

Supplementary information

High quality samples of La-substituted BiFeO₃ prepared by mechanosynthesis

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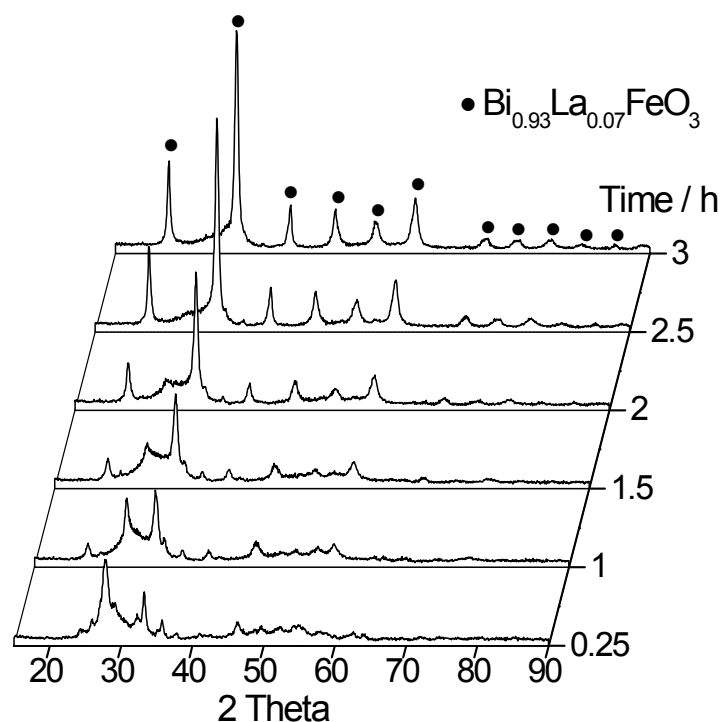


Figure S1. Diffraction patterns at different milling times of the solids obtained after milling under oxygen (7 bar) the stoichiometric amounts of the single oxides necessary for the composition $\text{Bi}_{0.93}\text{La}_{0.07}\text{FeO}_3$.

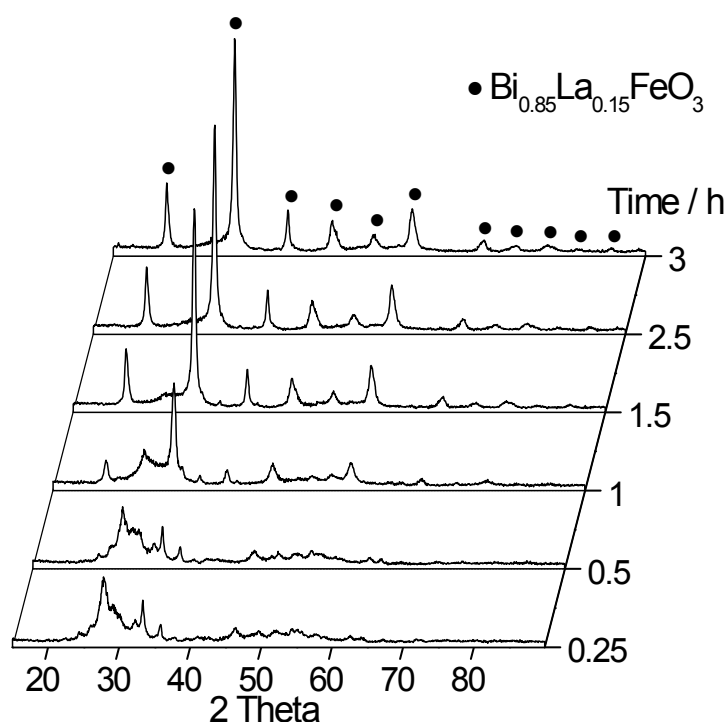


Figure S2. Diffraction patterns at different milling times of the solids obtained after milling under oxygen (7 bar) the stoichiometric amounts of the single oxides necessary for the composition $\text{Bi}_{0.85}\text{La}_{0.15}\text{FeO}_3$.

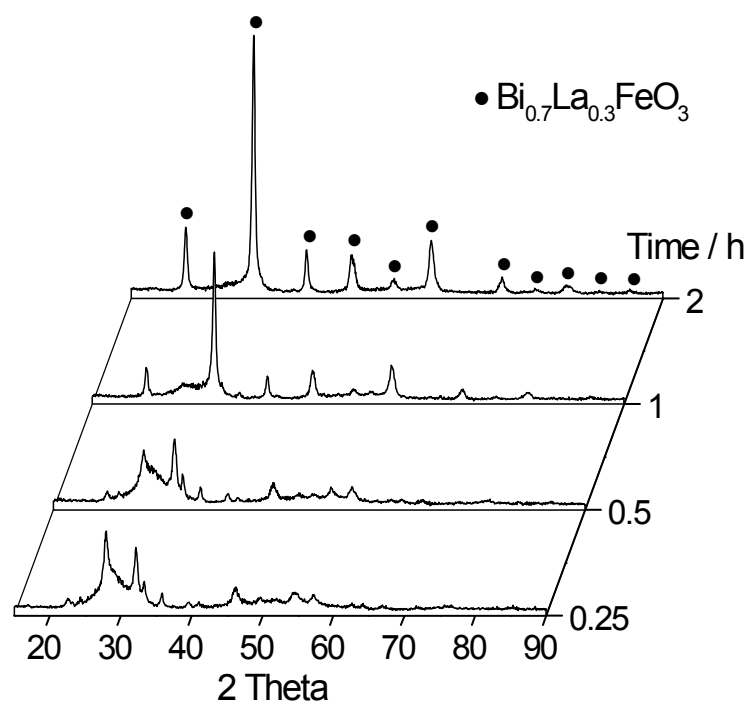


Figure S3. Diffraction patterns at different milling times of the solids obtained after milling under oxygen (7 bar) the stoichiometric amounts of the single oxides necessary for the composition $\text{Bi}_{0.70}\text{La}_{0.30}\text{FeO}_3$.

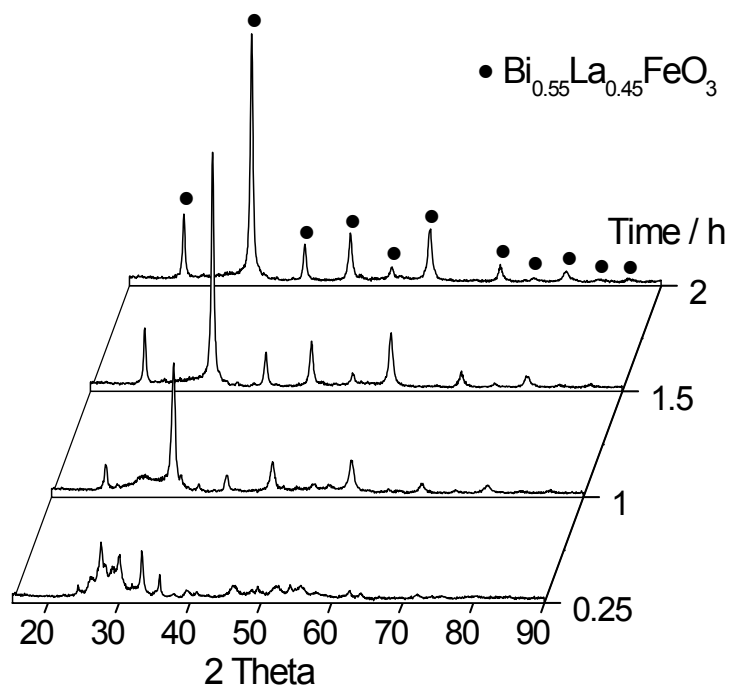


Figure S4. Diffraction patterns at different milling times of the solids obtained after milling under oxygen (7 bar) the stoichiometric amounts of the single oxides necessary for the composition $\text{Bi}_{0.55}\text{La}_{0.45}\text{FeO}_3$.

