

## Supplementary File for

### Observation of novel charge ordering and spin reorientation in perovskite oxide $\text{PbFeO}_3$

Xubin Ye<sup>1,2,#</sup>, Jianfa Zhao<sup>1,2,#</sup>, Hena Das<sup>3,4,#</sup>, Denis Sheptyakov<sup>5</sup>, Junye Yang<sup>5</sup>, Yuki Sakai<sup>6,3</sup>, Hajime Hojo<sup>7</sup>, Zhehong Liu<sup>1,2</sup>, Long Zhou<sup>1,2</sup>, Lipeng Cao<sup>1</sup>, Takumi Nishikubo<sup>3</sup>, Shogo Wakazaki<sup>3</sup>, Cheng Dong<sup>1,2</sup>, Xiao Wang<sup>8</sup>, Zhiwei Hu<sup>8</sup>, Hong-Ji Lin<sup>9</sup>, Chien-Te Chen<sup>9</sup>, Christoph Sahle<sup>10</sup>, Anna Efiminko<sup>10</sup>, Huibo Cao<sup>11</sup>, Stuart Calder<sup>11</sup>, Ko Mibu<sup>12</sup>, Michel Kenzelmann<sup>5</sup>, Liu Hao Tjeng<sup>8</sup>, Runze Yu<sup>\*1,2,4</sup>, Masaki Azuma<sup>\*3,6</sup>, Changqing Jin<sup>1,2,13</sup>, and Youwen Long<sup>\*1,2,13</sup>

<sup>1</sup>Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

<sup>2</sup>School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

<sup>3</sup>Laboratory for Materials and Structures, Tokyo Institute of Technology, 4259 Nagatsuta, Midori, Yokohama 226-8503, Japan

<sup>4</sup>Tokyo Tech World Research Hub Initiative (WRHI), Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8503, Japan

<sup>5</sup>Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, CH-5232 Villigen, Switzerland

<sup>6</sup>Kanagawa Institute of Industrial Science and Technology, 705-1 Shimoimaizumi, Ebina 243-0435, Japan

<sup>7</sup>Department of Advanced Materials and Engineering, Faculty of Engineering Sciences, Kyushu University, Kasuga 816-8580, Japan

<sup>8</sup>Max-Planck Institute for Chemical Physics of Solids, Nöthnitzer Straße 40, 01187 Dresden,  
Germany

<sup>9</sup>National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu 30076, Taiwan,  
R.O.C

<sup>10</sup>European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38043 Grenoble, France

<sup>11</sup>Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831,  
United States

<sup>12</sup>Graduate School of Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

<sup>13</sup>Songshan Lake Materials Laboratory, Dongguan, Guangdong 523808, China

#These authors contribute equally to this work.

\*Corresponding email: ywlong@iphy.ac.cn (Y.W.L.); yurz@iphy.ac.cn (R.Z.Y.); and  
mazuma@msl.titech.ac.jp (M.A.)

**Supplementary Table S1 | Crystallographic parameters of PbFeO<sub>3</sub> refined from SXRD pattern at RT<sup>a</sup>**

atom	site	<i>x</i>	<i>y</i>	<i>z</i>	100× <i>B</i> <sub>iso</sub> (Å)
Pb1	4 <i>c</i>	0	-0.0037(1)	0.25	0.78(1)
Pb2	4 <i>c</i>	0	0.4996(1)	0.25	0.78(1)
Pb3	4 <i>c</i>	0	0.8282(1)	0.25	0.78(1)
Pb4	4 <i>c</i>	0	0.1546(1)	0.25	0.78(1)
Pb5	4 <i>c</i>	0	0.3349(1)	0.25	0.78(1)
Pb6	4 <i>c</i>	0	0.6593(1)	0.25	0.78(1)
Fe1	8 <i>d</i>	0.25	0.25	0	0.22(2)
Fe2	16 <i>h</i>	0.2558(6)	0.5840(1)	0.9993(6)	0.22(2)
O1	8 <i>g</i>	0.301(4)	0.7756(8)	0.25	1.8(3)
O2	16 <i>h</i>	0.308(2)	0.6732(7)	0.053 (2)	1.8(3)
O3	8 <i>f</i>	0	0.2703(9)	-0.064(4)	1.8(3)
O4	8 <i>e</i>	0.277(4)	0	0	1.8(3)
O5	8 <i>f</i>	0	0.0763(10)	1.050(4)	1.8(3)
O6	8 <i>g</i>	0.187(4)	0.5869(8)	0.25	1.8(3)
O7	8 <i>f</i>	0	0.6082(9)	-0.038 (4)	1.8(3)
O8	8 <i>g</i>	0.283(4)	0.4047(7)	0.25	1.8(3)

<sup>a</sup>Space group *Cmcm* (No. 63), *Z* = 24. *a* = 7.88504(2)Å, *b* = 23.37741(8) Å, *c* = 7.70905(2) Å,  $\rho_{\text{cal}} = 8.723(1) \text{ g/cm}^3$ , *V* = 1421.023(1) Å<sup>3</sup>. *R*<sub>wp</sub> = 7.63%, *R*<sub>p</sub> = 5.30%,  $\chi^2 = 9.20$ .

