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Supplementary information

Large electrocaloric effect with high thermal and electric field cycling stability in solution-processed Y:HfO_2 thin films

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Table S1: The references for the data plotted in the comparison in Figure 1 in the article.

Code used	Material	T_m(K)	ΔT (K)	Pb-free	Reference
Single Crystals					
BT	$BaTiO_3$	288	1.33	✓	[1]
SBN	Ce-$Sr_xBa_{1-x}Nb_2O_6$	334	0.85	✓	[2]
BT	$BaTiO_3$	402	0.9	✓	[3]
PMN-PT	$0.7Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.3PbTiO_3$	403	2.7	×	[4]
BT	$BaTiO_3$	283	1.4	✓	[5]
BT–BMT	$BaTiO_3$-$Bi(Mg_{1/2}Ti_{1/2})O_3$	416	1.21	✓	[6]
BHT	$BaHf_{0.1}1Ti_{0.89}O_3$	343	0.35	✓	[7]
PST	$Pb(Sc_{1/2}Ta_{1/2})O_3$	300	3.7	×	[8]
BST	$Ba_{0.65}Sr_{0.35}TiO_3$	343	2.1	✓	[9]
PLZST	$Pb_{0.97}La_{0.02}(Zr_{0.80}Sn_{0.14}Ti_{0.06})O_3$	313	-12.9	×	[10]
PLZST	$Pb_{0.97}La_{0.02}(Zr_{0.80}Sn_{0.14}Ti_{0.06})O_3$	323	-14.1	×	[10]
BNT–BT	$0.94(Bi_{0.5}Na_{0.5})TiO_3$–$0.06BaTiO_3$	339	3.2	✓	[11]
PMN-PT	$0.7[PbMg_{1/3}Nb_{2/3}O_3]$-$0.3[PbTiO_3]$	429	2.7	×	[12]
Thin films					
HYO(ECE1)	Y-HfO_2	358	24.84	✓	This work
HYO(ECE2)	Y-HfO_2	358	24.35	✓	This work
HYO(ECE3)	Y-HfO_2	358	19.41	✓	This work
PZT	$PbZr_{0.95}Ti_{0.05}O_3$	495	12	×	[13]
PLZT(8/65/35)	$(Pb_{0.88}La_{0.08})(Zr_{0.65}Ti_{0.35})O_3$	318	40	×	[14]
PBZ*	$Pb_{0.8}Ba_{0.2}ZrO_3$	290	45.3	×	[15]
HSO	Si-HfO2	298	9.5	✓	[16]
HAO	Al-HfO2	295	5.7	✓	[17]
HGO	Gd-HfO2	295	3.1	✓	[17]
PMN–PT	$0.65[PbMg_{1/3}Nb_{2/3}O_3]$-$0.35[PbTiO_3]$	413	31	×	[18]
PLZST	$Pb_{0.97}La_{0.02}(Zr_{0.75}Sn_{0.2}Ti_{0.07})O_3$	306	33	×	[19]
HZO	$Hf_{0.2}Zr_{0.8}O_2$	298	13.4	✓	[20]
HZO	$Hf_{0.3}Zr_{0.7}O_2$	448	8.9	✓	[20]
Polymers					
P(VDF-TrFE-CFE)	P(VDF-TrFE-CFE)	303	15	✓	[21]
P(VDF-TrFE)	P(0.55VDF-0.45TrFE)	353	12.6	✓	[22]
P(VDF-TrFE)	P(0.7VDF–0.3TrFE)	390	21.2	✓	[23]
P(VDF-TrFE-CFE)	P(0.562VDF-0.363TrFE-0.076CFE)	350	21.6	✓	[23]
Special form					
Cascade	P(VDF-TrFE-CFE)	300	8.7	✓	[24]
Nanocubes	P(VDF-TrFE-CFE)/ $Ba_{0.67}Sr_{0.33}TiO_3$	316	9.1	✓	[25]
Nanowire	P(VDF-TrFE-CFE)/ $Ba_{0.67}Sr_{0.33}TiO_3$	300	32	✓	[25]
Molecular	Cyclohexylmethylammonium bromide	364	4.2	✓	[26]