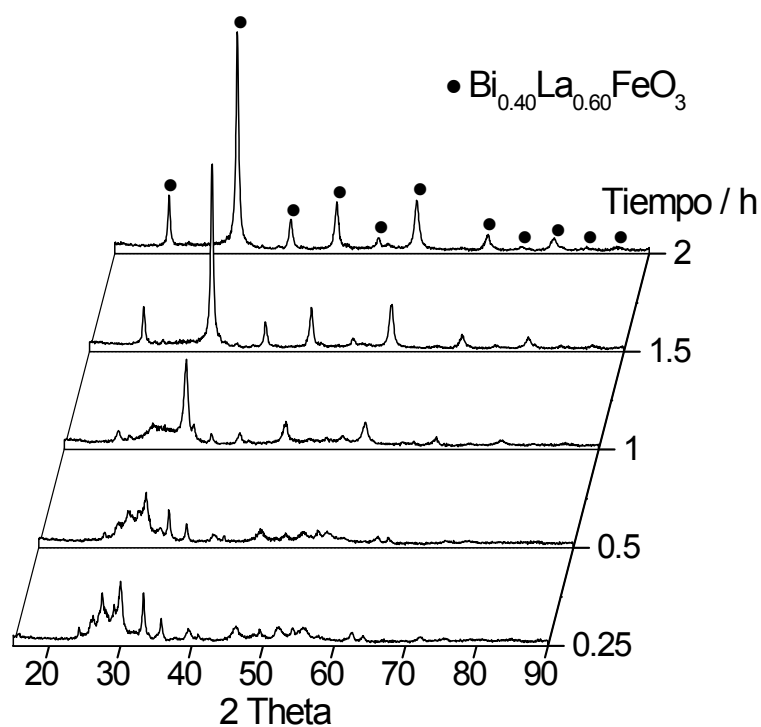


Figure S5. Diffraction patterns at different milling times of the solids obtained after milling under oxygen (7 bar) the stoichiometric amounts of the single oxides necessary for the composition $\text{Bi}_{0.40}\text{La}_{0.60}\text{FeO}_3$.

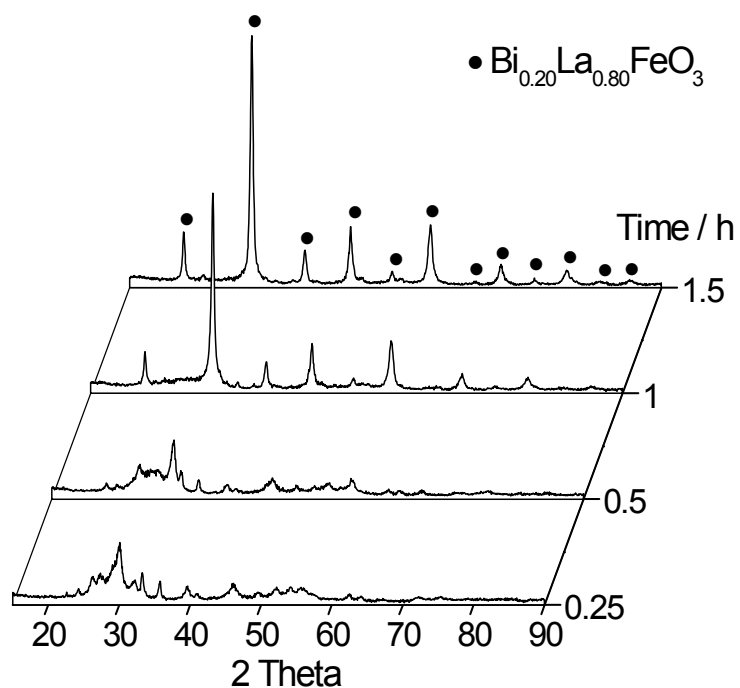


Figure S6. Diffraction patterns at different milling times of the solids obtained after milling under oxygen (7 bar) the stoichiometric amounts of the single oxides necessary for the composition $\text{Bi}_{0.20}\text{La}_{0.80}\text{FeO}_3$.

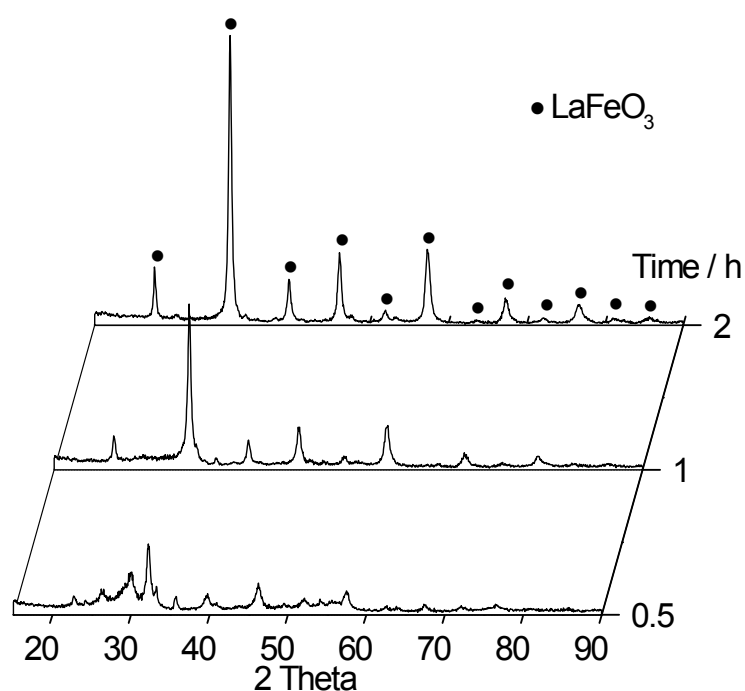


Figure S7. Diffraction patterns at different milling times of the solids obtained after milling under oxygen (7 bar) the stoichiometric amounts of the single oxides necessary for the composition LaFeO_3 .

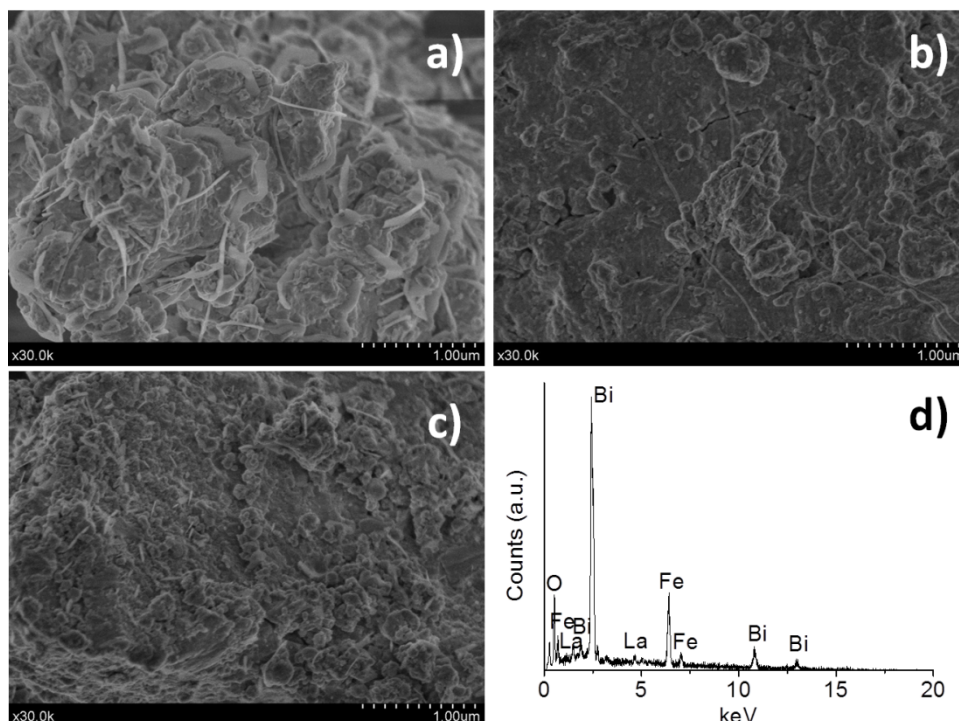


Figure S8. SEM micrographs corresponding to powders obtained after milling the single oxides necessary for the composition $\text{Bi}_{0.93}\text{La}_{0.07}\text{FeO}_3$. Micrographs were taken after milling (a) 0.5 h, (b) 1 h, (c) 3 h, (d) EDX spectrum of the product shown in (c).