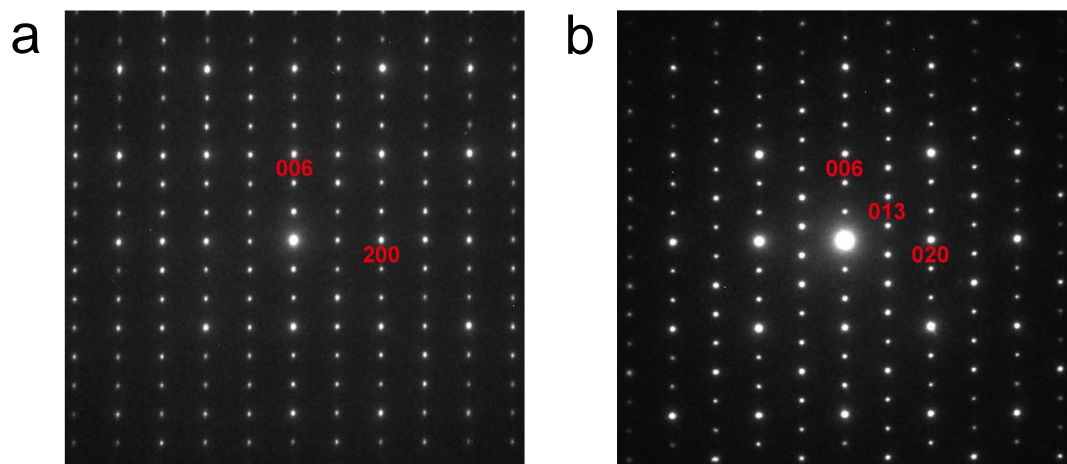
**Supplementary Table S2 | Pb-O and Fe-O bond lengths and BVSs for PbFeO<sub>3</sub>**  
**Refined from SXRD pattern at RT.**

	Distance (Å)		Average bond length (Å)	BVS
Fe1-O	1.897(2)	× 2	2.014	3.03
	2.058(2)	× 2		
	2.087(3)	× 2		
Fe2-O	1.952(3)		2.032	2.87
	1.973(3)			
	1.981(2)			
	2.009(3)			
	2.115(2)			
	2.165(2)			
Pb1-O	2.427(4)	× 2	2.771	1.94
	2.738(6)	× 2		
	2.866(6)	× 4		
	2.912(6)	× 2		
Pb2-O	2.516(4)	× 2	2.778	2.01
	2.611(5)	× 4		
	3.005(6)	× 2		
	3.148(6)	× 2		
Pb3-O	2.475(5)	× 2	2.774	2.23
	2.675(5)	× 2		
	2.712(6)	× 2		
	2.786(3)	× 4		
	3.213(3)	× 2		
Pb4-O	2.189(4)	× 4	2.588	3.72
	2.395(5)	× 2		
	2.933(4)	× 2		
	3.235(6)	× 2		
Pb5-O	2.092(4)	× 2	2.455	3.93
	2.107(4)	× 2		
	2.767(6)	× 2		
	2.853(5)	× 2		
Pb6-O	2.182(4)	× 2	2.541	3.52
	2.245(6)	× 2		
	2.521(4)	× 2		
	2.880(4)	× 4		

