

Supporting information

Improving energy storage performance enabled by composition-induced dielectric behavior in PbHfO₃-based ceramics under lower electric fields

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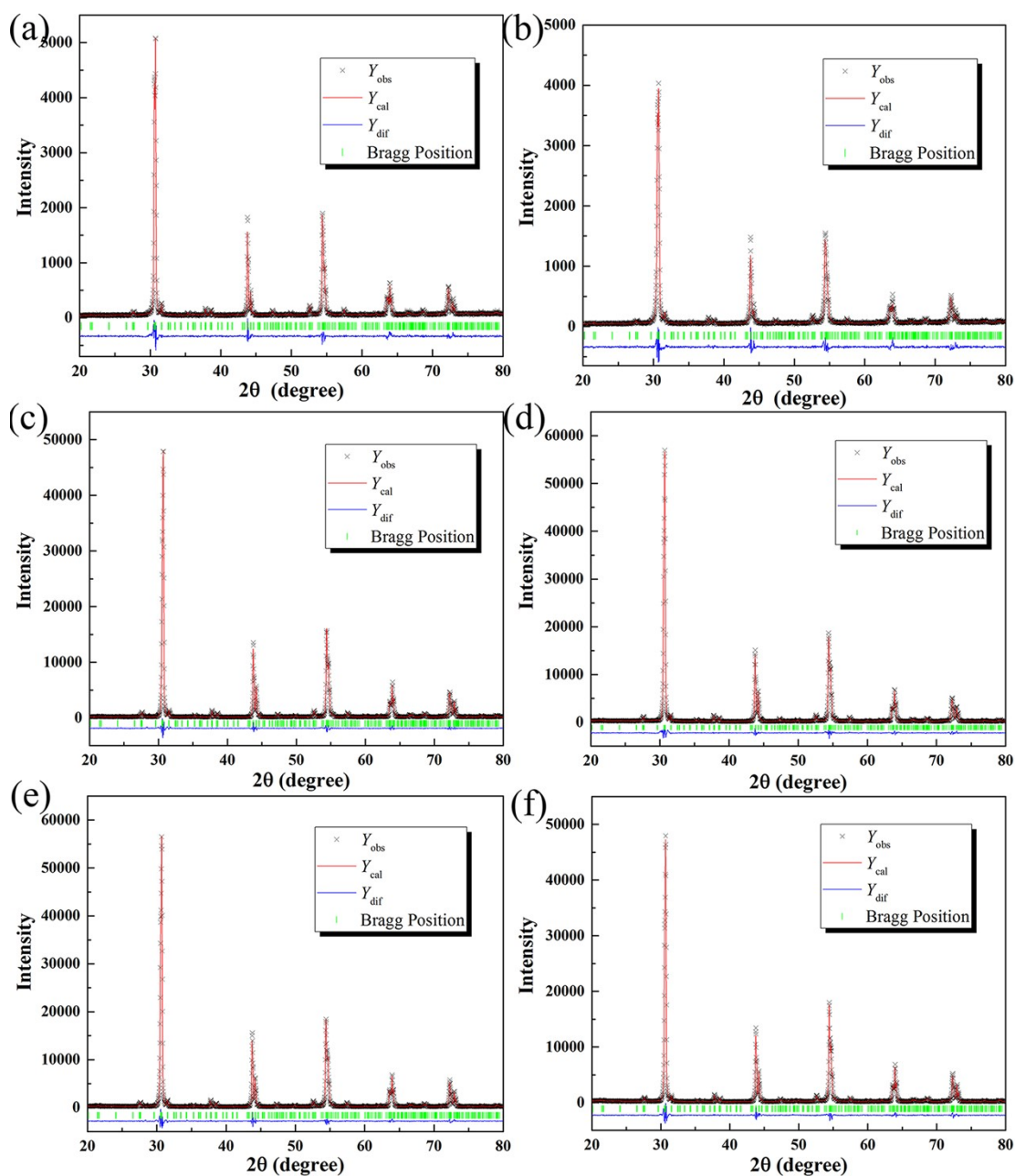


Fig. S1 The Rietveld refinement based on space group of Pbam of PHT_x ceramics, showing observed (cross), calculated (line) and difference (lower) profiles.

Table S1. The crystal and refined parameters of PHT_x ceramics.

