Supporting Information

Semi-empirical Estimation for Enhancing Negative Thermal Expansion in $PbTiO_3$-Based Perovskites

1. Methods

A series of $0.6PbTiO_3$–$0.4Bi(Ga_xFe_{1-x})O_3$ (x = 0–0.1) ceramics were synthetized by solid state reaction method. The analytic reagent grade raw materials, PbO, TiO_2, Bi_2O_3, Ga_2O_3, Fe_2O_3, were heated to dehydrate and then weighed at stoichiometric ratio. After ball-milling the mixture with ethanol for 24h, the dry powder was put into alumina crucible and calcined at 800°C for 5h. Then suitable binder was added to the calcined powder and fully grinded. The powder was pressed into plate by tablet machine. The plates were treated at 550°C for 2h to get rid of the binder and then sintered at 1050–1150°C for 2h. To avoid volatilization during reaction, the same composition powder needs to be covered on the plate. Finally, the pellets were sintered again at 600°C for 2h to release the mechanical strain.

The crystal structure and the thermal expansion behaviors 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. Structure refinement was adopted to Rietveld full spectrum fitting by FullProf. Experimental electron density distribution was obtained by the Rietveld refinement combined with MEM methods using RIETAN-FP and Dysnomia programs.

2. Calculating of average lattice distortion (k)

Figure S1 shows the change of volume at high and low temperatures. The blue rectangle represents cell parameters *a* and *c* on the ac plane of $PbTiO_3$-based compound at Room Temperature (T_R), while the red square presents isotropic cell parameters at Curie Temperature (T_C). When the temperature increases from T_R to T_C, the cell parameter of a changes from a to $a+\Delta a$. According to the calculation formula of thermal expansion coefficient:

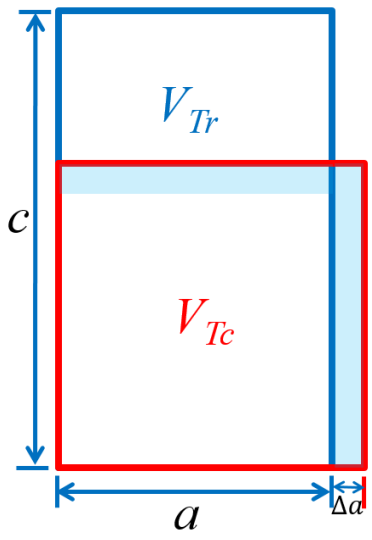
$$\alpha_V = \frac{\Delta V}{V \times \Delta T}$$

$$\alpha_V = \frac{(a+\Delta a)^3 - a^2 \times c}{(a^2 \times c) \times (T_C - T_R)}$$

We can get:

$$\alpha_V = \frac{(\frac{a}{c} + 3\frac{\Delta a}{c} + 3\frac{\Delta a^2}{a \times c} + \frac{\Delta a^3}{a^2 \times c}) - 1}{(T_c - T_R)}$$

T_C and T_R denote the Curie temperature and room temperature of the compound, respectively.



S2

Figure S1 Schematic diagram of ac plane of $PbTiO_3$-based compounds at room temperature and Curie temperature

According to the experimental results of $PbTiO_3$, in the process of changing from room temperature to Curie temperature, the change amount Δa of axis a is 0.067 Å, which is much smaller than the cell parameter a (3.90 Å) and c (4.15 Å) in $PbTiO_3$. As for higher order terms $\frac{\Delta a^2}{a \times c}$ and $\frac{\Delta a^3}{a^2 \times c}$, their omission made little difference to the result. Thus, when omit $3\frac{\Delta a}{c}$, $\frac{\Delta a^2}{a \times c}$ and $\frac{\Delta a^3}{a^2 \times c}$, we can get the simplified equation of

$$k = \frac{\frac{a}{c} - 1}{T_C - T_R}$$

Which is the definition of average lattice distortion (k).

