Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Large spontaneous polarization in polar perovskite of $PbTiO_3$-$Bi(Zn_{1/2}Ti_{1/2})O_3$

Zhao Pan[1,2,3], Xingxing Jiang[4], Jun Chen[2,*)], Lei Hu[2], Hajime Yamamoto[3], Linxing Zhang[2], Longlong Fan[2], Xi'an Fan[1], Yawei Li[1], Guangqiang Li[1], Yang Ren[5], Zheshuai Lin[4], Masaki Azuma[3] and Xianran Xing[2]

[1]*State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China*

[2]*Department of Physical Chemistry, University of Science and Technology Beijing, Beijing 100083, China*

[3]*Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama, 226-8503, Japan*

[4]*Center for Crystal R&D, Key Laboratory of Functional Crystals and Laser Technology, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

[5]*X-Ray Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States*

[*)]Author to whom correspondence should be addressed. Electronic mail: junchen@ustb.edu.cn.

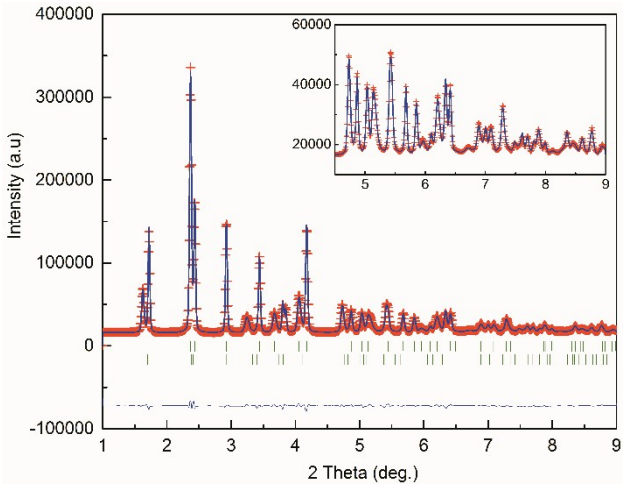

Figure S1. Rietveld full profile refinement of SXRD patterns of tetragonal $0.9PbTiO_3$-$0.1Bi(Zn_{0.5}Ti_{0.5})O_3$ at room temperature. Observed (red, +), calculated (blue line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks. For structural refinement of $PbTiO_3$-based ferroelectrics, it cannot ignore the profile broadening and asymmetry induced by the large lattice distortion. In order to achieve a high quality fit of the SXRD data, a two-phase Rietveld refinement has been used in present large tetragonal $(1-x)PbTiO_3$-$xBi(Zn_{0.5}Ti_{0.5})O_3$ system, where the majority or bulk phase is a perovskite with a large *c*/*a* ratio and a minority phase is a perovskite with a smaller *c*/*a*. In order to make the structural refinement stable and reliable, the coordinates of atoms for the minor tetragonal phase are assumed to be the same as those of the major tetragonal one. If the atomic coordinates of minor tetragonal phase are refined independently, the refined values will be fluctuated and unreasonable. In present system, the two-phase model gives a much better fitting result than the single tetragonal phase one. The *c*/*a* ratios in Figure 1(b) were derived from the majority phase of the two-phase refinement results. The present adopted two-phase model has also been successfully utilized in parent $PbTiO_3$ and nano-$BaTiO_3$ materials (*Phys. Rev. Lett.*, 2007, 98: 107601; *J. Phys. Soc. Jpn.*, 2002, 71: 1218).