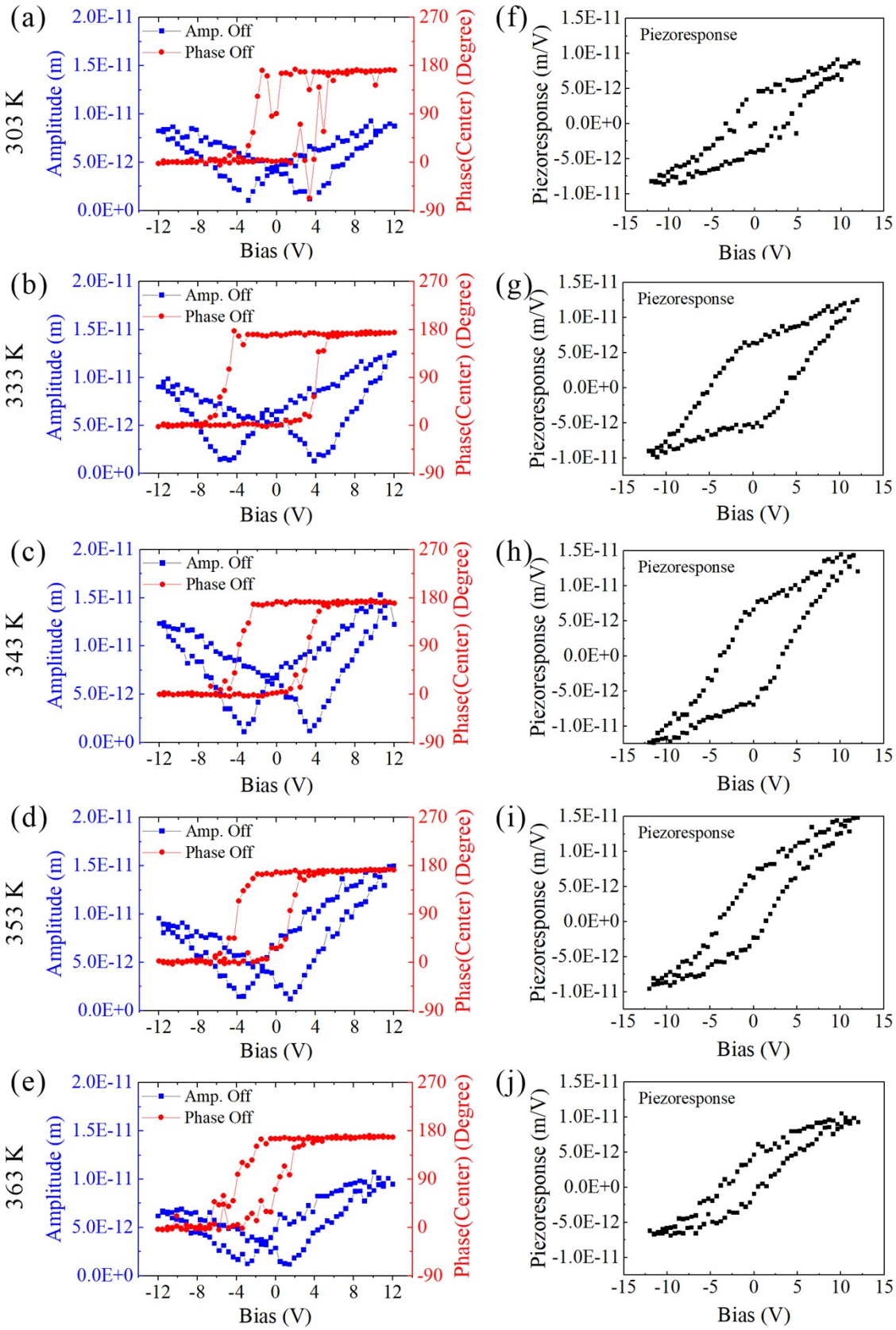
(a)
303 K
Amplitude (m)
Phase(Center) (Degree)
Amp. Off
Phase Off
Bias (V)
(b)
333 K
(c)
343 K
(d)
353 K
(e)
363 K
(f)
Piezoresponse
Piezoresponse (m/V)
(g)
(h)
(i)
(j)

Figure S1: (a)-(e) PFM local hysteresis at temperature 303, 333, 343, 353 and 363 K. (f)-(j) Local piezo-response at those specified temperatures.