Compo sitions	PHT0	PHT0.5	PHT1	PHT2	PHT3	PHT4
Space group	Pbam	Pbam	Pbam	Pbam	Pbam	Pbam
Unit cell dimensions	a=5.8404Å b=11.7057 Å c=8.1751 Å	a=5.8448 Å b=11.716 Å c=8.1948 Å	a=5.8499Å b=11.7162 Å c=8.2017 Å	a=5.8442 Å b=11.7030 Å c=8.1939 Å	a=5.8387 Å b=11.6913 Å c=8.1859 Å	a=5.8364 Å b=11.6863 Å c=8.1829 Å

Volume	558.90 Å ³	561.16 Å ³	562.13 Å ³	560.42 Å ³	558.79 Å ³	558.12 Å ³
Refining parameters	R _{wp} =0.1117 R _p =0.0827 χ^2 =1.458	R _{wp} =0.1098 R _p =0.0898 χ^2 =1.681	R _{wp} =0.1007 R _p =0.0646 χ^2 =1.223	R _{wp} =0.0989 R _p =0.0629 χ^2 =1.548	R _{wp} =0.0947 R _p =0.0647 χ^2 =1.580	R _{wp} =0.0998 R _p =0.0683 χ^2 =1.575

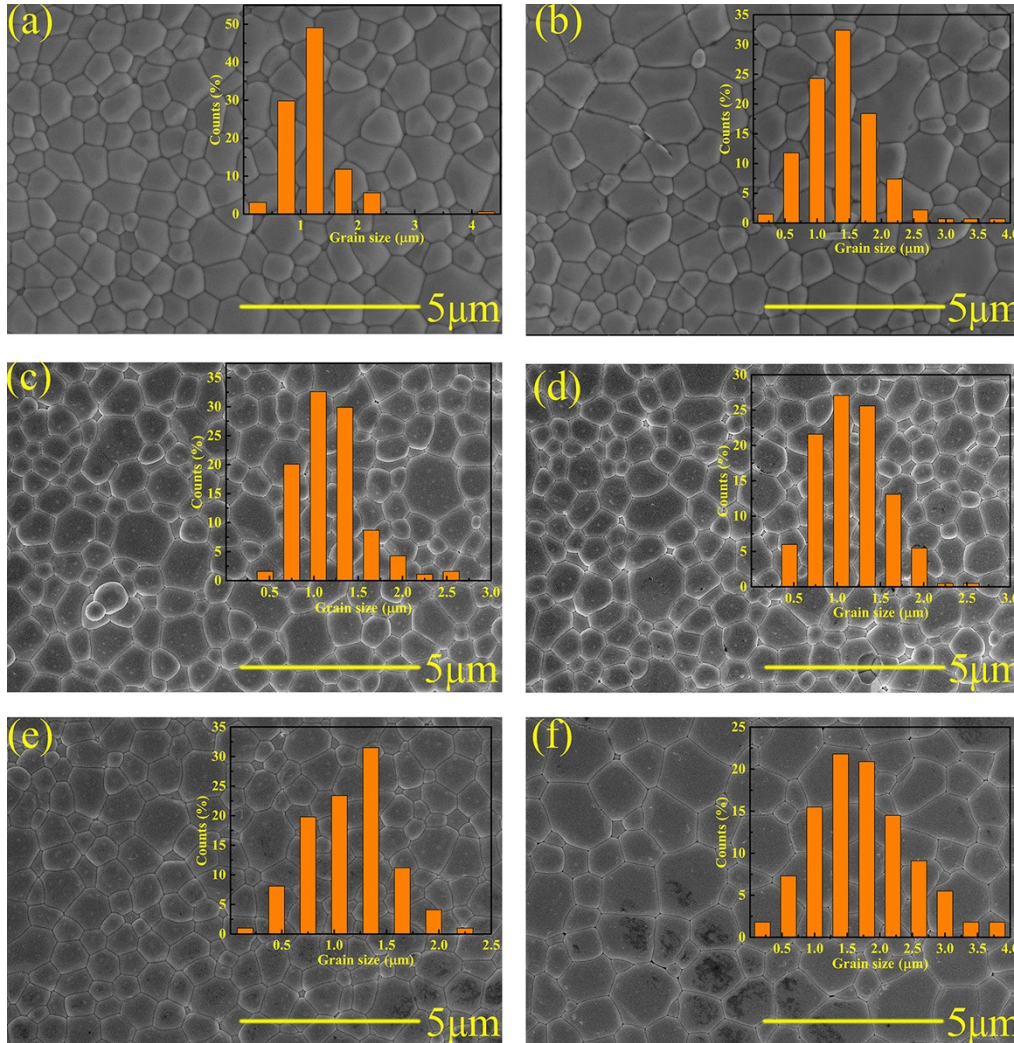


Fig. S2 The surface microstructure images and grain size distribution of the PHT_x ceramics.