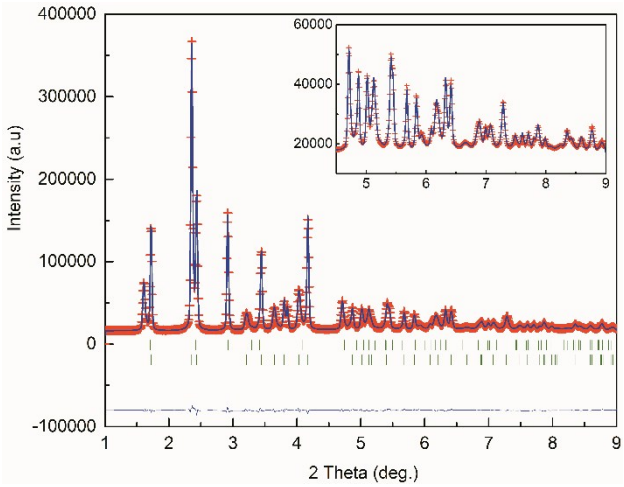

Figure S2. Rietveld full profile refinement of SXRD patterns of tetragonal $0.8PbTiO_3$-$0.2Bi(Zn_{0.5}Ti_{0.5})O_3$ at room temperature. Observed (red, +), calculated (blue line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

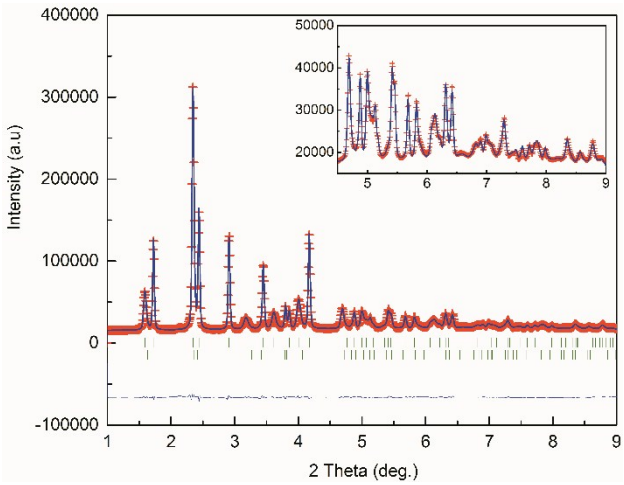

Figure S3. Rietveld full profile refinement of SXRD patterns of tetragonal $0.7PbTiO_3$-$0.3Bi(Zn_{0.5}Ti_{0.5})O_3$ at room temperature. Observed (red, +), calculated (blue line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

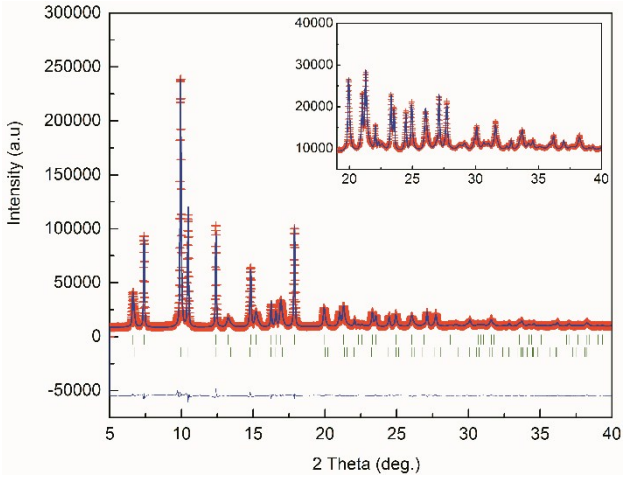

Figure S4. Rietveld full profile refinement of SXRD patterns of tetragonal $0.6PbTiO_3$-$0.4Bi(Zn_{0.5}Ti_{0.5})O_3$ at room temperature. Observed (red, +), calculated (blue line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

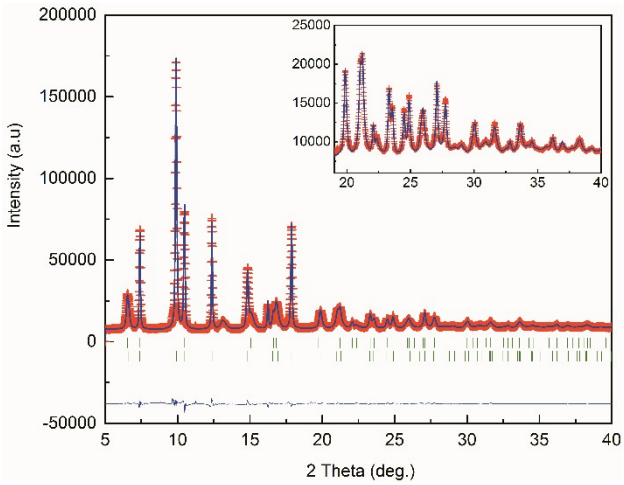

Figure S5. Rietveld full profile refinement of SXRD patterns of tetragonal $0.5PbTiO_3$-$0.5Bi(Zn_{0.5}Ti_{0.5})O_3$ at room temperature. Observed (red, +), calculated (blue line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

