SUPPORTING INFORMATION FOR

Anomalous dispersion X-ray diffraction study of Pb/Bi ordering/disordering states in $PbTiO_3$-based perovskite oxides

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Calculation details:

Binding energy was calculated for structures in the 2 × 2 × 2 cells of different Pb/Bi positions, based on density functional theory within the Perdew-Burke-Ernzerhof approximation, [1] as implemented in the Vienna *ab-initio* simulation package.[2] Interactions between ion cores and valence electrons are described by the projector augmented wave method.[3] Plane waves with a kinetic energy cutoff of 400 eV are used as the basis set. Integration over the Brillouin zone is done with the Monkhorst-Pack scheme[4] of 5 × 5 × 5 grid points. All of the structures are fully relaxed until the maximum residual ionic force is below 0.01 eV/ Å.

Figures:

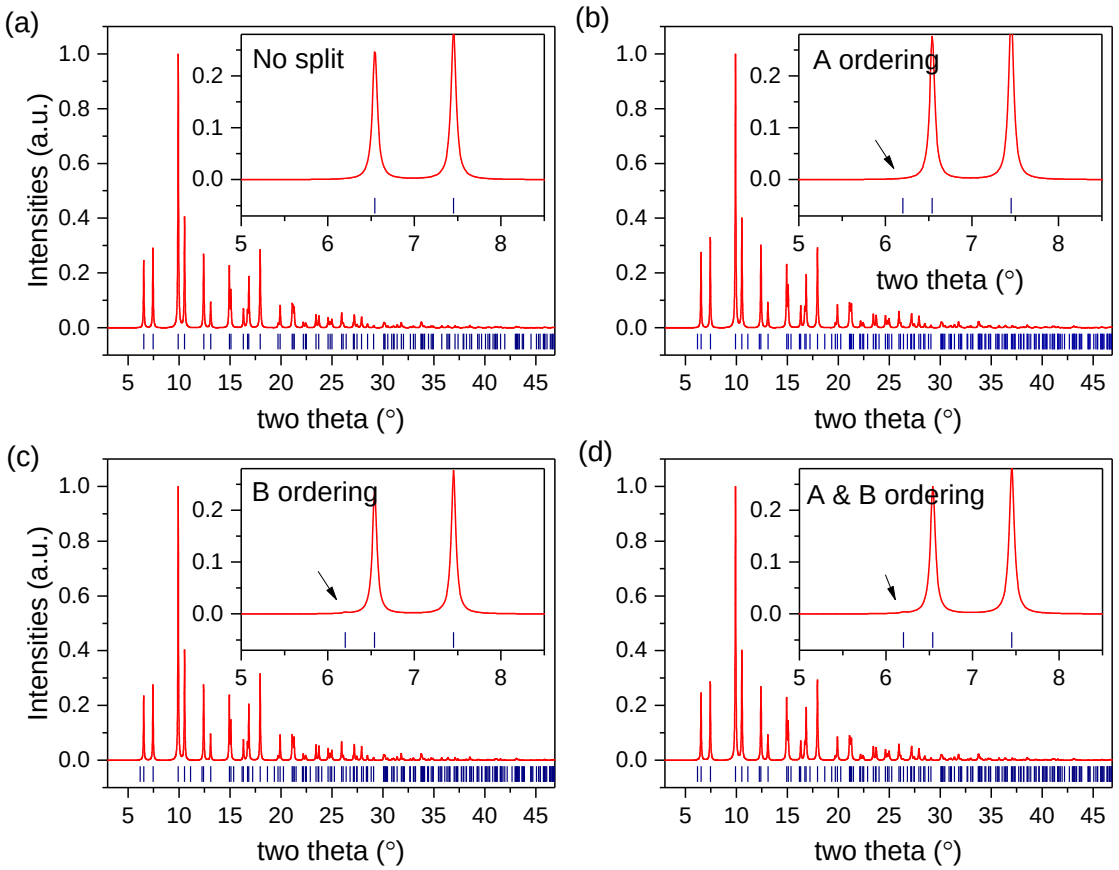

Fig. S1 Full range of simulated SPD patterns at λ = 0.5003 Å for PTBF50 using different structural models. (a-d) correspond to model **I**-**IV** in Fig. 1. Inset shows the low angle range of 5° – 8.5°, corresponding to interplanar spacing *d* ranges from 3.4 Å to 5.7 Å. The arrows indicate superstructure reflections of <101> exerted by the A- or B-site ordering.

