

## Supplemental Materials:

### Negative thermal expansion and the role of hybridization in perovskite-type $\text{PbTiO}_3$ - $\text{Bi}(\text{Cu}_{0.5}\text{Ti}_{0.5})\text{O}_3$

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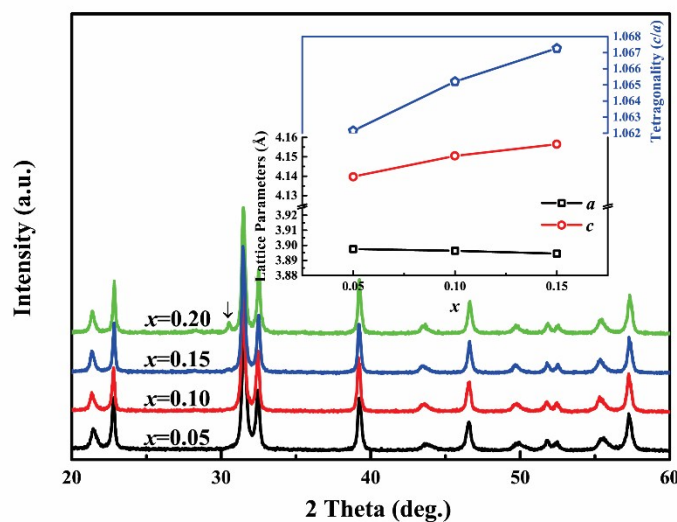


FIG. S1 Lab X-ray diffraction patterns of the  $(1-x)\text{PT}$ - $x\text{BCT}$  powder samples in a selected short range of  $2\theta$ . The inset pattern is the change of lattice parameters and tetragonality ( $c/a$ ) with the variation of  $\text{Bi}(\text{Cu}_{0.5}\text{Ti}_{0.5})\text{O}_3$  content.

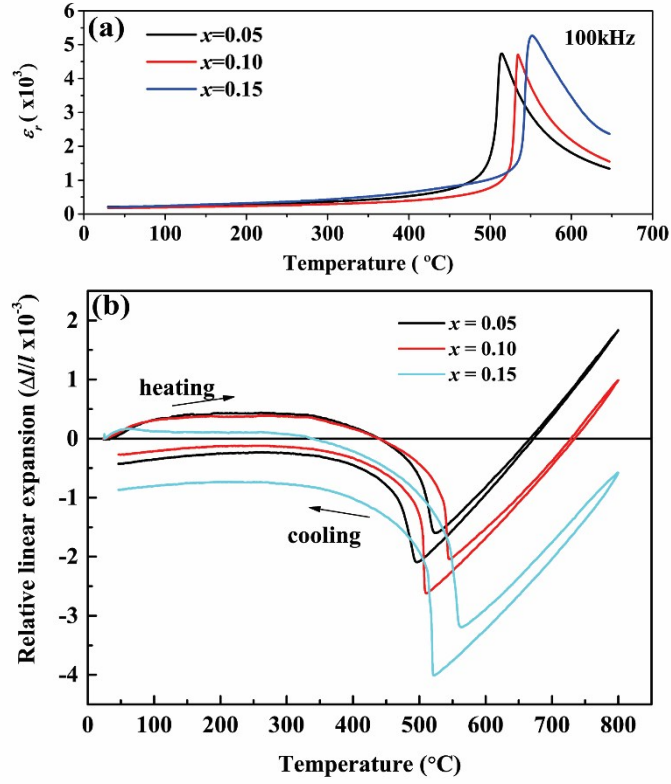


FIG. S2 The temperature dependence of (a) dielectric constant and (b) relative linear expansion of (1-x)PT-xBCT ceramics ( $x = 0.05, 0.1$ , and  $0.15$ ).

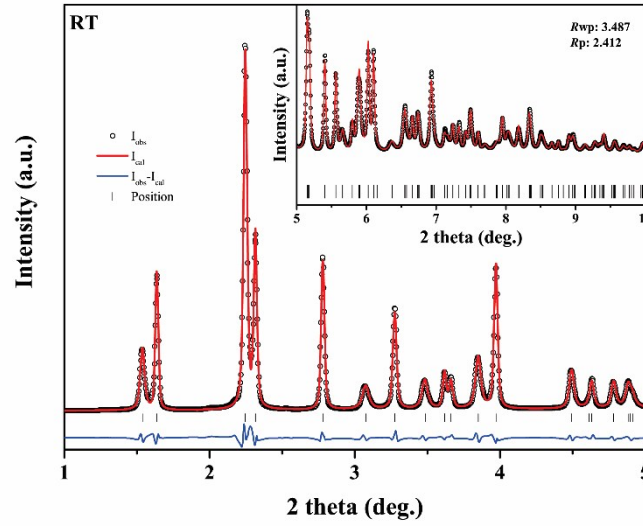


FIG. S3 Rietveld fitting patterns of synchrotron powder diffraction data of tetragonal 0.85PT-0.15BCT at room temperature. Wavelength of synchrotron X-ray was 0.11538  $\text{\AA}$ . The high-angular region is enlarged and shown in the inset.