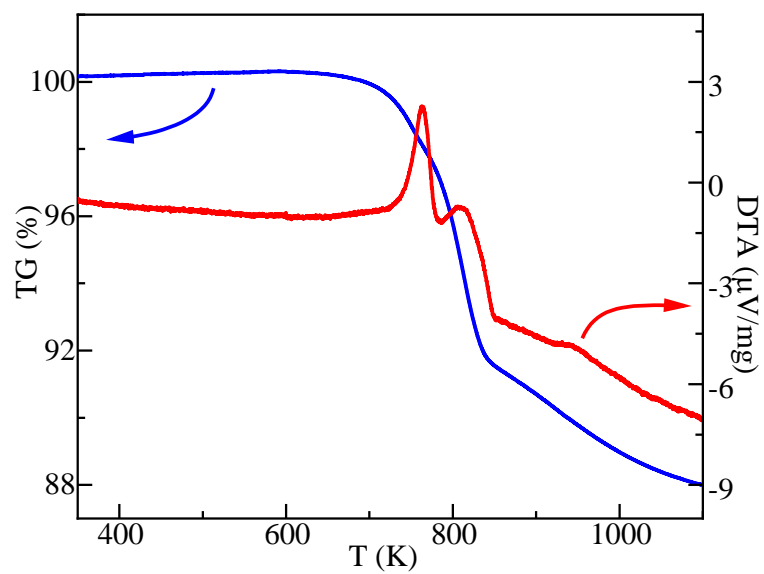


**Supplementary Table S3 | Peak area ratio for each peak and calculated average Pb valence for HAXPES data.**

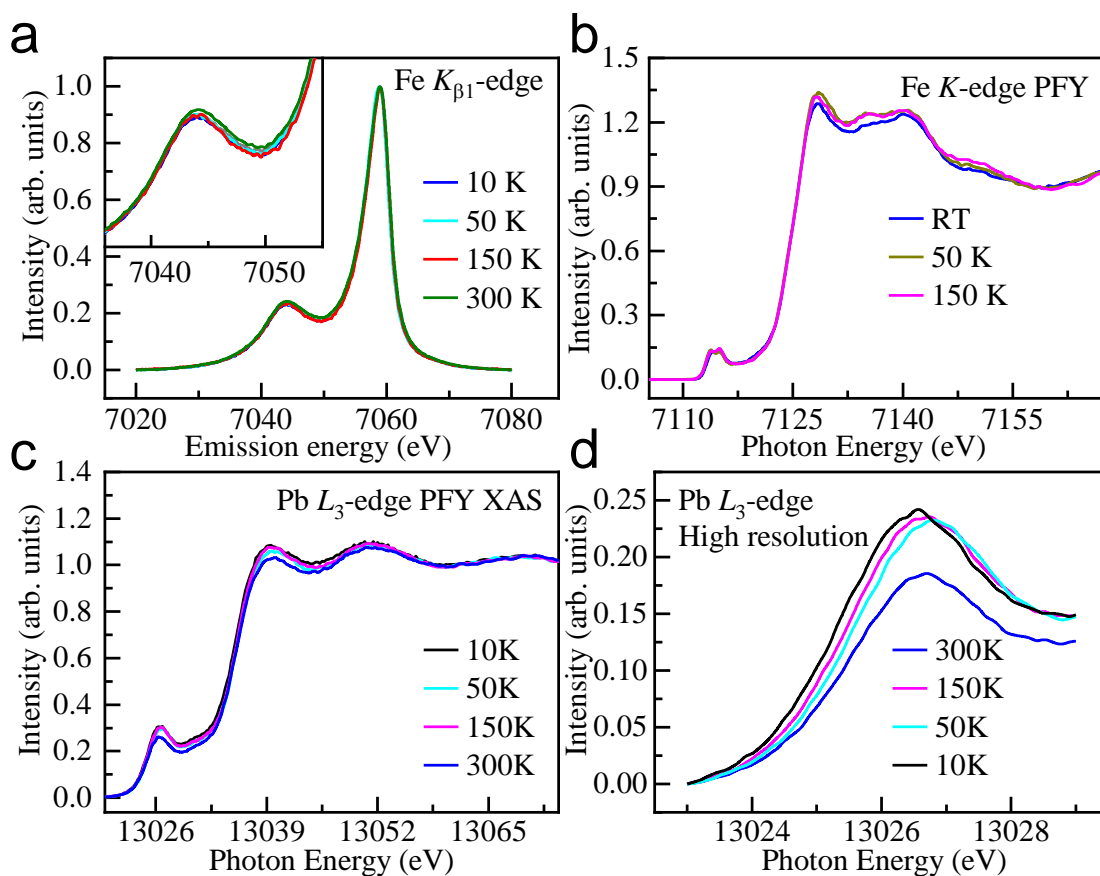
	$4f_{5/2}$		$4f_{7/2}$	
PbCrO <sub>3</sub>	0.61	0.39	0.61	0.39
PbFeO <sub>3</sub>	0.59	0.41	0.58	0.42
PbCoO <sub>3</sub>	0.48	0.52	0.45	0.55



