**Supplemental Materials:**

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

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**FIG. S1** Lab X-ray diffraction patterns of the (1-x)PT-xBCT powder samples in a selected short range of 2θ. The inset pattern is the change of lattice parameters and tetragonality (c/a) with the variation of Bi(Cu$_{0.5}$Ti$_{0.5}$)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 Å. 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 Å$^{-3}$, respectively, and contours are from 0.3 to 2.3 Å$^{-3}$ by 0.1 Å$^{-3}$ step.