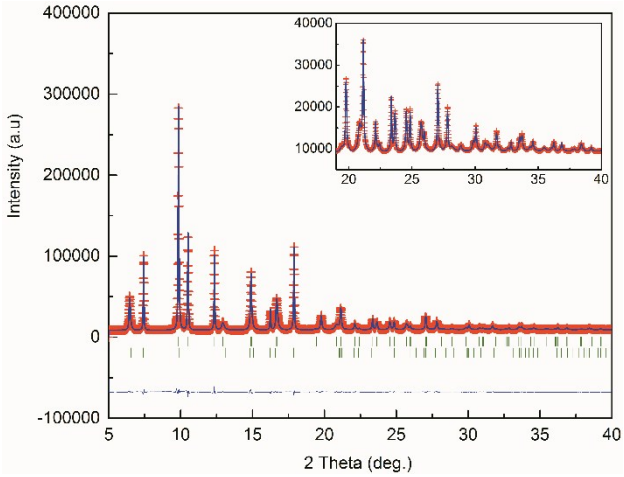

Figure S6. Rietveld full profile refinement of SXRD patterns of tetragonal $0.4PbTiO_3$-$0.6Bi(Zn_{0.5}Ti_{0.5})O_3$ at room temperature. Observed (red, +), calculated (blue line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

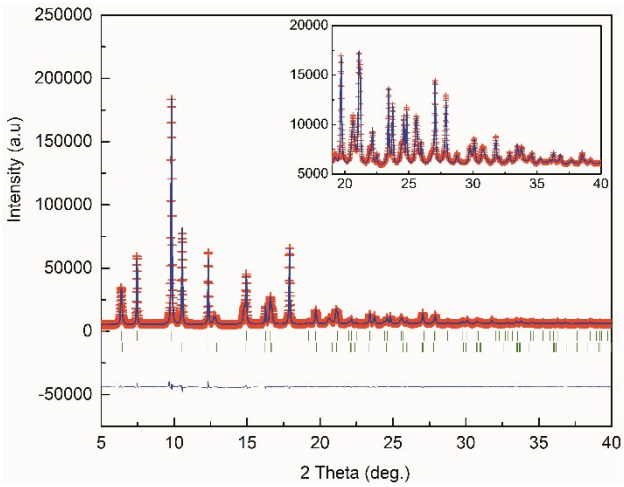

Figure S7. Rietveld full profile refinement of SXRD patterns of tetragonal $0.3PbTiO_3$-$0.7Bi(Zn_{0.5}Ti_{0.5})O_3$ at room temperature. Observed (red, +), calculated (blue line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

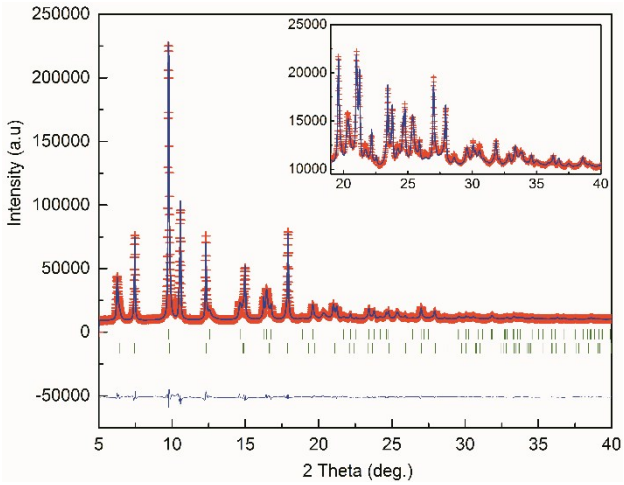

Figure S8. Rietveld full profile refinement of SXRD patterns of tetragonal $0.2PbTiO_3$-$0.8Bi(Zn_{0.5}Ti_{0.5})O_3$ at room temperature. Observed (red, +), calculated (blue line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