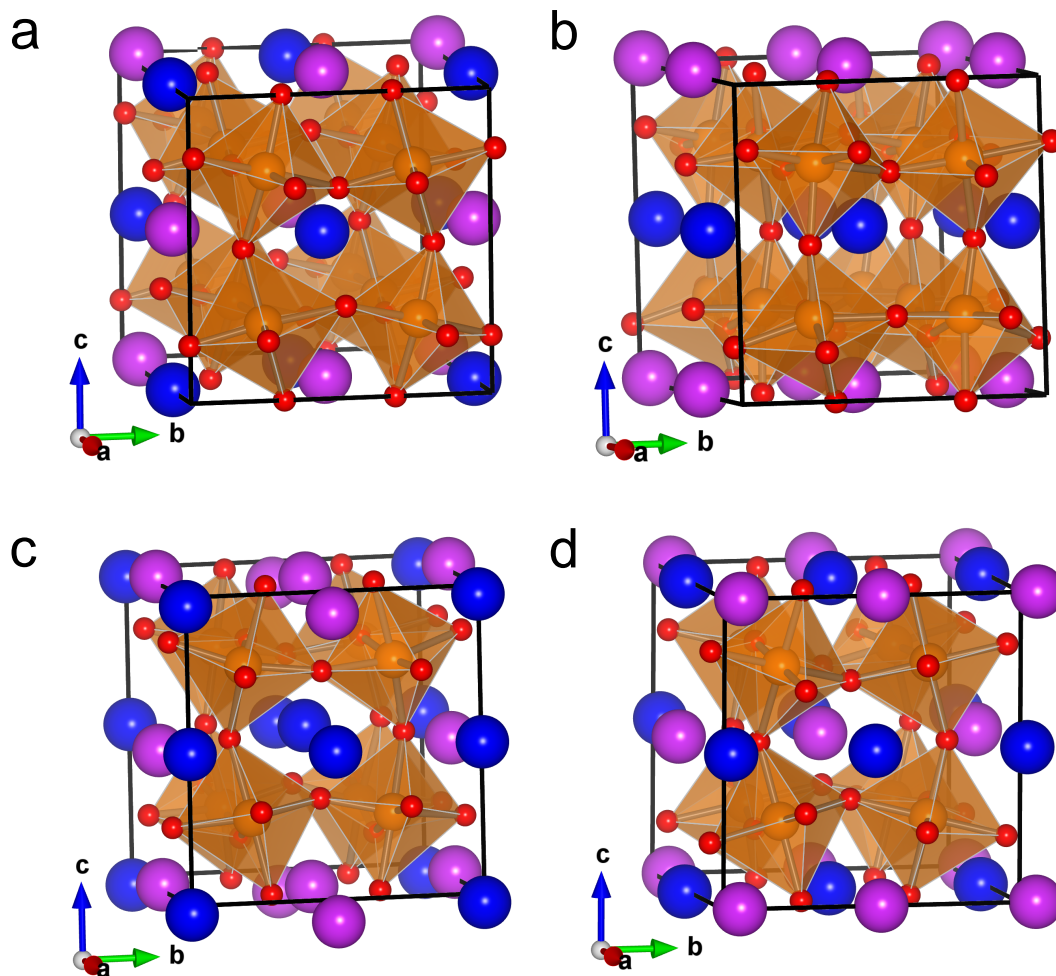
**Supplementary Figure S1 | ED patterns along the pseudocubic zone axis at RT for PbFeO<sub>3</sub>. (a) [100] and (b) [001] axis. Multiple scattering effects make it possible to observe  $h00$  reflections with  $h = \text{odd}$  at [010].**



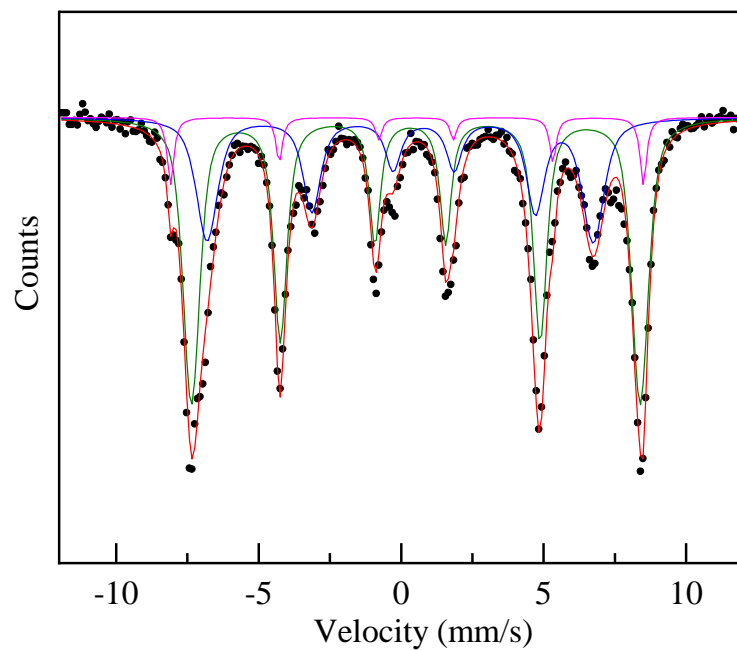
**Supplementary Figure S2 | Temperature dependence of thermogravimetry (TG) and differential thermal analysis (DTA) for  $\text{PbFeO}_3$ .**



