Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Evidence to the enhanced negative thermal expansion in $(1-x)PbTiO_3$-$xBi(Zn_{2/3}Ta_{1/3})O_3$

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1. **Experimental section**

A series of (1-*x*)$PbTiO_3$-*x*Bi($Zn_{2/3}Ta_{1/3}$)O_3 (*x* = 0~0.2) ceramics were synthetized by solid state reaction method. The analytic reagent grade raw materials, PbO, TiO_2, Bi_2O_3, ZnO, Ta_2O_5, were treated to evaporate water before weighed at stoichiometric ratio. After ball-milled the mixture with ethanol for 24h. dried powders were put into alumina crucible and calcining at 800^oC for 5h. Then add suitable binder and grind the calcined powders fully. The product was pressed into plate by tablet machine. Sintered the plate at 550^oC for 2h to get rid of the binder, then treated it at 1100^oC for 2h to obtain hard ceramics. Cover the plate with powders before sintered to avoid volatilization during reaction. To release the mechanical strain during the sintering and grinding procedures, the pellets were sintered again at 600^oC for 2h finally.

The crystal structure and properties of thermal expansion were investigated by the X-ray diffraction (XRD) technique on a diffractometer (model X'pert PRO, PANalytical, Netherlands). To get precise X-ray diffraction peaks, silicon standard was used to rectify the system and sample error. To achieve accurate data of diffraction, synchrotron XRD patterns of the powder were collected at the beamline BL44B2 in Japan Spring-8. The Raman spectroscopy were obtained at high-precision modular tertiary Raman spectrometer (JYT64000). Structure refinement were adopted to Rietveld full spectrum fitting by software of FullProf. Charge dentist were calculated by VASP using the method of first principle calculate.

First principle calculation was performed based on density functional using VASP package. Exchange correlation function adopt Generalized Gradient Approximation (GGA), and exchange correlation potential adopt PBE pseudo potential method. The calculating parameters were optimized at the beginning. The plane-wave energy cutoff were selected at 500eV. The integrations of the Brillouin-zone use the method of Monkhorst-Pack special k point sampling, 4×4×4 k-point mesh were applied for Brillouin-zone integrations. To get the proper proportions approach the practical situation, 3×3×3 supercell were established. The theoretical model $Pb_{24}Ti_{24}O_{72}$-$Bi_3Zn_2Ta_1O_9$ is pretty close to the actual model $0.9PbTiO_3$-$0.1Bi(Zn_{2/3}Ta_{1/3})O_3$, which exhibit the feature of enhanced negative thermal expansion. Structural optimization was carried out for the theoretical model, and then got the structure and electron density. Also, the related calculation of $PbTiO_3$ is treated in the same way.