3. Results and discussion

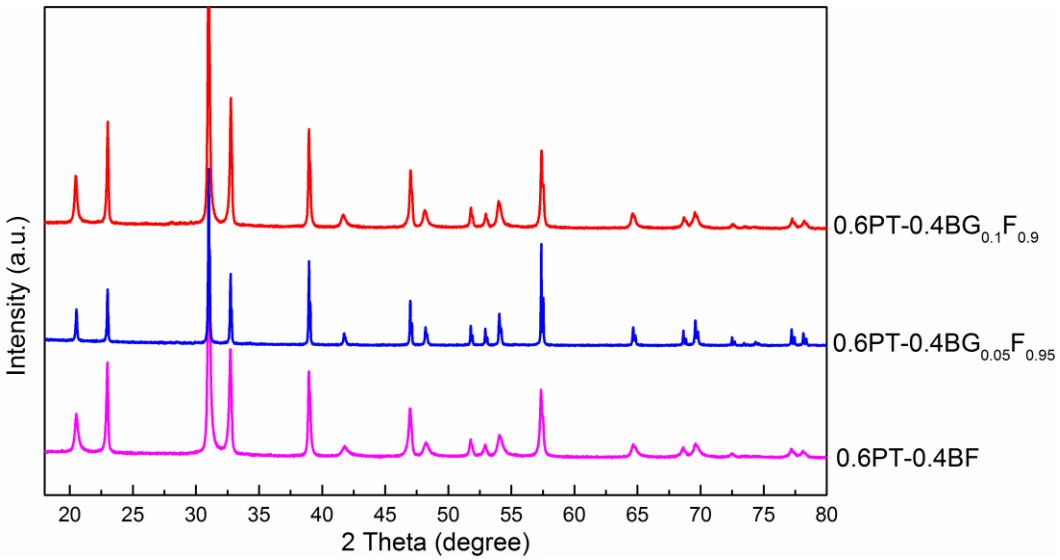


Figure S2 XRD patterns of $0.6PbTiO_3$–$0.4Bi(Ga_xFe_{1-x})O_3$ (x = 0–0.1) at room temperature.

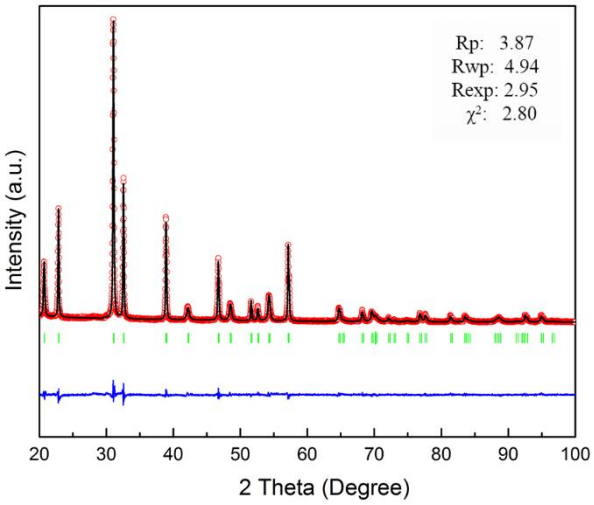


Figure S3 Rietveld refinement of XRD patterns of $0.6PbTiO_3–0.4Bi(Zn_{1/2}Ti_{1/2})O_3$