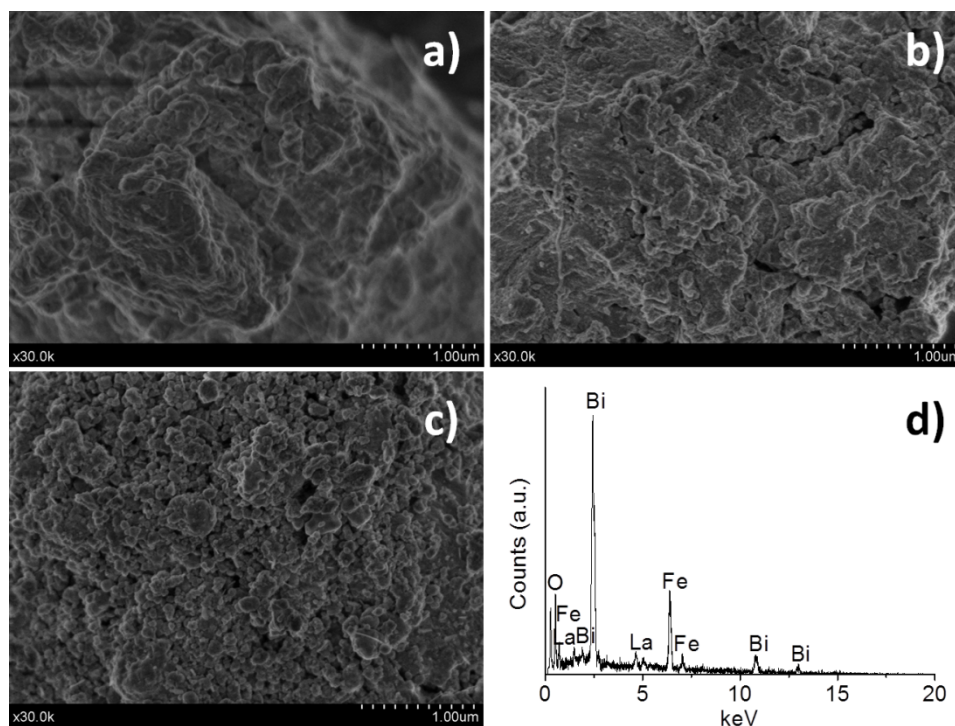


Figure S9. SEM micrographs corresponding to powders obtained after milling the single oxides necessary for the composition $\text{Bi}_{0.85}\text{La}_{0.15}\text{FeO}_3$. Micrographs were taken after milling (a) 0.5 h, (b) 1.5 h, (c) 3 h, (d) EDX spectrum of the product shown in (c).

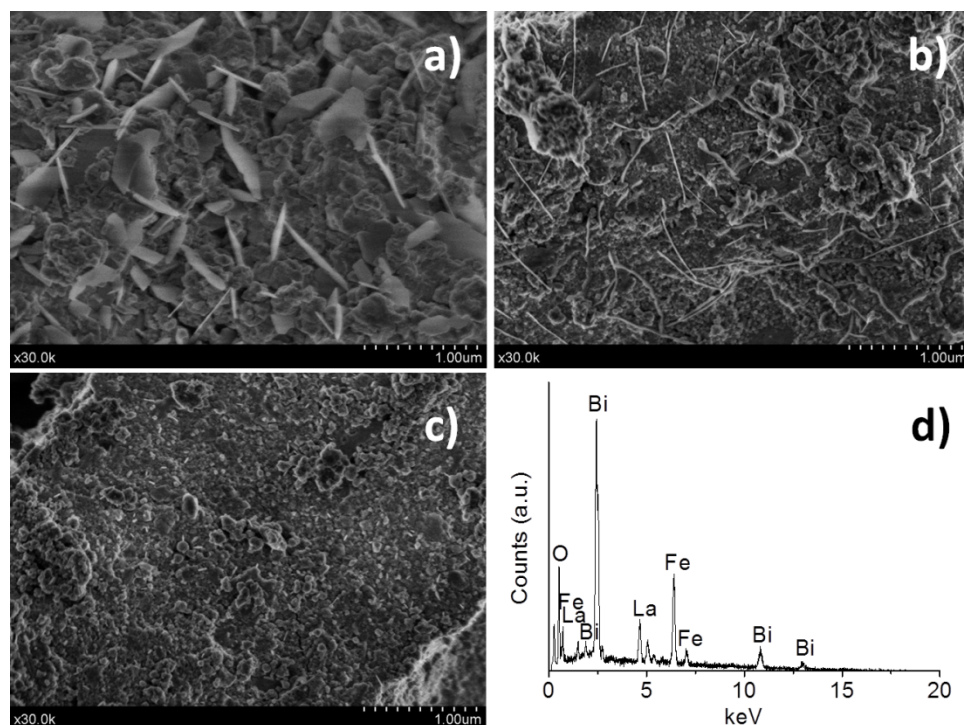


Figure S10. SEM micrographs corresponding to powders obtained after milling the single oxides necessary for the composition $\text{Bi}_{0.70}\text{La}_{0.30}\text{FeO}_3$. Micrographs were taken after milling: (a) 0.25 h, (b) 1 h, (c) 2 h, (d) EDX spectrum of the product shown in (c).

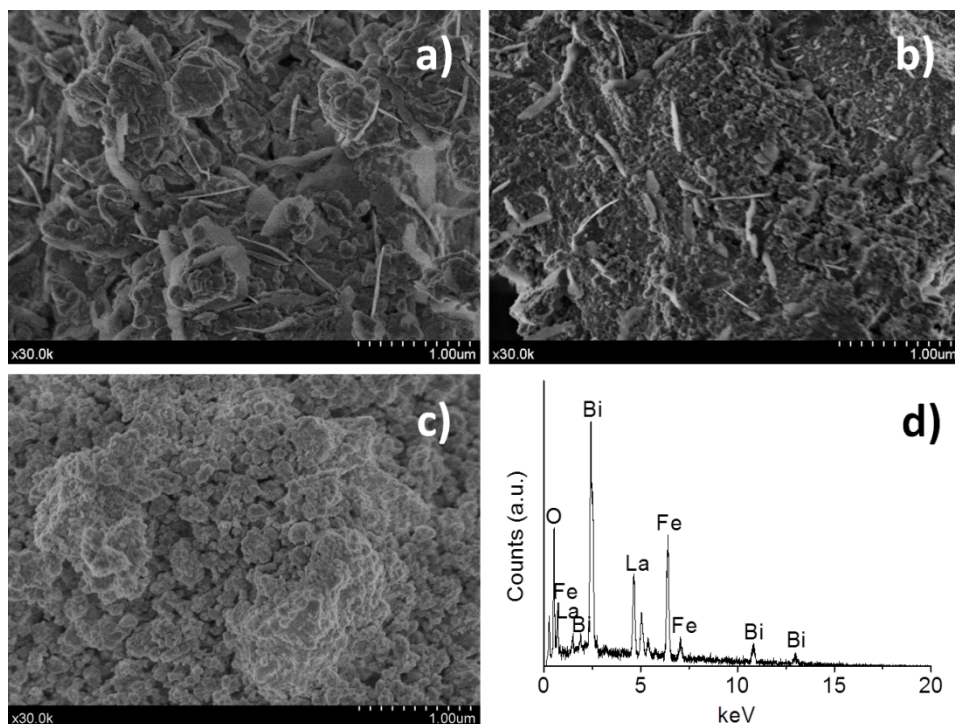


Figure S11. SEM micrographs corresponding to powders obtained after milling the single oxides necessary for the composition $\text{Bi}_{0.55}\text{La}_{0.45}\text{FeO}_3$. Micrographs were taken after milling: (a) 0.5 h, (b) 1 h, (c) 2 h, (d) EDX spectrum of the product shown in (c).