2. **Results and discussion**

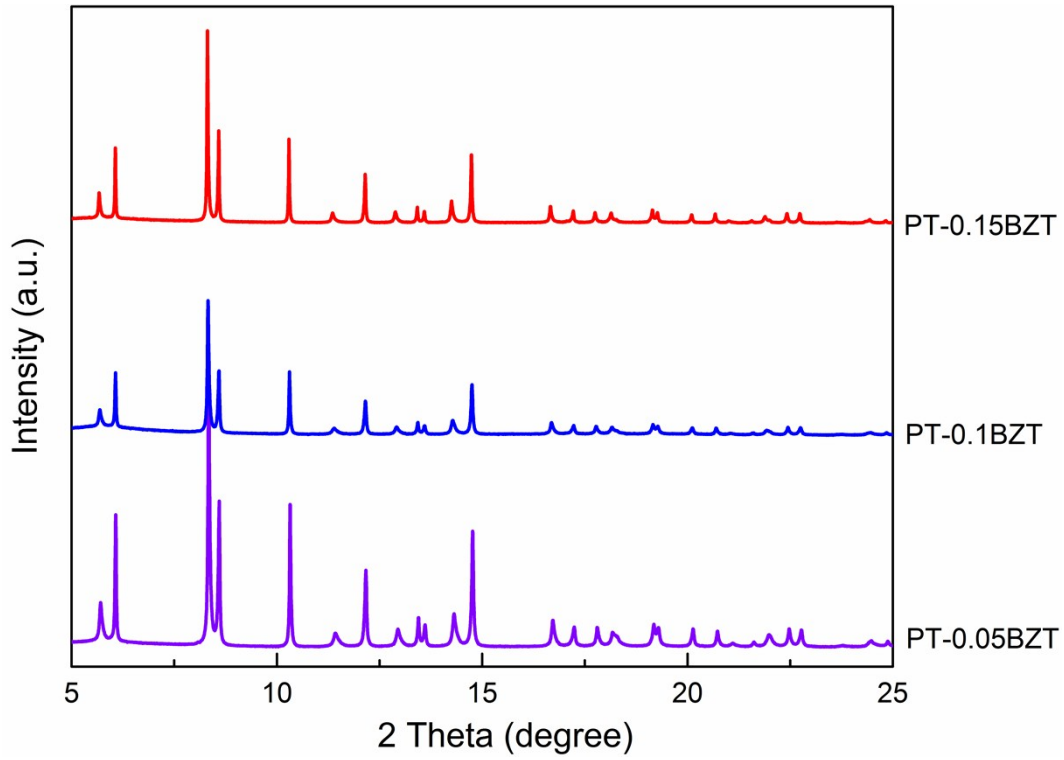

Figure S1 The synchrotron XRD patterns of (1-*x*)$PbTiO_3$- *x*$Bi(Zn_{2/3}Ta_{1/3})O_3$ (*x* = 0~0.2) at room temperature.