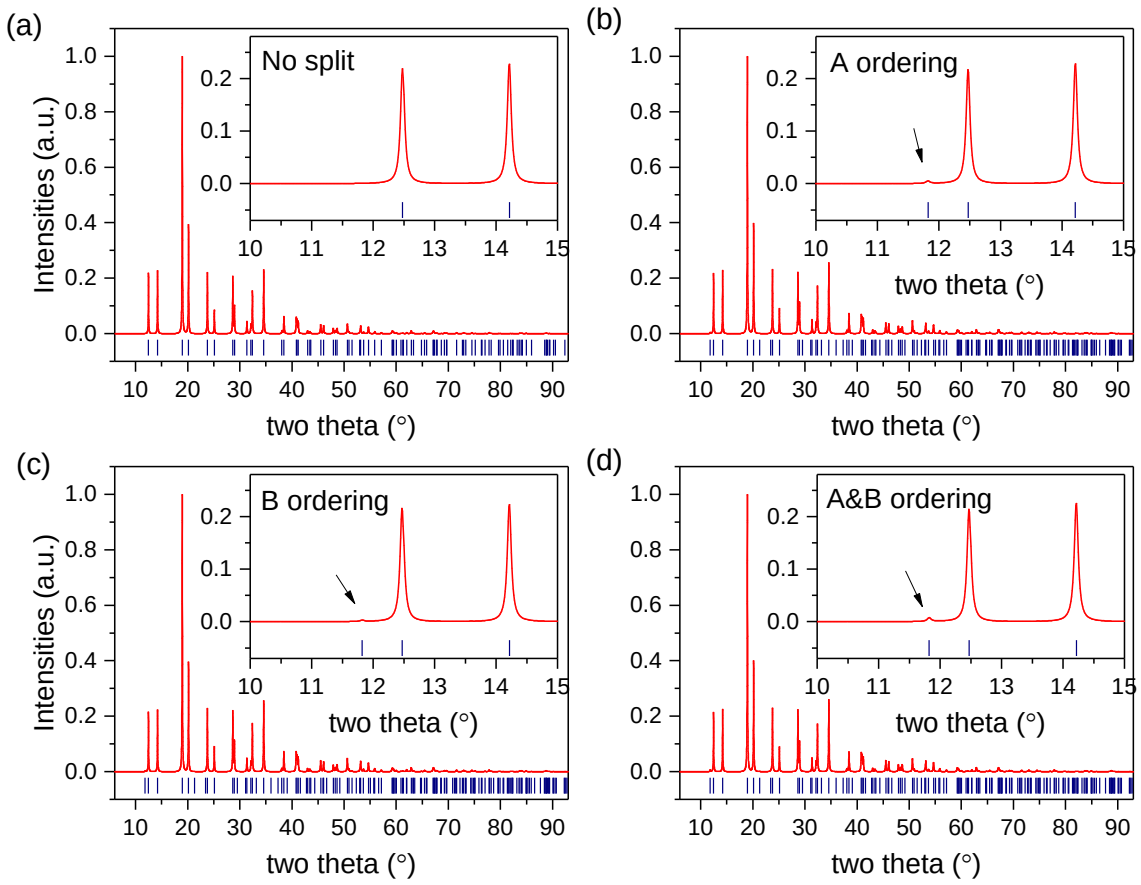

Fig. S2 Full range of simulated ADSPD patterns at λ = 0.9527 Å for PTBF50 using different structural models. (a-d) correspond to model **I**-**IV** in Fig. 1. Inset shows the low angle range of 10° – 15°, corresponding to interplanar spacing *d* ranges from 3.6 Å to 5.4 Å. The arrows indicate superstructure reflections of <101> exerted by the A- or B-site ordering.