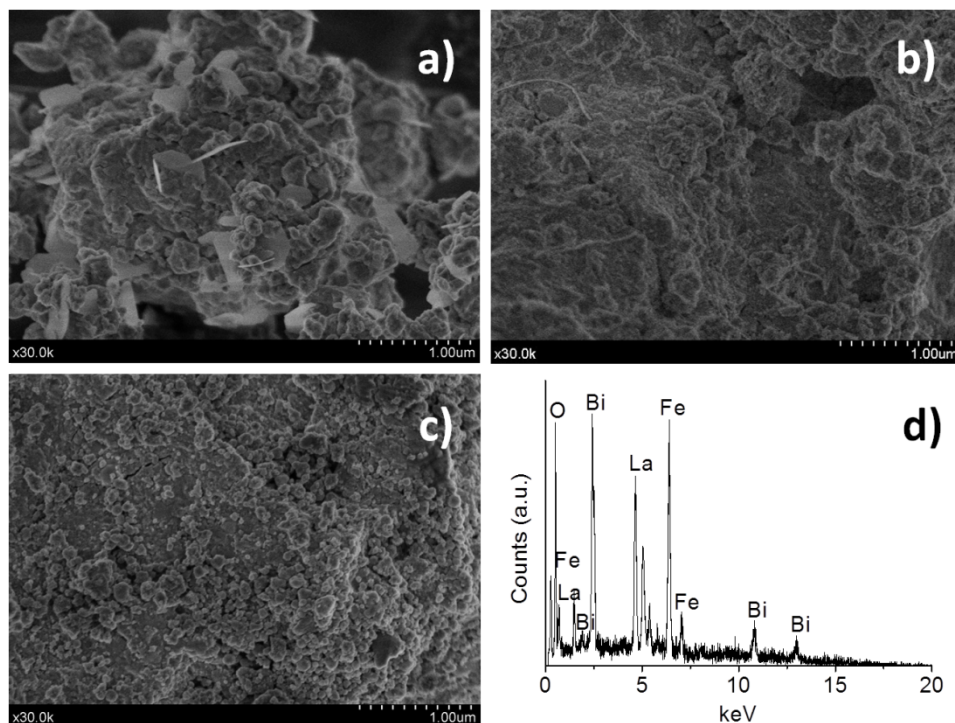


Figure S12. SEM micrographs corresponding to powders obtained after milling the single oxides necessary for the composition $\text{Bi}_{0.40}\text{La}_{0.60}\text{FeO}_3$. Micrographs were taken after milling: (a) 0.5 h, (b) 1 h, (c) 2 h, (d) EDX spectrum of the product shown in (c).

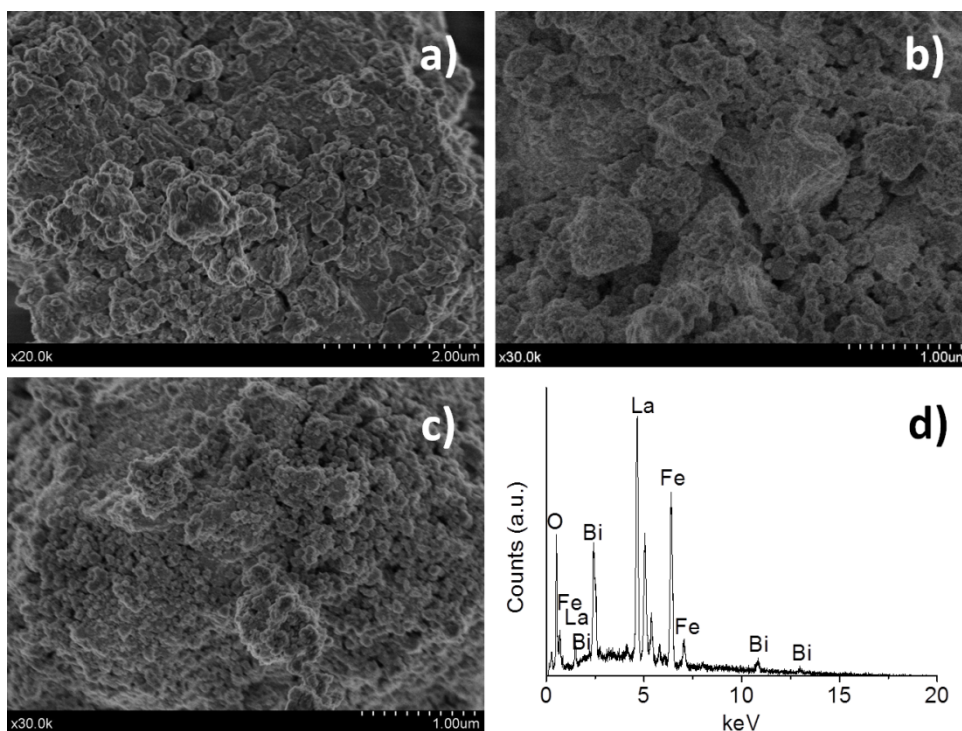


Figure S13. SEM micrographs corresponding to powders obtained after milling the single oxides necessary for the composition $\text{Bi}_{0.20}\text{La}_{0.80}\text{FeO}_3$. Micrographs were taken after milling: (a) 0.25 h, (b) 1 h, (c) 1.5 h, (d) EDX spectrum of the product shown in (c).

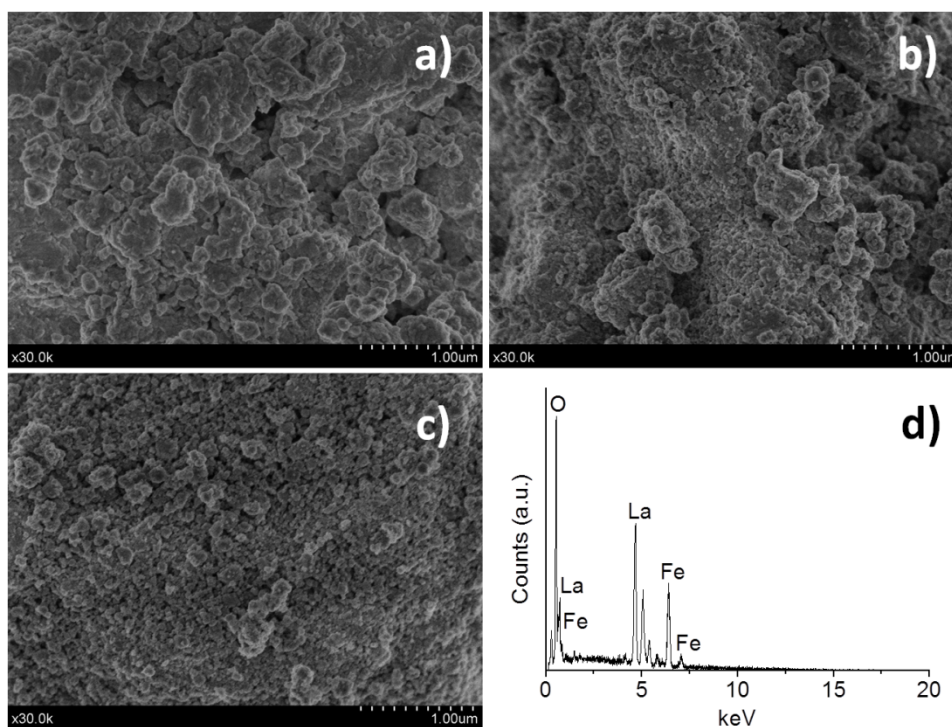


Figure S14. SEM micrographs corresponding to powders obtained after milling the single oxides necessary for the composition LaFeO_3 . Micrographs were taken after milling: (a) 0.5 h, (b) 1 h, (c) 2 h, (d) EDX spectrum of the product shown in (c).