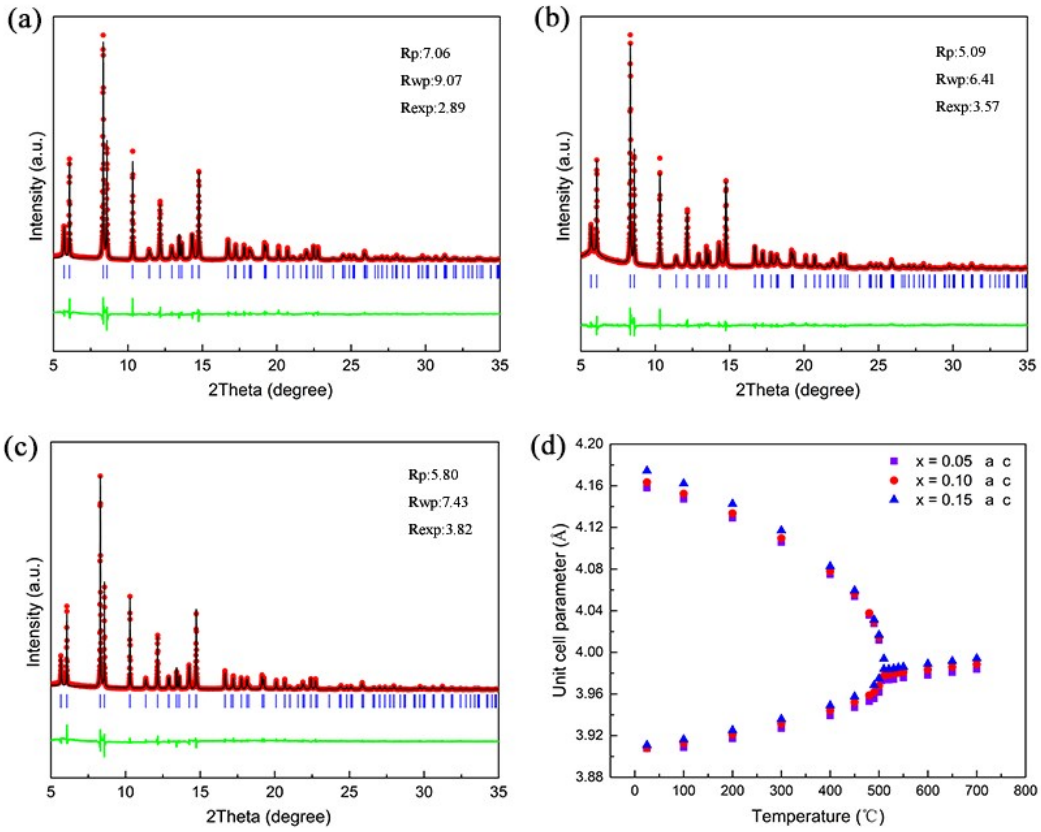

Figure S2 Rietveld refinement of the synchrotron XRD patterns of (1-*x*)$PbTiO_3$-*x*$Bi(Zn_{2/3}Ta_{1/3})O_3$ ((a): $x = 0.05$; (b): $x = 0.10$; (c): $x = 0.15$) at room temperature. (d) Temperature dependence of *a, c* axis with different contents of $Bi(Zn_{2/3}Ta_{1/3})O_3$.

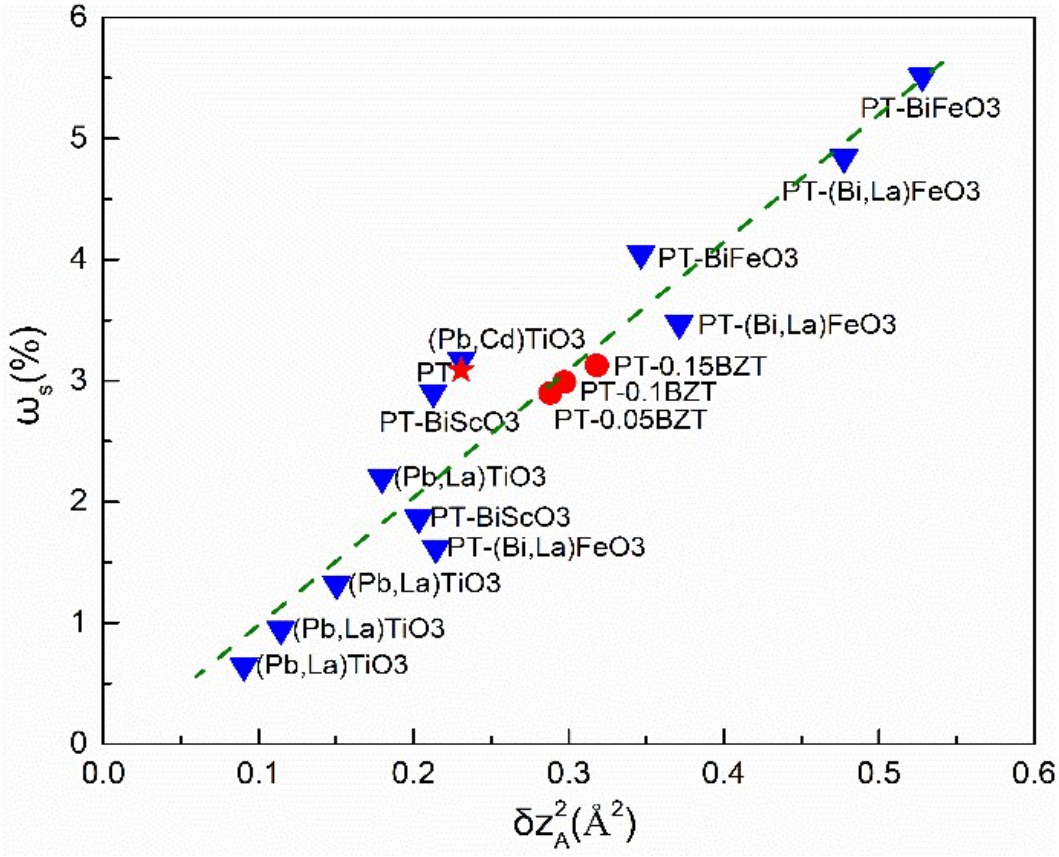

Figure S3 The correlation between the spontaneous volume ferroelectrostriction (ω_s) and square of P_S displacement (δz_A^2) for PT-based tetragonal NTE ferroelectrics according to SVFS throry.[1]