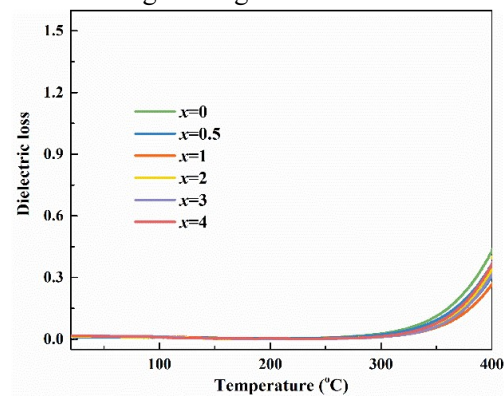


Fig. S3 The dielectric loss as a function of temperature

Table S2 The average ionic radii of A-site and B-site cations and tolerance factor of PHT x ceramics.

Composition (x mol%)	$R_{A\text{-site}}$ (Å)	$R_{B\text{-site}}$ (Å)	Tolerance factor
0	1.49	0.71	0.9661
0.5	1.49	0.7095	0.9663
1	1.49	0.709	0.9665
2	1.49	0.708	0.9670
3	1.49	0.707	0.9674
4	1.49	0.706	0.9679

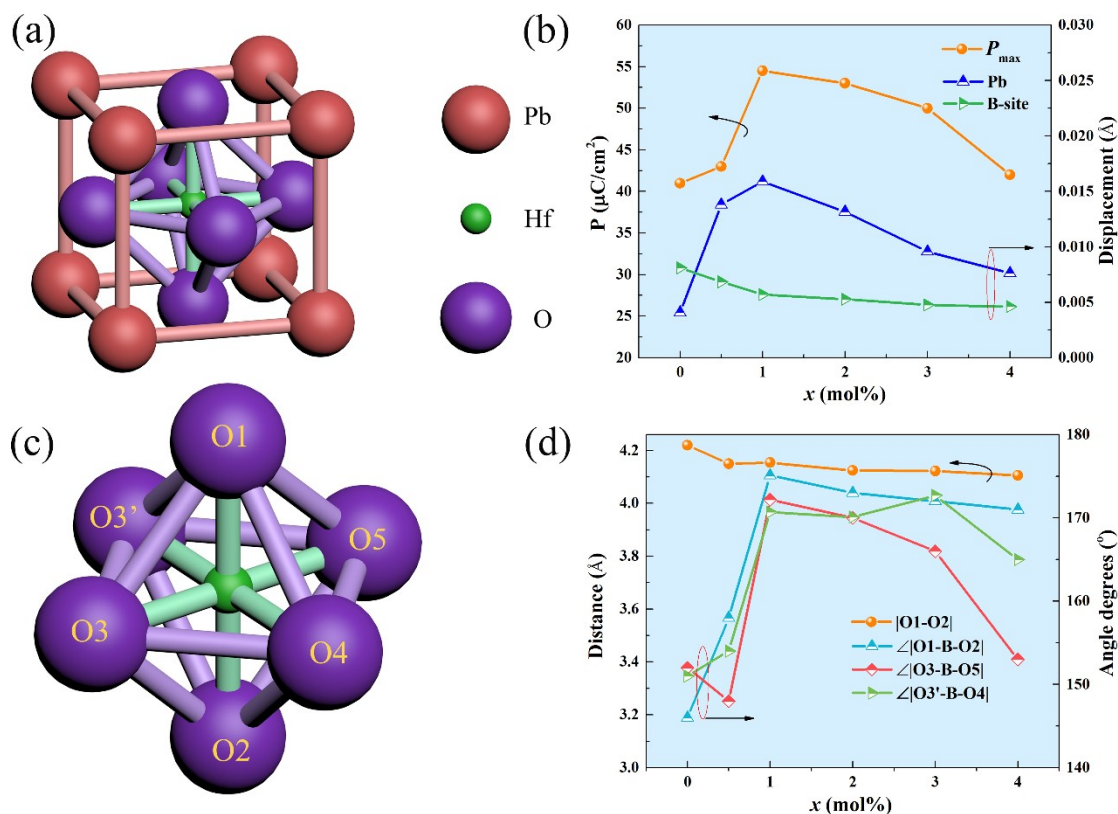


Fig S4 (a)The general perovskite structure of PbHfO₃ ceramics. (b) The evolution of maximum polarization and average displacement of Pb and B-site cations as a function of Ti content. (c) The model of BO₆ octahedral of PbHfO₃ system. and (d) The variation of distance of $|O1-O2|$ and angle degrees of $\angle|O1-B-O2|$, $\angle|O3-B-O5|$, and $\angle|O3'-B-O4|$ as a function of Ti content.

