Supplementary data

Effect of Fe-doping on structure and magnetoelectric properties of (Ba$_{0.85}$Ca$_{0.15}$)(Ti$_{0.9}$Zr$_{0.1}$)O$_3$ synthesized by chemical route

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Rietveld Refinement procedure

The starting atomic parameters for the tetragonal and rhombohedral phases, described in the space group (SG) $P4mm$, and $R3m$, respectively, were taken from Kwei et al.$^1$. In the Rietveld refinements, were refined the following parameters: scale-factors and zero-point; the
background profile was modelled using a 10th order shifted Chebyshev polynomial function; unit cell parameters and profile coefficients – one Gaussian ($G_W$), an angle-independent term and two Lorentzian terms $L_X$ and $L_Y$ – peak correction for asymmetry, and sample displacement effects. Furthermore, atomic positions and isotropic displacement parameters ($U_{iso}$) were also refined; occupancies of Ba and Ca were constrained to be 0.85 and 0.15, respectively, in all the refinements, according to the stoichiometry of the synthesis. Furthermore, the same atomic positions and $U_{iso}$ were given to these two atoms, and restrained to be identical. Similarly, following the stoichiometry of the synthesis, the occupancies of the BO$_6$ octahedral site were constrained to be 0.9 and 0.1 for Ti and Zr in BCTZO sample (restraining their atomic position and $U_{iso}$ to be the same); likewise, in samples were iron was present, the occupancies were also constrained to be the same as those of the synthesis, i.e. 0.88, 0.02, and 0.1 for Ti, Fe, and Zr, respectively, in case of Fe-2 (with Ti, Zr, and Fe having restrained the same atomic positions and $U_{iso}$).

Once the bond lengths and bond angles were calculated from the listing of distances and bond angles from GSAS, they were used to obtain a 3D rendering of the tetragonal phase, by means of the VESTA software package 2. Also, the distortion index ($D$) and quadratic elongation (QE) of the BO$_6$ octahedral site in the tetragonal phase were calculated, according to the formalisms of Baur 3, and Robinson et al. 4, respectively.