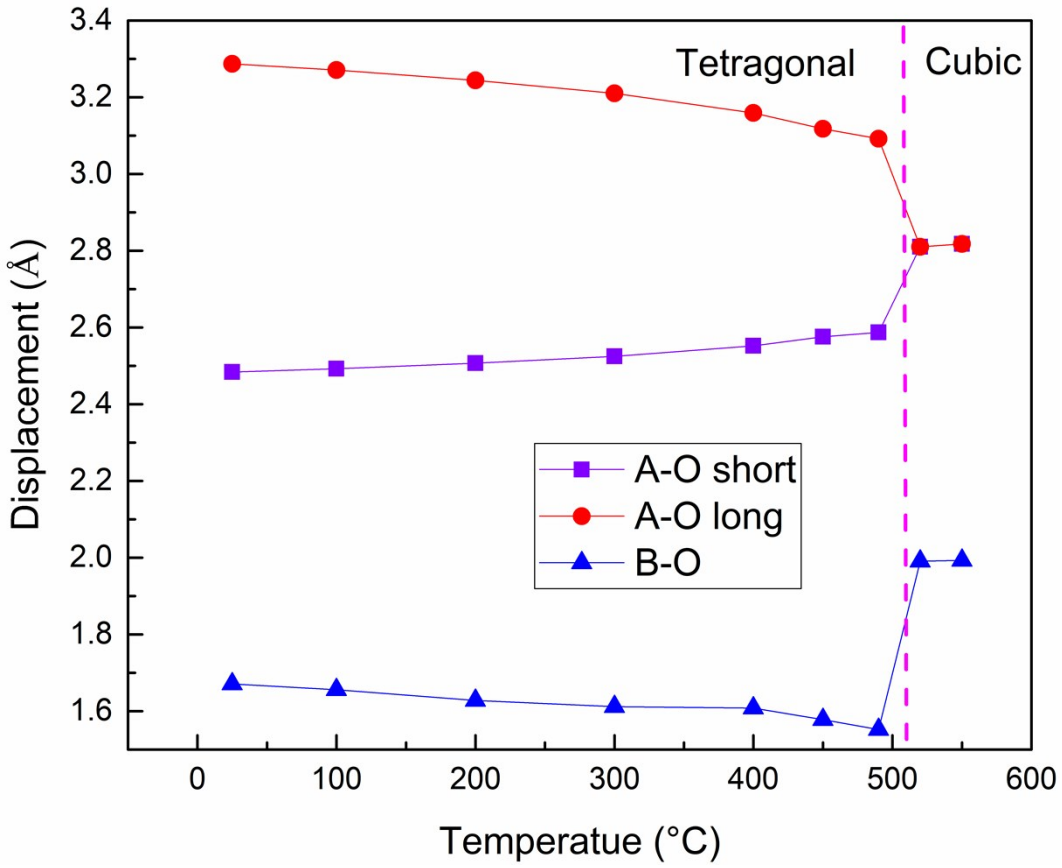

Figure S4 The temperature dependent of the displacement of A-site to O2 short, A-site to O2 long and B-site to O1 in $0.85PbTiO_3$-$0.15Bi(Zn_{2/3}Ta_{1/3})O_3$. Because of charge disproportionation existed, the bong length changes with the increasing of temperature.