To better understand the origin of high polarization and the evolution of BO₆ octahedral rotation, the general perovskite structure model of PbHfO₃ ceramics and BO₆ octahedral were established based on the Rietveld refinement results as shown in Fig S4a and c. The displacement of Pb²⁺ cations display almost identical trend with the

P_{\max} of different Ti^{4+} contents, but the displacement of B-site ions is not the same as that for the displacement of A-site, which is in good agreement with the results in Fig 1.

Two factors contribute to the large polarization intensity, the major contribution is the enhanced displacement of A-site cations, the second contribution is the torsion of oxygen octahedral. As the Ti^{4+} content continuous increase, the volume of the BO_6 octahedral increases, which leading to the position change of A-site cations and further leading to the total displacement dipole strength increase. The maximum polarization firstly presents a rising trend with the increase of Ti content. With the increase of Ti content, the Ti-O bond binding capacity is gradually enhanced, resulting in a decrease in volume. As the displacement of the A-site ions becomes smaller, the polarization strength further decreases, which is consistent with the results in Fig 3a. The distance between O1 and O2 also shows the same trend as in Fig. S4d. We have marked oxygen atoms in different positions in Fig S4c. With the Ti content increases, the angle of $\angle|\text{O1-B-O2}|$ also shows a similar trend with the change of P_{\max} , however, the angle of $\angle|\text{O3-B-O5}|$ and $\angle|\text{O3'-B-O4}|$ have been declined. Combine the information of Fig S4b and d, it could be concluded that the BO_6 octahedral is more likely to twist along the c axis (polar axis) rather than a and b axes. These results further illustrate that the high spontaneous polarization is highly possible rooted in the large displacement of A-site cations in PbHfO_3 ceramics. Corrections have been made in the revised version and supporting information.

Table S3. The free energy coefficients of PHTx ceramics.

Composition(x mol%)	PHT0	PHT0.5	PHT1	PHT2	PHT3	PHT4
$a_1(10^6 \text{ N m C}^{-2})$	3.5	3.5	3.5	3.5	3.5	3.5
$a_{11}(10^6 \text{ N m}^6 \text{ C}^{-4})$	20.0	20.0	5.0	5.0	5.0	5.0
$a_{111}(10^6 \text{ N m}^{10} \text{ C}^{-6})$	40.0	40.0	20.0	20.0	40.0	40.0
$g(10^6 \text{ N m C}^{-2})$	35.0	24.5	19.3	14.0	14.0	10.5

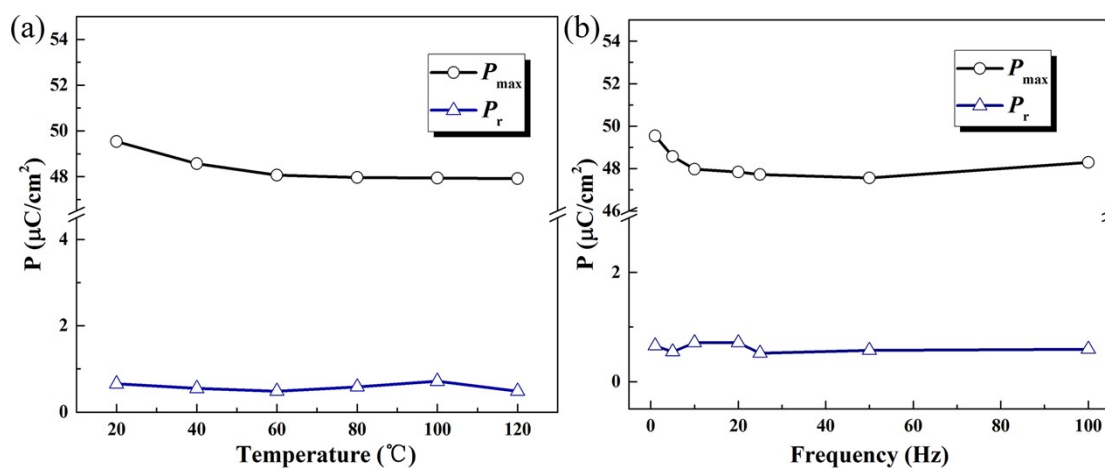


Fig. S5 P_{\max} and P_r of PHT1 composition as a function of (a) temperature (20-120 $^{\circ}\text{C}$) and (b) frequency (1-100 Hz).