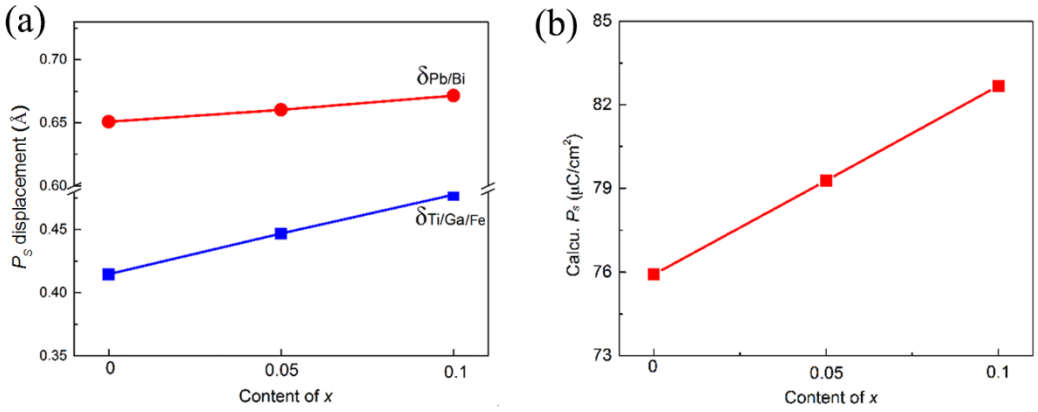


Figure S4 (a) P_S displacement at A-site ($\delta z_{Pb/Bi}$) and *B*-site ($\delta z_{Ti/Ga/Fe}$), (b) P_S $0.6PbTiO_3–0.4Bi(Ga_xFe_{1-x})O_3$ (x = 0–0.1), determined by structure refinement.

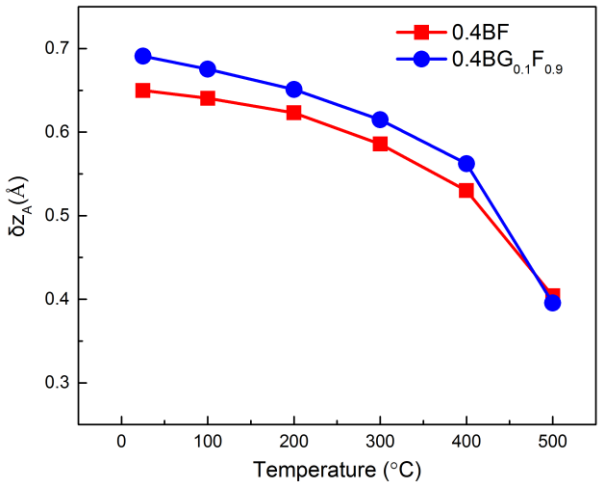


Figure S5 Temperature dependence of $\delta z_{Pb/Bi}$ with $0.6PbTiO_3–0.4Bi(Ga_xFe_{1-x})O_3$

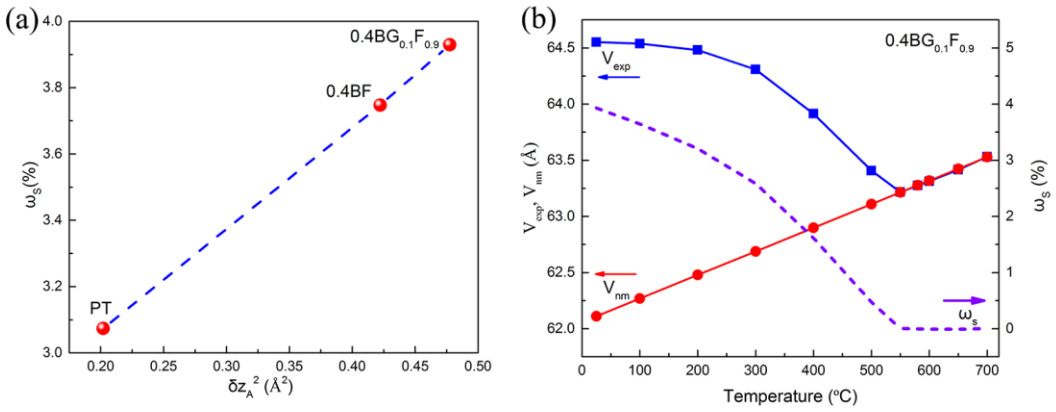


Figure S6 (a) Correlation between the SVFS (ω_s) and the square of the P_S displacement $\delta z_{Pb/Bi}^2$, (b) Temperature dependence of ω_s in the system of $0.6PbTiO_3–0.4Bi(Ga_{0.1}Fe_{0.9})O_3$