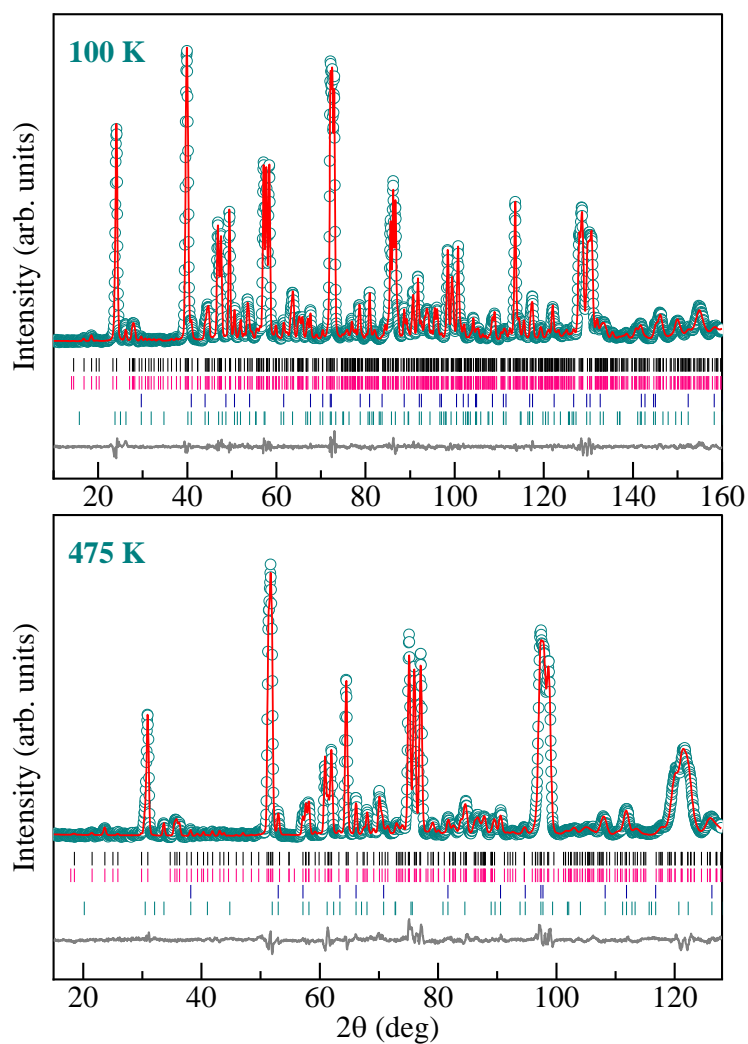
**Supplementary Figure S3 | Temperature dependent XAS measurement for  $\text{PbFeO}_3$ .** (a) Fe  $K_{\beta 1}$ -edge for  $\text{PbFeO}_3$ . (b) Fe  $K$ -edge for  $\text{PbFeO}_3$  in PFY model. (c) Pb  $L_3$ -edge for  $\text{PbFeO}_3$  in PFY model. (d) High resolution Pb  $L_3$ -edge for  $\text{PbFeO}_3$ .



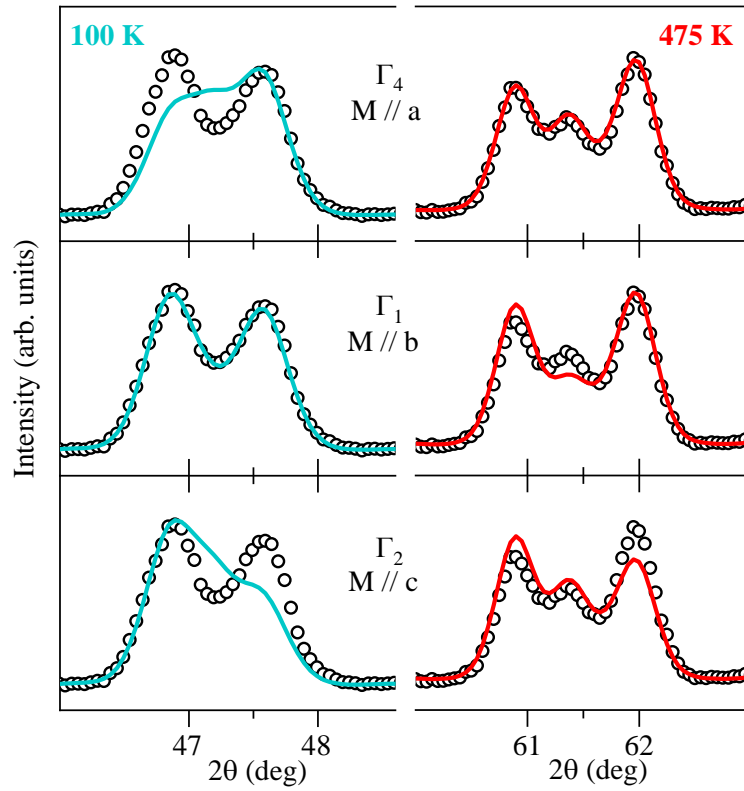
**Supplementary Figure S4 | Represents the  $\text{Pb}^{2+}/\text{Pb}^{4+}$  for different charge-order phases. (a) rock-salt ( $Cm$ ), (b) layered ( $Pc$ ), (c) mixed ( $Pm$ ) and (d) columnar ( $Pmmn$ ).**