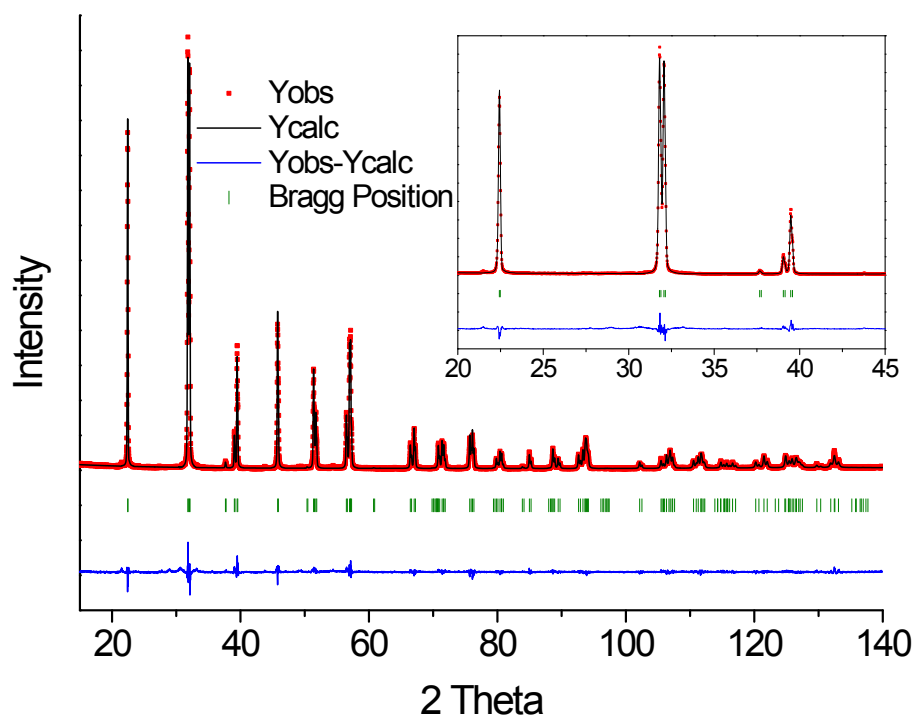


Figure S15. Diffraction pattern corresponding to the sample $\text{Bi}_{0.93}\text{La}_{0.07}\text{FeO}_3$ obtained after milling the single oxides for 3 hours, and heated to 800°C (dots). The solid lines are the results of the Rietveld refinement. The inset shows a detail of the refinement in the range $20\text{--}45^\circ$ where the maxima peaks are observed.

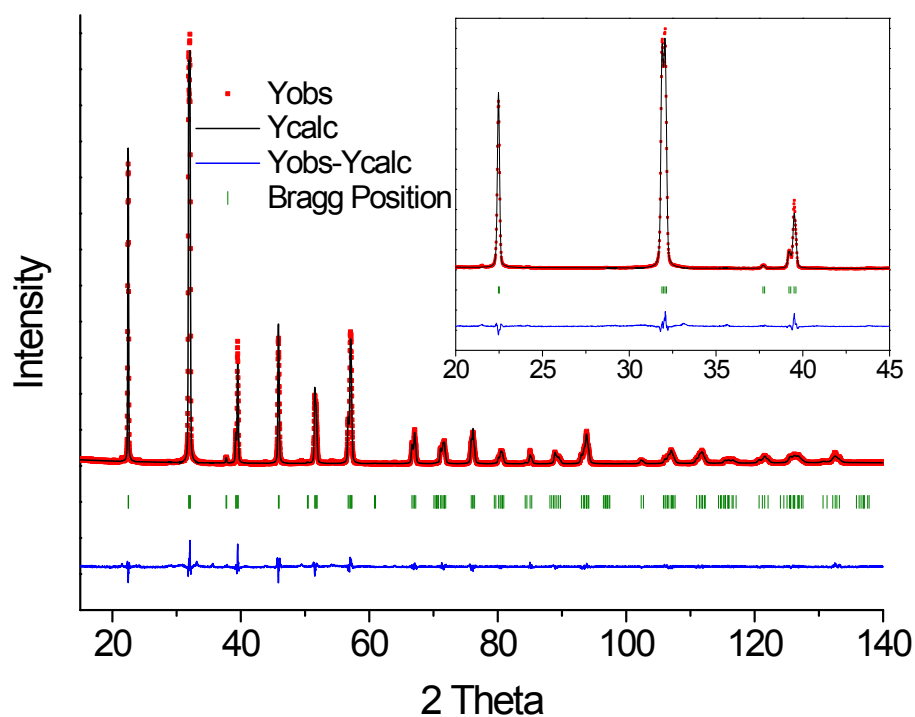


Figure S16. Diffraction pattern corresponding to the sample $\text{Bi}_{0.85}\text{La}_{0.15}\text{FeO}_3$ obtained after milling the single oxides for 3 hours, and heated to 800°C (dots). The solid lines are the results of the Rietveld refinement. The inset shows a detail of the refinement in the range $20\text{--}45^\circ$ where the maxima peaks are observed.

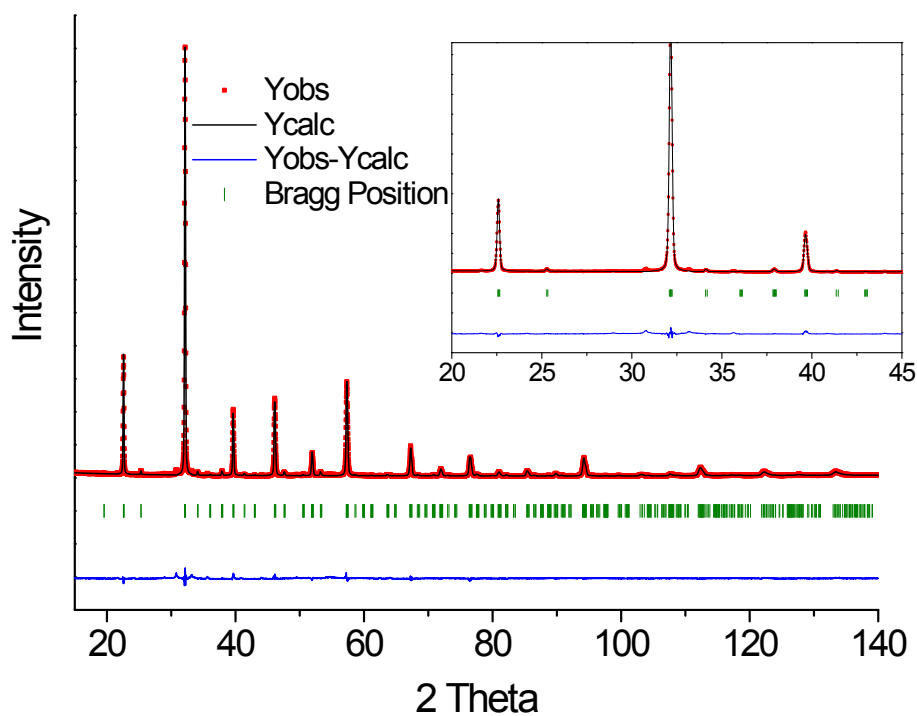


Figure S17. Diffraction pattern corresponding to the sample $\text{Bi}_{0.55}\text{La}_{0.45}\text{FeO}_3$ obtained after milling the single oxides for 2 hours, and heated to 800°C (dots). The solid lines are the results of the Rietveld refinement. The inset shows a detail of the refinement in the range $20-45^\circ$ where the maxima peaks are observed.