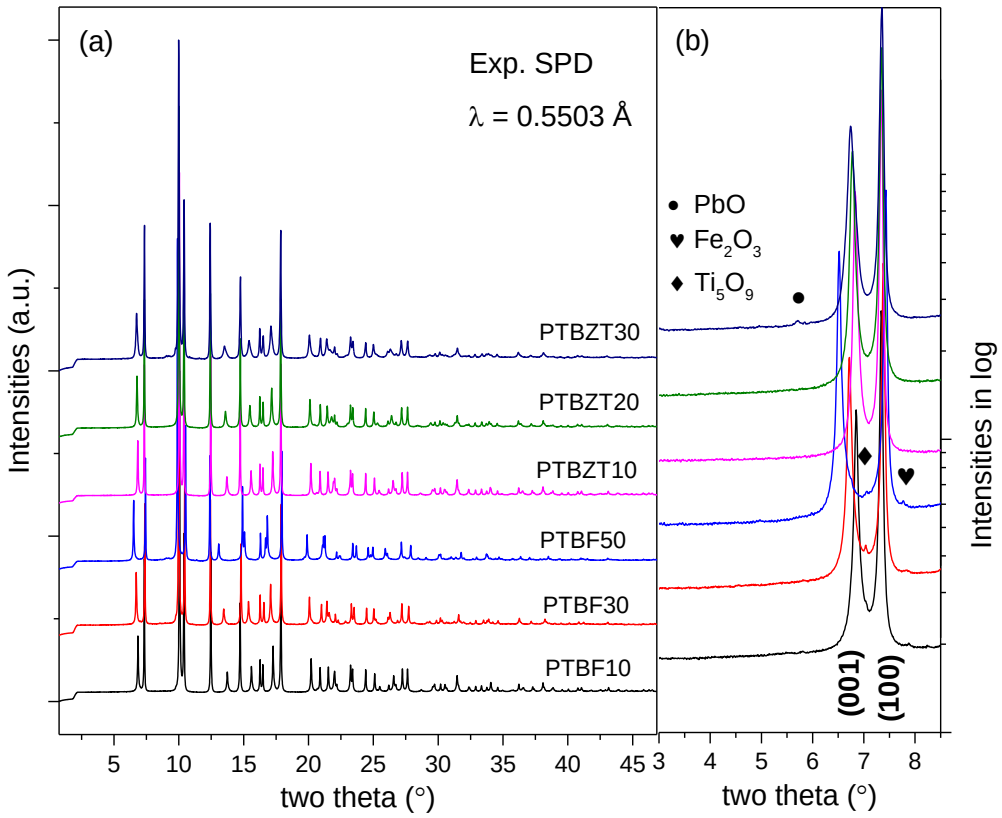

Fig. S3 (a) Experimental SPD data at λ = 0.5003 Å for PTBF10, PTBF30, PTBF50, PTBZT10, PTBZT20, and PTBZT30. (b) shows the low two theta region ranges from 3˚ to 8.5˚ (3.4 Å to 9.6 Å). The peak intensities in (b) are scaled in log in order to show the weak superstructure peaks more clearly. Some minor impurities are marked.

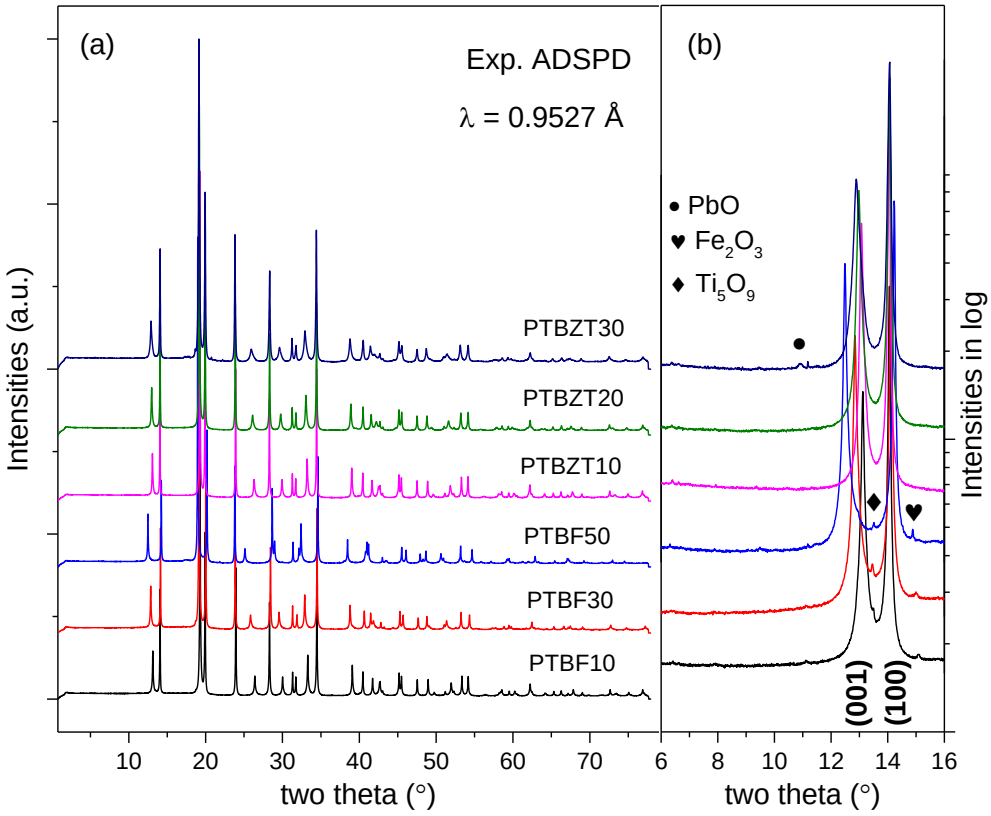

Fig. S4 (a) Experimental ADSPD data at λ = 0.9527 Å for PTBF10, PTBF30, PTBF50, PTBZT10, PTBZT20, and PTBZT30. (b) shows the low two theta region ranges from 6˚ to 16˚ (3.4 Å to 9.1 Å). The peak intensities in (b) are scaled in log in order to show the weak superstructure peaks more clearly. Some minor impurities are marked.