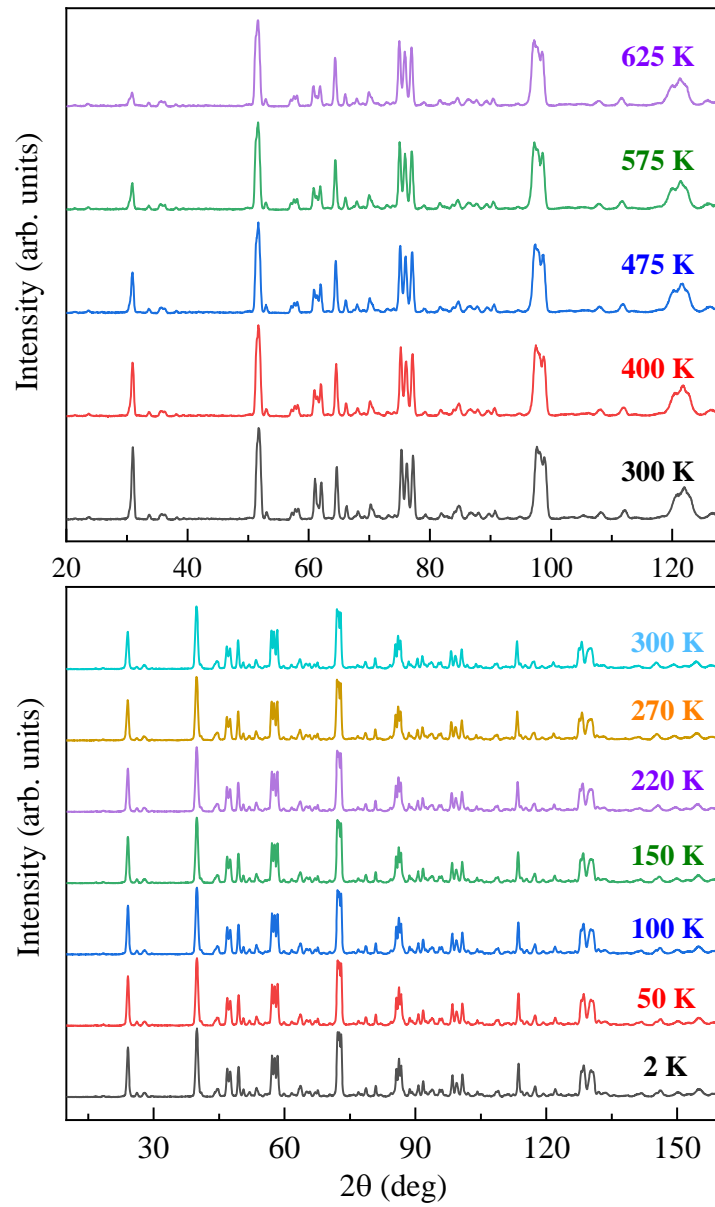
**Supplementary Figure S5 | Mössbauer spectrum for the  $^{57}\text{Fe}$ -enriched powder sample at 300 K.** The spectrum can be fitted with three sets of magnetically-split sextets, which are attributed to Fe at the  $16h$  site (olive, 60%),  $8d$  site (blue, 34%), and at  $\alpha\text{-Fe}_2\text{O}_3$  impurities (pink, 6%).



**Supplementary Figure S6 | The NPD patterns and the refinement results at 100 K and 475 K for  $\text{PbFeO}_3$ .** The observed (dark cyan circles), calculated (red line), and difference (dark gray) values are shown. The ticks correspond to the allowed nuclear (black), magnetic (pink) Bragg peaks of  $\text{PbFeO}_3$  and allowed nuclear (navy), magnetic (green) Bragg reflections of the impurity phase  $\text{Fe}_2\text{O}_3$  (~5 wt %), respectively.

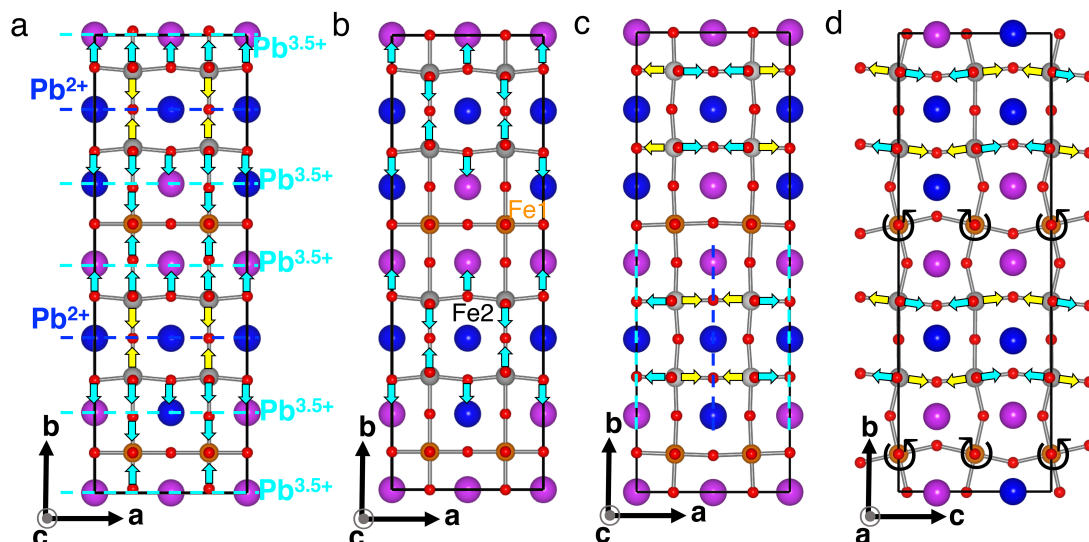


**Supplementary Figure S7 | Magnetic Bragg peaks and the fitting curves using the three different spin models at 100 K (left panel) and 475 K (right panel) for several characteristic peaks of NPD patterns of  $\text{PbFeO}_3$ . The gray balls and solid curves correspond to measured data and fitted results, and three spin models ( $\Gamma_4$ ,  $\Gamma_1$  and  $\Gamma_2$ ) are represented from up to down, respectively.**