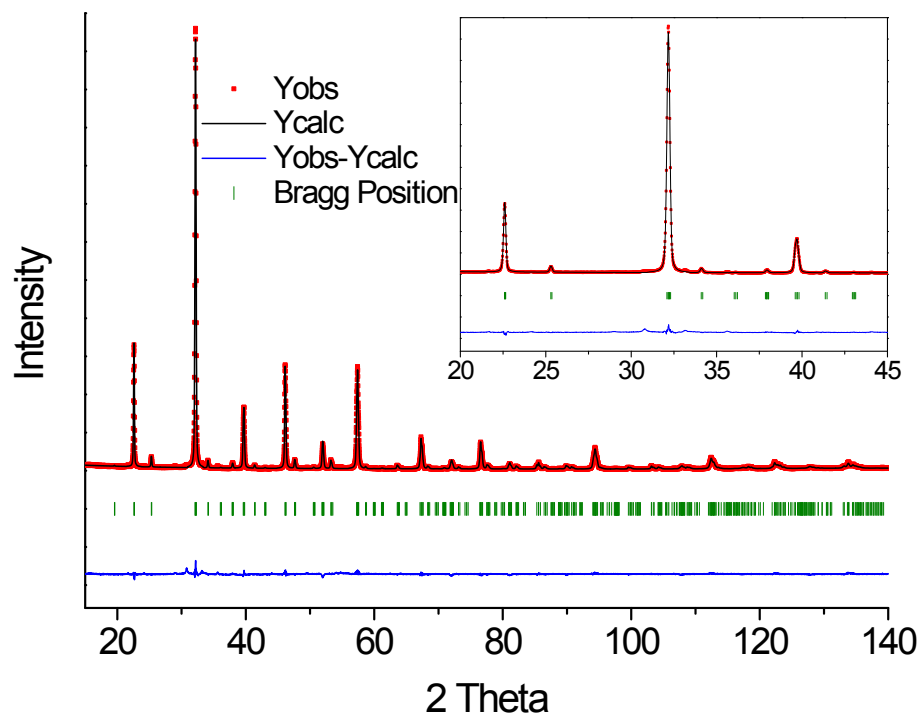


Figure S18. Diffraction pattern corresponding to the sample $\text{Bi}_{0.40}\text{La}_{0.60}\text{FeO}_3$ obtained after milling the single oxides for 2 hours and heated to 800°C (dots). The solid lines are the results of the Rietveld refinement. The inset shows a detail of the refinement in the range $20-45^\circ$ where the maxima peaks are observed.

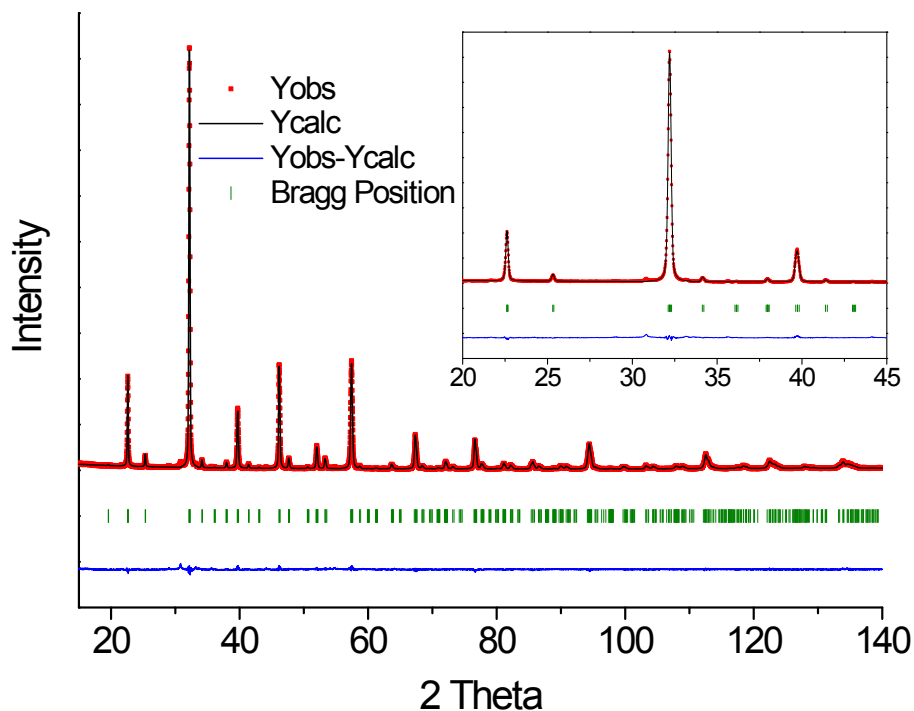


Figure S19. Diffraction pattern corresponding to the sample $\text{Bi}_{0.20}\text{La}_{0.80}\text{FeO}_3$ obtained after milling the single oxides for 2 hours and heated to 800°C (dots). The solid lines are the results of the Rietveld refinement. The inset shows a detail of the refinement in the range $20\text{--}45^\circ$ where the maxima peaks are observed.

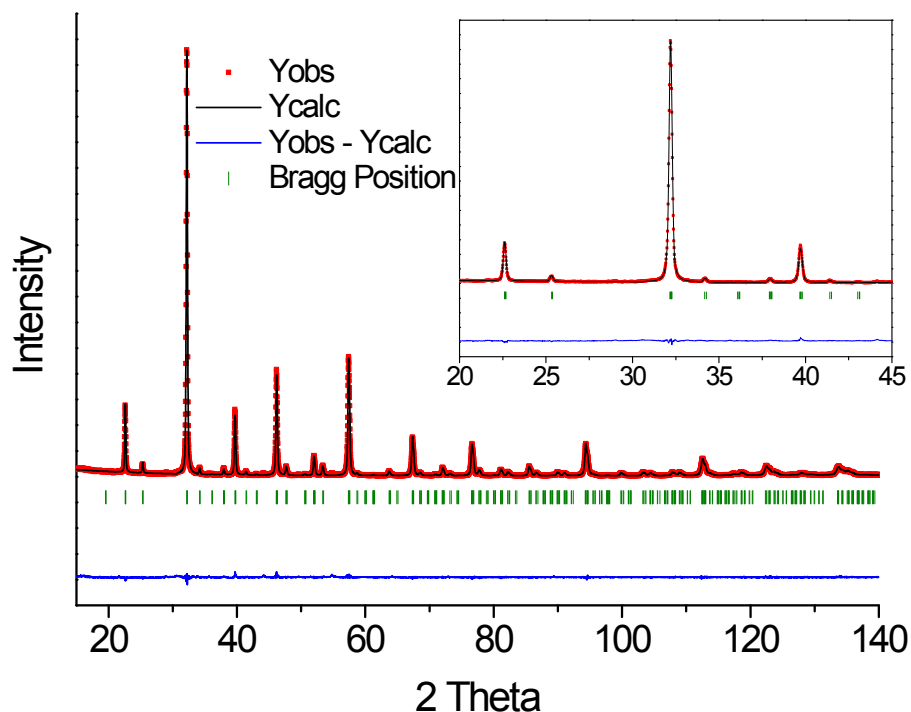


Figure S20. Diffraction pattern corresponding to the sample LaFeO_3 obtained after milling the single oxides for 2 hours and heated to 800°C (dots). The solid lines are the results of the Rietveld refinement. The inset shows a detail of the refinement in the range $20\text{--}45^\circ$ where the maxima peaks are observed.