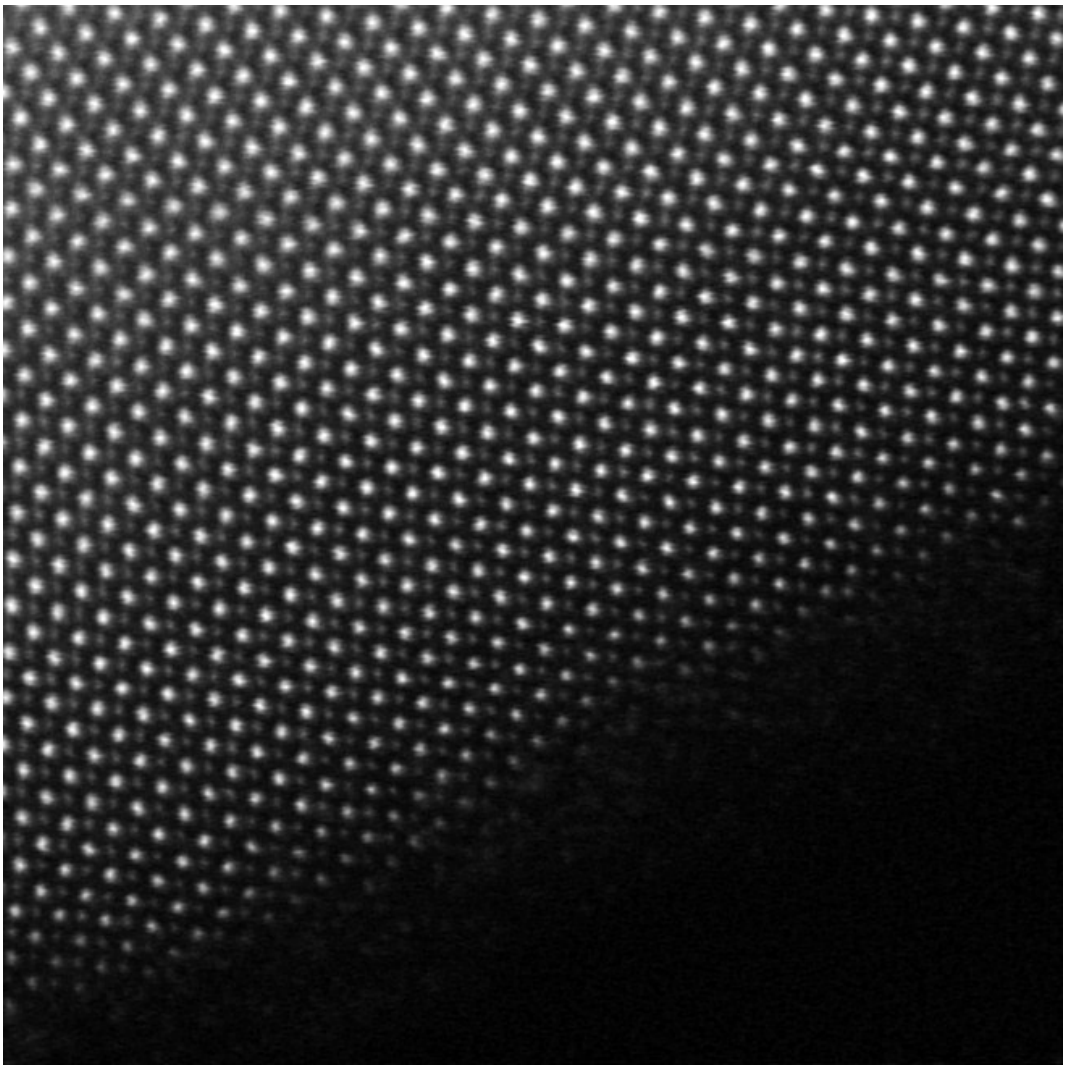

Figure S5 The STEM image of $0.85PbTiO_3$-$0.15Bi(Zn_{2/3}Ta_{1/3})O_3$.

1. J. Chen, L. Hu, J. Deng, X. Xing, Negative Thermal Expansion in Functional Materials: Controllable Thermal Expansion by Chemical Modifications, *Chem. Soc. Rev.,* 2015, **44**, 3522-3567.