Synergistic design of a new PbHfO$_3$-based antiferroelectric solid solution with high energy storage and large strain performances under low electric fields

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In order to suppress the formation of the secondary phases PbWO$_4$ and Pb$_2$WO$_5$, as well as the pyrochlore phase in the final product, the ZnWO$_4$ precursor phase needs to be first synthesized. **Fig. S1** shows the XRD pattern of the as-prepared ZnWO$_4$ precursor, exhibiting excellent agreement between the diffraction peaks of PDF # 15-0774 of ZnWO$_4$. This confirms the successful formation of the ZnWO$_4$ precursor phase.

**Fig. S1.** XRD result of the B-site precursor ZnWO$_4$. The pattern agrees well with the PDF # 15-0774 of ZnWO$_4$.

The orthorhombic $Pbam \sqrt{2}a \times 2\sqrt{2}a \times 2a$ lattice is converted into the pseudocubic $a_p \times a_p \times a_p$ lattice setting ($a_p = $ cell dimension of PEC phase) by the following matrix:

$$
\begin{pmatrix}
\frac{1}{2} & -\frac{1}{2} & 0 \\
\frac{1}{4} & \frac{1}{4} & 0 \\
0 & 0 & \frac{1}{2}
\end{pmatrix}
= \begin{pmatrix}
h_p \\
k_p \\
l_p
\end{pmatrix}
$$

(S1)

It is observed from **Fig. S2** that a PbO$_2$-typed secondary phase marked by black solid circles appears when the concentration of PZnW reaches 0.25, indicating that the solubility limit is achieved.
Table S1. Refined crystal structural parameters for the (1-x)PHf-xPZnW ceramics

<table>
<thead>
<tr>
<th>Composition</th>
<th>Space group</th>
<th>Lattice parameters</th>
<th>R-factors</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>a (Å)</td>
<td>b (Å)</td>
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<td>0.10</td>
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<tr>
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<td>5.84481</td>
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<tr>
<td>0.20</td>
<td>Pbam</td>
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Fig. S2. Room temperature XRD patterns of the (1-x)PHf-xPZnW (x = 0.00 and 0.25) ceramics.

Fig. S3-A(a) - (e) illustrates the surface morphology of the (1-x)PHf-xPZnW ceramics with various compositions. The pure PHf ceramics display smaller grain sizes and some pores. The partial substitution of PZnW for PHf results in a significant increase in the average grain size and a reduction in porosity, leading to a denser microstructure. Similar features are observed in the fracture images displayed in Fig. S3-B(a) - (e). The PHf ceramics exhibit a mixture of intergranular and transgranular fractures, while the solid solution ceramics show primarily an intergranular fractural surface. The relative density initially increases and then decreases as the PZnW content
increases, with the highest relative density of 98% achieved in \( x = 0.10 \), indicating the optimal PZnW content for the densification of the ceramics. The substitution of PZnW significantly promotes grain growth and enhances the relative density, probably due to the presence of some low melting point intermediate and transient phases (Pb\(_2\)WO\(_5\), m.p. = 935 °C) in addition to the reagents (PbO, m.p. = 888 °C) that formed a liquid phase in the (1-x)PHf-xPZnW system at high temperatures. The liquid phase can be clearly observed at the grain boundaries in the ceramics of \( x \geq 0.10 \), as shown in Fig. S3-B. The average grain size increases with the increase in PZnW amount, as the liquid phase at the grain boundaries accelerates grain growth. However, a higher PZnW content inhibits grain growth and results in smaller grain sizes. Fig. S3-C presents the grain size distribution of the (1-x)PHf-xPZnW ceramics with different PZnW contents. The average grain size first increases and then decreases as the \( x \) value increases. The ceramics with \( x = 0.05 \) and 0.10 show a more uniform grain size distribution and dense microstructure, which provide a basis for achieving high energy storage and electric field-induced strain performance under relatively low electric fields.
Fig. S3-A. Microstructure of the surfaces of the (1-x)PHf-xPZnW ceramics with (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$, and (e) $x = 0.20$. Fig. S3-B. Microstructure of the fractures of the (1-x)PHf-xPZnW ceramics with (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$, (d) $x = 0.15$, and (e) $x = 0.20$. The liquid phases in the grain boundary are marked by the cycles. Fig. S3-C. (a)-(e) The average grain size distributions of the (1-x)PHf-xPZnW ceramics with different PZnW contents.

Fig. S4(a) - (e) illustrates the $P-E$ hysteresis loops and the corresponding current versus electric field ($I-E$) curves of the (1-x)PHf-xPZnW ceramics under ±200 kV/cm (10 Hz) at room temperature. An electric field of ±200 kV/cm is insufficient to induce
the AFE-FE phase transition in the pure PHf ceramic due to its large $E_{cr}$. As a result, the $P$-$E$ loop exhibits a linear behavior, and the $I$-$E$ curves lack significant peaks, leading to a small maximum electric field-induced polarization of ±3.93 μC/cm$^2$. This unfavorable outcome hampers energy storage capabilities. In contrast, the (1-$x$)PHf-$x$PZnW ceramic samples with $x = 0.05 \sim 0.20$ possess typical double $P$-$E$ hysteresis loops with a high $P_{max}$ and a low $P_r$, fully displaying the AFE characteristics.