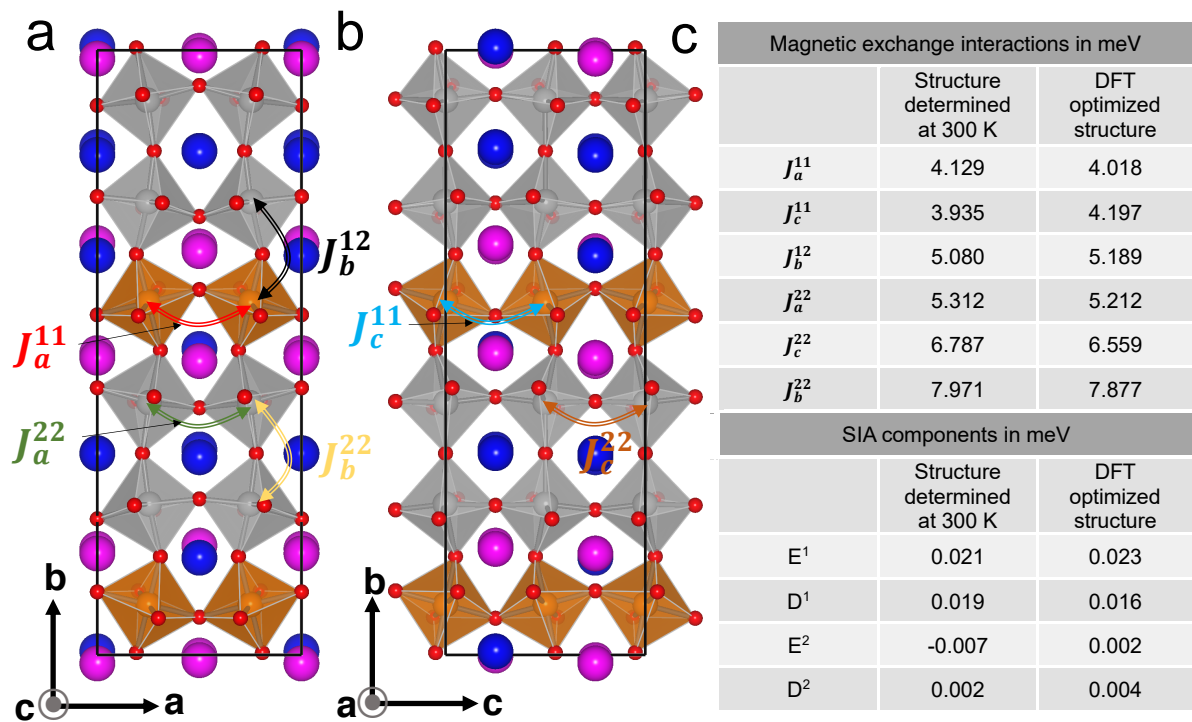


**Supplementary Figure S8 | The NPD patterns measured at 2 - 625 K for  $\text{PbFeO}_3$ .**

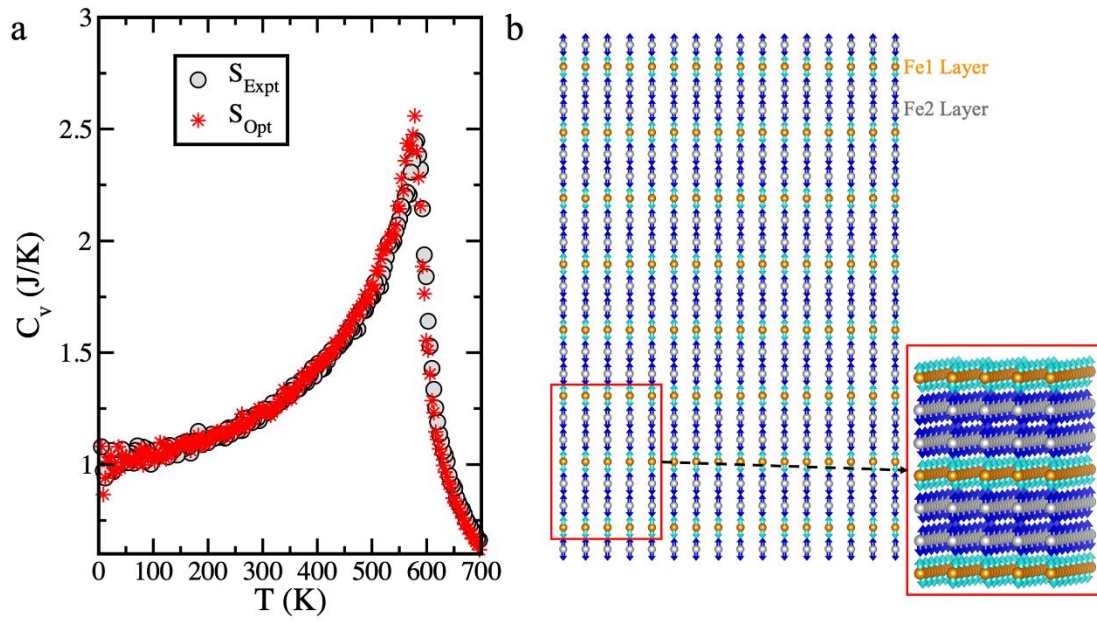




**Supplementary Figure S9 | Symmetric distortions which owe their origin to the special arrangements of Pb cations.** The symmetric distortions that correspond to *DT1* (transforms  $Pm\bar{3}m \rightarrow P4/mmm$ , (a)), *DT2* (transforms  $Pm\bar{3}m \rightarrow Pmmm$ , (b)), *Z4* (transforms  $Pm\bar{3}m \rightarrow Cmmm$ , (c)) and *Z4* (transforms  $Pm\bar{3}m \rightarrow Pmma$ , (d)). Blue and cyan layers represent average 2+ and 3.5+ oxidation state of Pb ions, respectively. The Fe and oxygen movements are denoted by yellow and cyan arrows, respectively. The in-phase oxygen octahedra rotations at the Fe1 layers around *a* axis is denoted by black arrow.

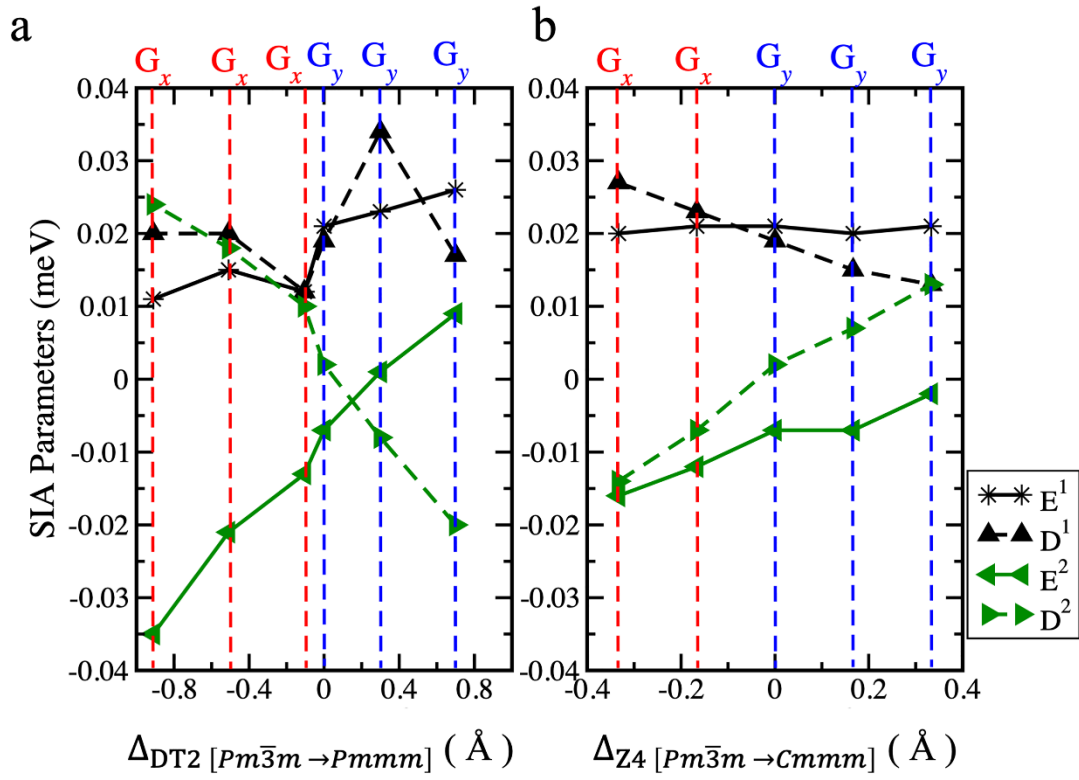


**Supplementary Figure S10 | Parameterize the spin Hamiltonian.