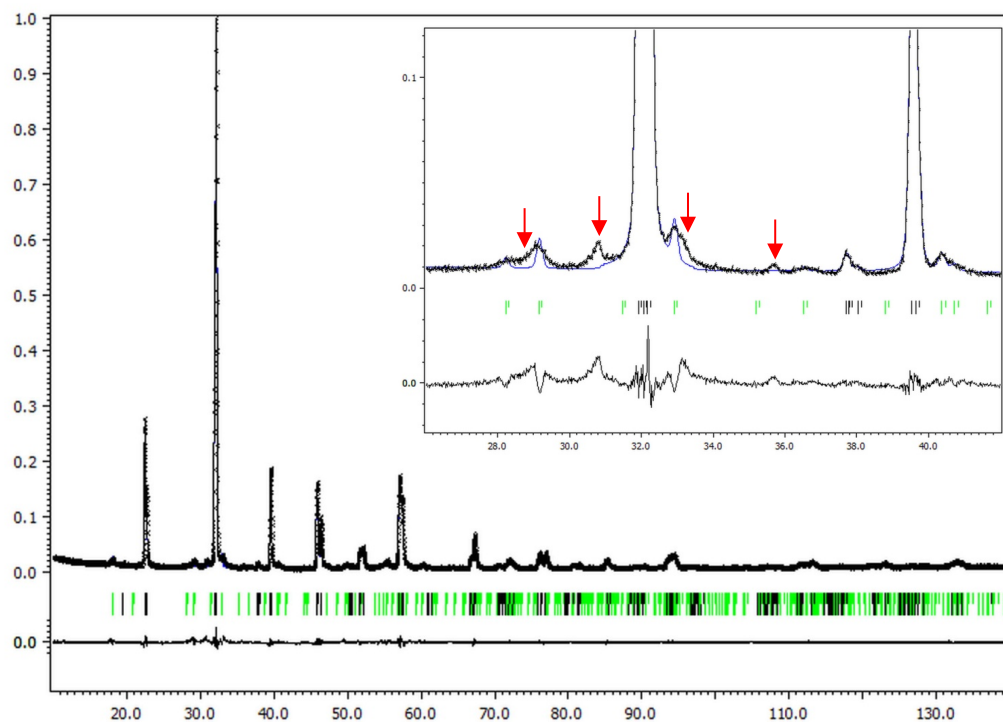


Figure S21. Diffraction pattern corresponding to the sample $\text{Bi}_{0.70}\text{La}_{0.30}\text{FeO}_3$ obtained after milling the single oxides for 2 hours and heated to 800°C (dots). The refinement of the pattern with Jana2006 in LeBail pattern match mode was performed considering the superspace group $\text{Imma}(00\gamma)s00$. The inset shows a detail of the refinement in the range $26\text{--}42^\circ$. The red arrows indicate the satellite peaks not fitted by this super structure.

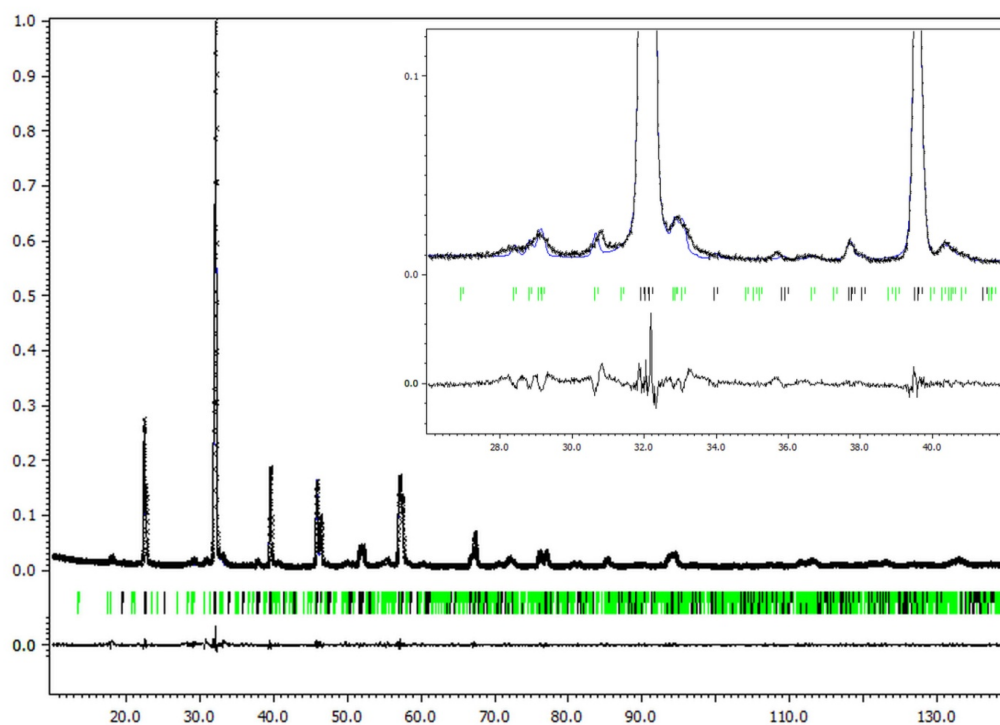


Figure S22. Rietveld refinement of the pattern of the sample $\text{Bi}_{0.70}\text{La}_{0.30}\text{FeO}_3$ with Jana2006 in LeBail pattern match mode considering the superspace group $\text{Pn}2_1\text{a}(00\gamma)\text{s}00$. The inset shows a detail of the refinement in the range $26\text{--}42^\circ$. All satellite peaks are fitted by this super structure.

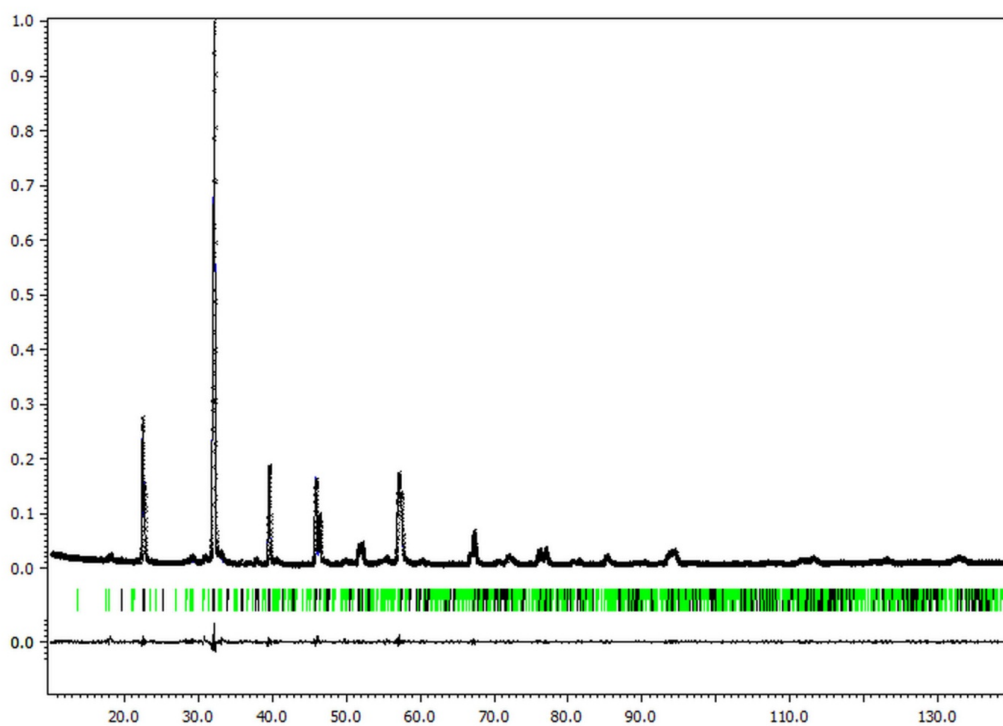


Figure S23. Full Rietveld refinement of the pattern of the sample $\text{Bi}_{0.70}\text{La}_{0.30}\text{FeO}_3$ with Jana2006 considering the superspace group $\text{Pn}2_1\text{a}(00\gamma)\text{s}00$.