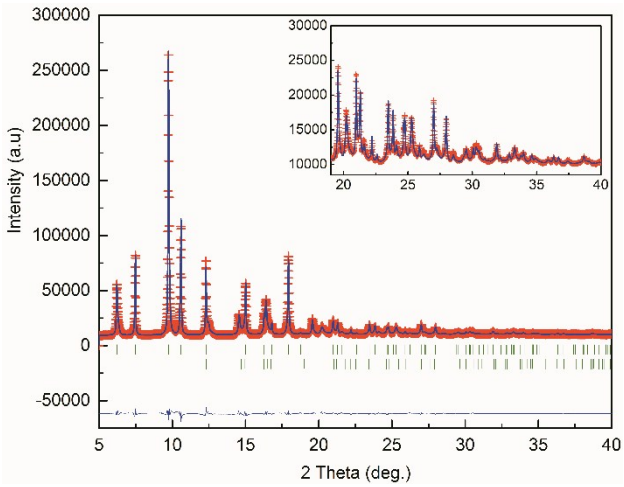

Figure S9. Rietveld full profile refinement of SXRD patterns of tetragonal $0.1PbTiO_3$-$0.9Bi(Zn_{0.5}Ti_{0.5})O_3$ at room temperature. Observed (red, +), calculated (blue line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

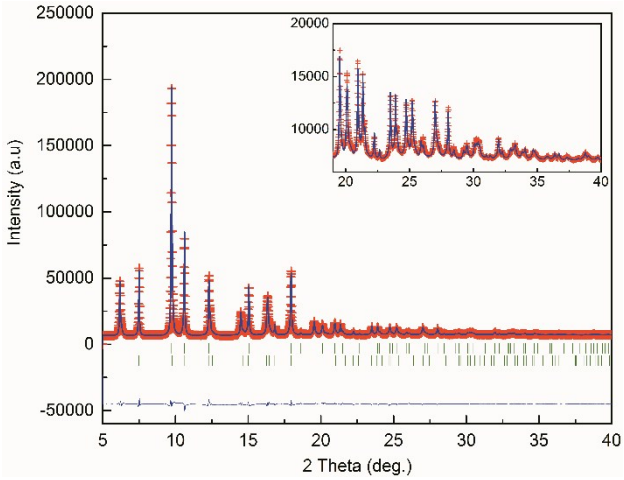

Figure S10. Rietveld full profile refinement of SXRD patterns of tetragonal $Bi(Zn_{0.5}Ti_{0.5})O_3$ at room temperature. Observed (red, +), calculated (blue line), and their difference profiles (bottom line) are shown. The Bragg reflection positions are indicated by the green ticks.

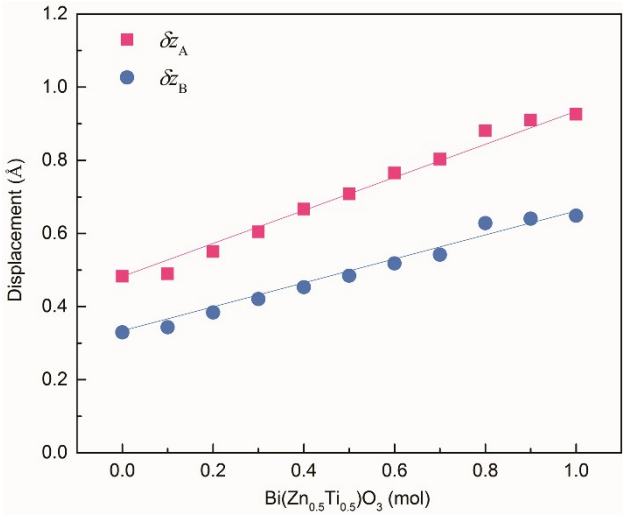

Figure S11. P_S displacement of δz_A and δz_B of (1-x)$PbTiO_3$-$x$$Bi(Zn_{0.5}Ti_{0.5})O_3$ as a function of x.