**Fig. S4.** (a) - (e) $P$-$E$ loops and the corresponding $I$-$E$ curves of the (1-$x$)PHf-$x$PZnW ceramics measured at 10 Hz.

**Fig. S5** presents the enlarged view of the XRD patterns of the (1-$x$)PHf-$x$PZnW ceramics with different PZnW contents. It is observed that the intensity of the $1/4(hkl)_{pc}$ superlattice reflection peaks slightly decreases with the increase of PZnW content. This trend suggests that the substitution of Hf$^{4+}$ by $(Zn_{1/2}W_{1/2})^{4+}$ reduces the driving force for the antiparallel displacement of Pb$^{2+}$ along the [110]$_{pc}$ direction, indicating some degrees of dipole frustration. Additionally, notable changes are observed in a new $1/2(hkl)_{pc}$ superlattice reflection peak at $(3/2,1/2,0)_{pc}$ (marked as red pentagrams) in the (1-$x$)PHf-$x$PZnW solid solutions, particularly with a higher PZnW content ($x \geq 0.10$).
These changes suggest the formation of partial chemical ordering on the B site due to the addition of PZnW.

Fig. S5. Enlarged view of the XRD patterns of the (1-x)PHf-xPZnW ceramics with different PZnW contents at room temperature.

To determine the local structural evolution and the chemical ordering of the (1-x)PHf-xPZnW ceramics, XRD patterns, and Raman spectra are measured from 10 to 40 degrees and from 50 to 1000 cm\(^{-1}\) at RT, respectively. Because of the very low intensities of the diffraction peaks associated with the chemical ordering, the scanning speed in the XRD experiment was set as slow as 3500 s per step. The results are shown in Fig. S6(a) and (b). As shown in Fig. S5 and Fig. S6(a), a new 1/2\((hkl)_{pc}\) superlattice reflection peak (marked as red pentagrams) associated with the chemical ordering of B site is obviously observed in the (1-x)PHf-xPZnW solid solutions with a high PZnW content \((x \geq 0.10)\), implying that the substitution of PZnW leads to a partial chemical ordering on the B site. In addition, the Raman spectra of (1-x)PHf-xPZnW ceramics are illustrated in Fig. S6(b). The Raman spectra of the (1-x)PHf-xPZnW solid solution exhibit similarities to that of pure PHf, indicating that the substitution of PZnW does
not change the crystal structure symmetry of PHf in the range of \( x = 0.00 \sim 0.20 \). Among the Raman peaks, one marked with the dark-blue arrow at 122 cm\(^{-1}\) associated with the oxygen octahedral tilt vibration exists in all of the composition, and its intensity and wavenumber do not vary obviously with increasing PZnW content. However, additional Raman peaks marked by the red arrows at around 842 and 927 cm\(^{-1}\) are activated for the \( x = 0.05 \sim 0.20 \). These peaks are attributed to the partial chemical ordering on the B site, resulting from the substitution of the Zn\(^{2+}\) and W\(^{6+}\) ions for the Hf\(^{4+}\) ion. The intensity of those peaks increases with increasing PZnW content, indicating that the degree of order is enhanced by the substitution of PZnW for PHf. Those peaks can be assigned to the stretching of the highly rigid Zn-O-W bonds consisting, in fact, of a totally symmetric breathing vibration of the oxygen octahedra.

Compared to XRD diffraction, Raman spectroscopy is especially sensitive to small domains. Therefore, Raman scattering is capable of detecting B-site ordering even in the composition with low PZnW content, where the B-site ordering domains are too small to be detected by XRD.
**Fig. S6.** (a) The (1/2,1/2,1/2)_{PC} superlattice reflection peaks of the (1-x)PHf-xPZnW solid solutions were revealed by a very slow scan on a laboratory X-ray diffractometer. (b) Room temperature Raman spectra of the (1-x)PHf-xPZnW ceramics.

**Fig. S7** shows the temperature dependence of the dielectric properties from RT to 300 °C for (1-x)PHf-xPZnW ceramics with different compositions upon heating. It is evident that all the ceramic samples exhibit two dielectric peaks, corresponding to the phase transitions from the AFE_{I} (O_{1}) phase to the AFE_{II} (O_{2}) IM phase, and subsequently to the PE_{C} phase. Meanwhile, both phase transition temperatures decrease with progressively PZnW content. It is worth mentioning that no obvious frequency dispersion of the maximum dielectric constant is observed for any of the samples, although there is a slight decrease with increasing frequency.

**Fig. S7.** (a)-(e) Temperature dependence of the dielectric properties of the (1-x)PHf-xPZnW ceramics (x = 0.00, 0.05, 0.10, 0.15, and 0.20) measured at various frequencies upon heating.

**Fig. S8** shows the P-E hysteresis loops of the (1-x)PHf-xPZnW ceramics measured at RT, and elevated temperatures of 140, 170, and 210 °C. The measurements were
conducted under an applied electric field of $\pm 100$ kV/cm at 10 Hz. All compositions exhibit similar trends with increasing temperature, except for pure PHf, which is due to the higher $E_{cr}$ of PHf. It is noteworthy that the IM phase of all compositions exhibits AFE characteristics.

**Fig. S8.** (a)-(e) $P$-$E$ loops of the (1-$x$)PHf-$x$PZnW ceramics measured at different temperatures under 10 Hz.
Table S2. Lattice parameters in the various phases of the $x = 0.10$ ceramic at different temperatures.

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<th>Lattice parameters</th>
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