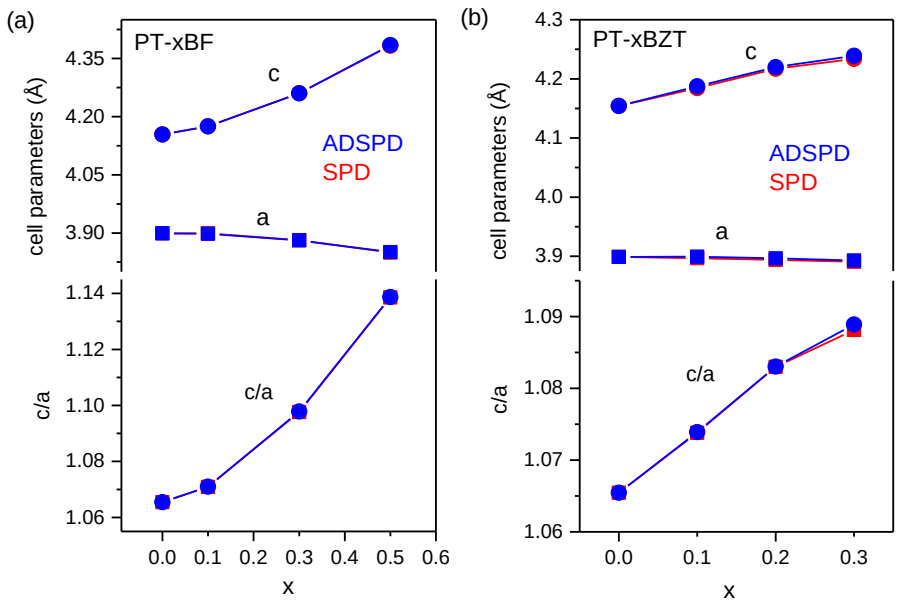

Fig. S5 Cell parameters and tetragonal distortion (c/a) as a function of x for (1-x)$PbTiO_3$–$x$$BiFeO_3$ (x = 0.1, 0.3, 0.5) (a) and (1-x)$PbTiO_3$–$x$$Bi(Zn_{1/2}Ti_{1/2})O_3$ (x = 0.1, 0.2, 0.3) (b). The red and blue colors correspond to SPD and ADSPD results, respectively.

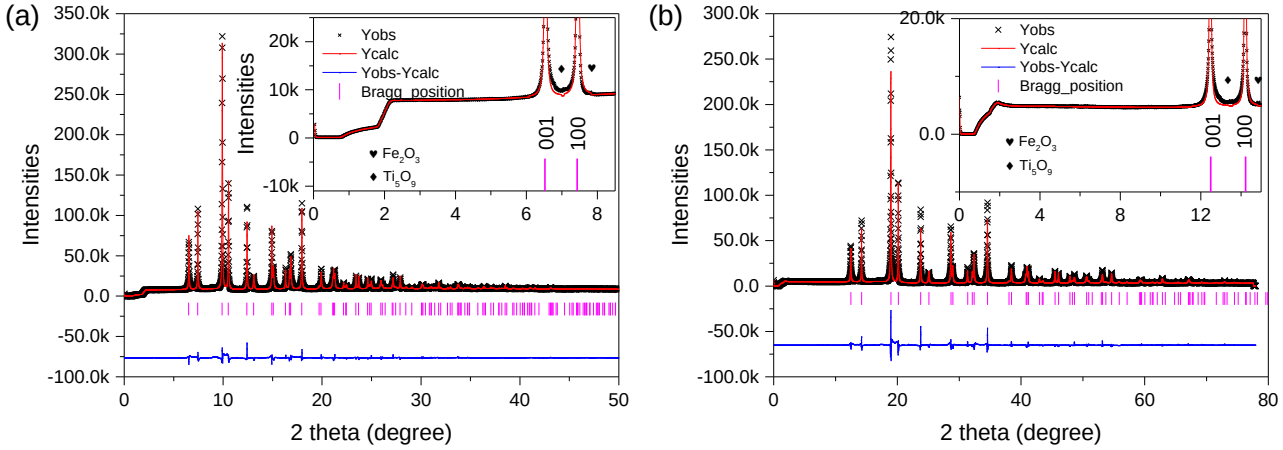

Fig. S6 Rietveld fitting of PTBF50 using disordered model **I** against SPD (a) and ADSPD (b) data. The R factors are R_{wp} = 5.10%, GOF = 5.52 in (a) and R_{wp} = 9.74%, GOF =7.43 in (b).

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