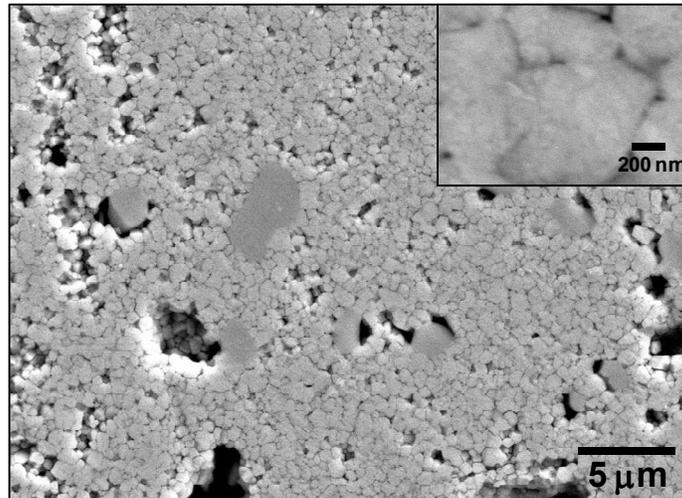


Figure S7. FESEM micrograph on the polished and etched surface of the $\text{Ti}:\text{BiFeO}_3$ material sintered at 1173 K/8h.