** (a) and (b) Super-exchange interaction paths between Fe spins. (c) Estimated values of the symmetric exchange interactions between Fe spins and single ion magnetic anisotropy energies of Fe1 ( $E^1$  and  $D^1$ ) and Fe2 ( $E^2$  and  $D^2$ ) ions.



**Supplementary Figure S11 | Results of finite temperature Monte Carlo simulations.**

(a) Exhibits magnetic phase transition  $\sim 580$  K for both  $S_{\text{Expt}}$  and  $S_{\text{Opt}}$  structures. (b) Denotes the  $G$ -type ( $G_y$ ) antiferromagnetic structure at 20 K. The cyan and blue arrows represent Fe1 and Fe2 spins, respectively.



**Supplementary Figure S12 | Stability of various magnetic phases as modulation of structural distortions.** (a) and (b) Estimated single ion anisotropy (SIA) parameters associated with Fe1 ( $E^1$  and  $D^1$ ) and Fe2 ( $E^2$  and  $D^2$ ) magnetic sublattices as a function of  $DT2$  ( $Pm\bar{3}m \rightarrow Pmmm$ ) and  $Z4$  ( $Pm\bar{3}m \rightarrow Cmmm$ ) distortions, respectively. The magnetic phases stabilized in the Monte Carlo simulations considering the estimated SIA parameters below the magnetic phase transition are also shown.