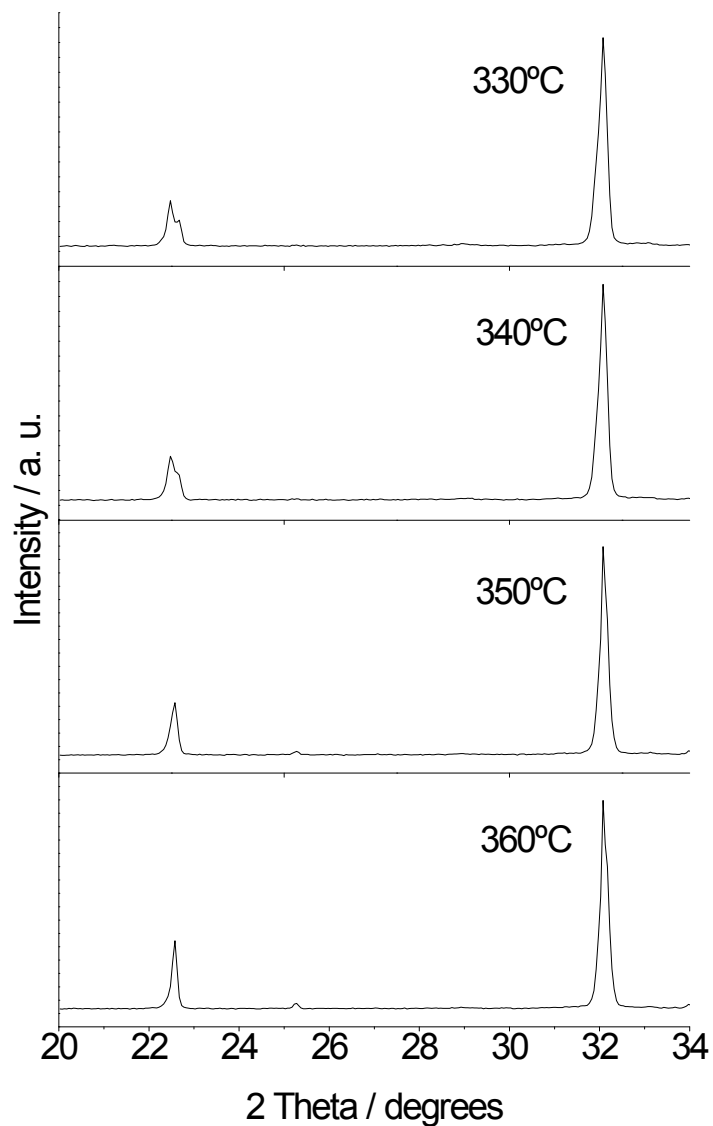


Figure S24. Detail of the XRD patterns measured at different temperatures (between 320°C and 360°C) for $\text{Bi}_{0.70}\text{La}_{0.30}\text{FeO}_3$. From 350°C the double peak at about 22.5° transforms to a single peak and a new peak at 25.3° appears. The new phase can be indexed as Pnma, as was observed for compositions $x \leq 0.15$ above T_C . Other phase transitions at higher temperatures were not observed.

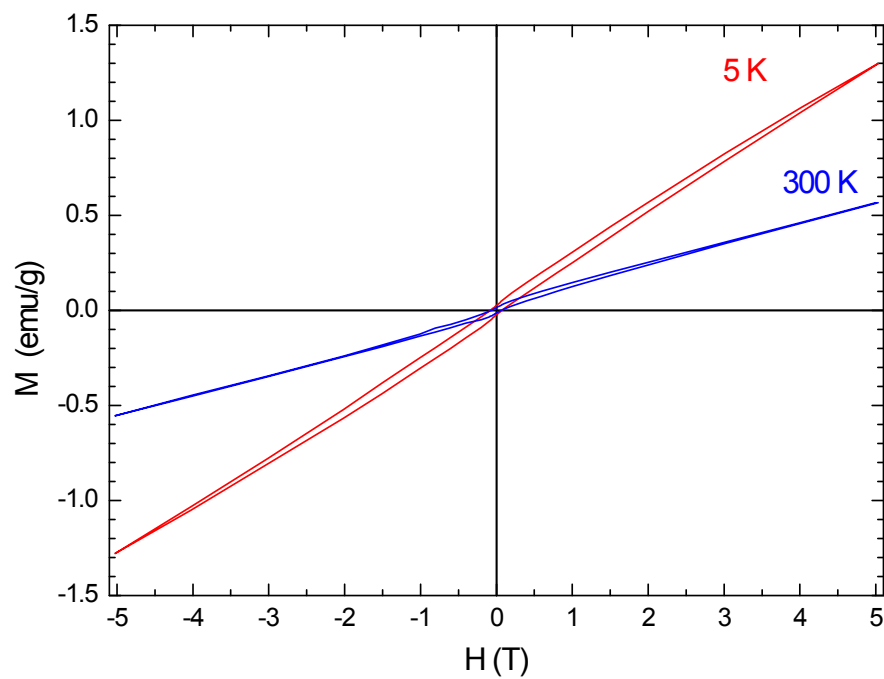


Figure S25. Magnetic field dependence of the magnetization at 5 K and 300 K for BiFeO₃ nanoparticles.

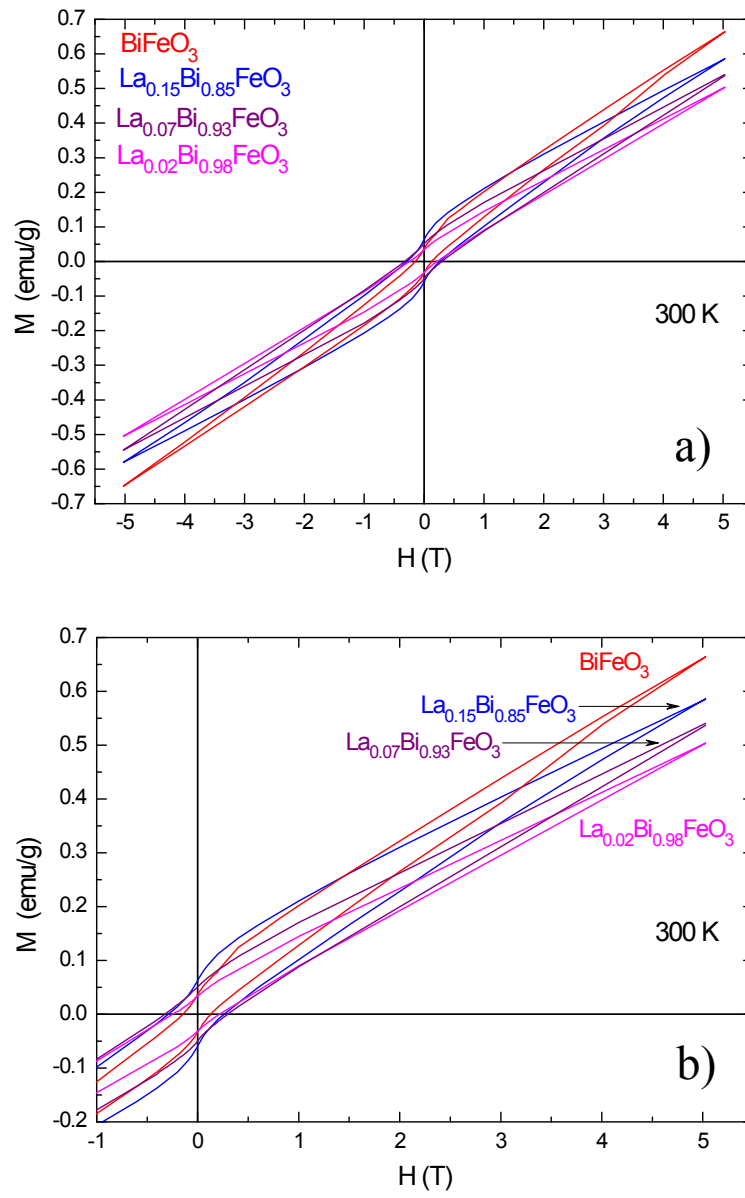


Figure S26. (a) Hysteresis loops obtained at 300 K for $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ samples with $x=0, 0.02, 0.07$ and 0.15 . (b) Zoom of the hysteresis loops.