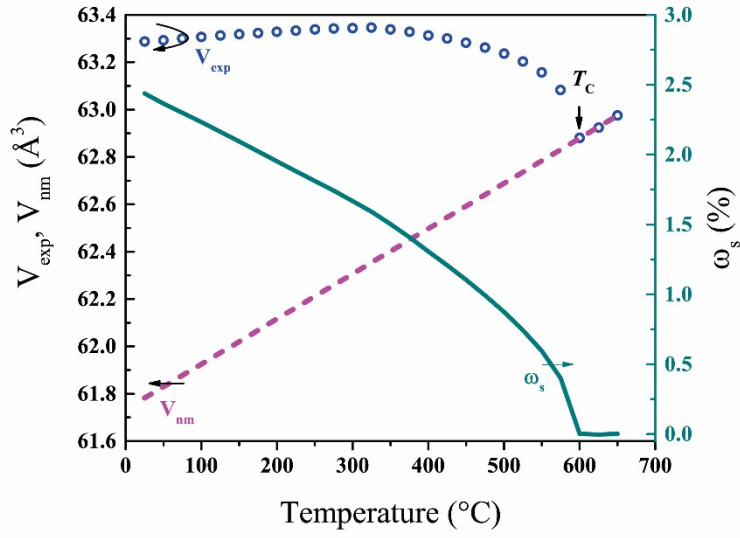


FIG. S4 Temperature dependent  $V_{\text{exp}}$ ,  $V_{\text{nm}}$  and spontaneous volume ferroelectrostriction contribution of tetragonal 0.85PT-0.15BCT to NTE from ferroelectricity,  $\omega_s$ . The  $V_{\text{exp}}$  is the observed unit cell volume and  $V_{\text{nm}}$  is a nominal one calculated by extrapolation from paraelectric to ferroelectric phase,  $\omega_s$  is calculated as  $(V_{\text{exp}} - V_{\text{nm}})/V_{\text{nm}} \times 100\%$ .

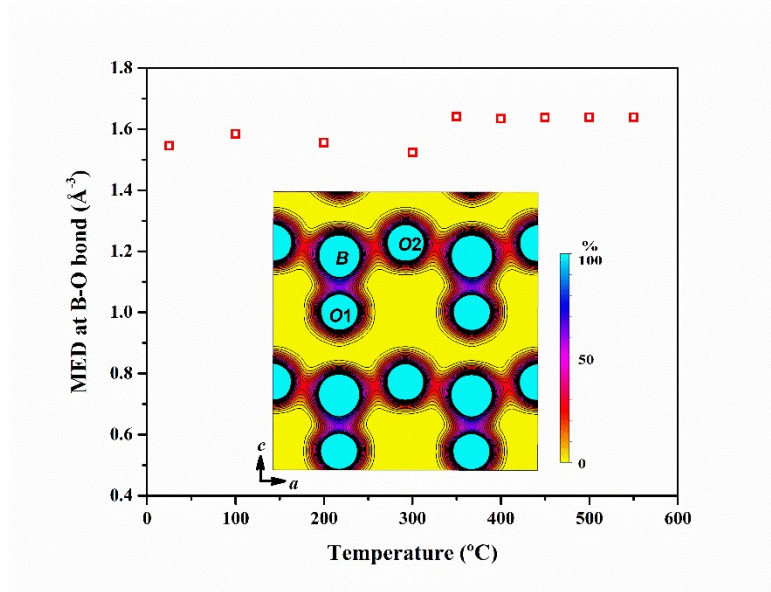


FIG. S5 The evolution of minimum electron density at B-O1(Ti/Cu-O1) bonds as a function of temperature. Electron density distributions on the  $ac$  planes ( $y = 1/2$ ) of tetragonal 0.85PT-0.15BCT from synchrotron data measured at RT is shown in inset. The 0 and 100% in color scale correspond to 0.3 and  $2.3 \text{ \AA}^{-3}$ , respectively, and contours are from  $0.3$  to  $2.3 \text{ \AA}^{-3}$  by  $0.1 \text{ \AA}^{-3}$  step.