References

1. Li, J., et al., *Near-Room-Temperature Large Electrocaloric Effect in Barium Titanate Single Crystal Based on the Electric Field–Temperature Phase Diagram.* physica status solidi (RRL) – Rapid Research Letters, 2021. **15**(8).
2. Le Goupil, F., et al., *Effect of Ce doping on the electrocaloric effect of SrxBa1−xNb2O6 single crystals.* Applied Physics Letters, 2014. **104**(22).222911.
3. Moya, X., et al., *Giant electrocaloric strength in single-crystal $BaTiO_3$.* Adv Mater, 2013. **25**(9).1360-5.
4. Chukka, R., et al., *Enhanced cooling capacities of ferroelectric materials at morphotropic phase boundaries.* Applied Physics Letters, 2011. **98**(24).242902.
5. Bai, Y., et al., *The electrocaloric effect around the orthorhombic- tetragonal first-order phase transition in $BaTiO_3$.* AIP Advances, 2012. **2**(2).022162.
6. Li, M.-D., et al., *Giant electrocaloric effect in $BaTiO_3$–$Bi(Mg_{1/2}Ti_{1/2})O_3$ lead-free ferroelectric ceramics.* Journal of Alloys and Compounds, 2018. **747**.1053-1061.
7. Li, J., et al., *Large room-temperature electrocaloric effect in lead-free $BaHf_xTi_{1-x}O_3$ ceramics under low electric field.* Acta Materialia, 2016. **115**.58-67.
8. Nouchokgwe, Y., et al., *Giant electrocaloric materials energy efficiency in highly ordered lead scandium tantalate.* Nat Commun, 2021. **12**(1).3298.
9. Liu, X.Q., et al., *Enhanced Electrocaloric Effects in Spark Plasma-Sintered $Ba_{0.65}Sr_{0.35}TiO_3$-Based Ceramics at Room Temperature.* Journal of the American Ceramic Society, 2013. **96**(4).1021-1023.
10. Zhuo, F., et al., *Giant Negative Electrocaloric Effect in (Pb,La)(Zr,Sn,Ti)O3 Antiferroelectrics Near Room Temperature.* ACS Appl Mater Interfaces, 2018. **10**(14).11747-11755.
11. Zhang, L., et al., *Electrocaloric refrigeration capacity in BNT-based ferroelectrics benefiting from low depolarization temperature and high breakdown electric field.* Journal of Materials Chemistry A, 2021. **9**(21).12772-12781.
12. Rožič, B., et al., *Influence of the critical point on the electrocaloric response of relaxor ferroelectrics.* Journal of Applied Physics, 2011. **110**(6).
13. Mischenko, A.S., et al., *Giant electrocaloric effect in thin-film $PbZr_{0.95}Ti_{0.05}O_3$.* Science, 2006. **311**(5765).1270-1.
14. Lu, S.G., et al., *Organic and inorganic relaxor ferroelectrics with giant electrocaloric effect.* Applied Physics Letters, 2010. **97**(16).162904.
15. Peng, B., H. Fan, and Q. Zhang, *A Giant Electrocaloric Effect in Nanoscale Antiferroelectric and Ferroelectric Phases Coexisting in a Relaxor $Pb_{0.8}Ba_{0.2}ZrO_3$ Thin Film at Room Temperature.* Advanced Functional Materials, 2013. **23**(23).2987-2992.
16. Hoffmann, M., et al., *Ferroelectric phase transitions in nanoscale HfO_2 films enable giant pyroelectric energy conversion and highly efficient supercapacitors.* Nano Energy, 2015. **18**.154-164.

17. Park, M.H., et al., *Effect of acceptor doping on phase transitions of HfO_2 thin films for energy-related applications.* Nano Energy, 2017. **36**.381-389.
18. Saranya, D., et al., *Electrocaloric effect of PMN-PT thin films near morphotropic phase boundary.* Bulletin of Materials Science, 2009. **32**(3).259-262.
19. Hao, X., Y. Zhao, and Q. Zhang, *Phase Structure Tuned Electrocaloric Effect and Pyroelectric Energy Harvesting Performance of (Pb0.97La0.02)(Zr,Sn,Ti)O3Antiferroelectric Thick Films.* The Journal of Physical Chemistry C, 2015. **119**(33).18877-18885.
20. Park, M.H., et al., *Toward a multifunctional monolithic device based on pyroelectricity and the electrocaloric effect of thin antiferroelectric $Hf_xZr_{1-x}O_2$ films.* Nano Energy, 2015. **12**.131-140.
21. Li, X., et al., *Tunable temperature dependence of electrocaloric effect in ferroelectric relaxor poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene terpolymer.* Applied Physics Letters, 2011. **99**(5).052907.
22. Neese, B., et al., *Large electrocaloric effect in ferroelectric polymers near room temperature.* Science, 2008. **321**(5890).821-3.
23. Liu, P.F., et al., *Huge electrocaloric effect in Langmuir–Blodgett ferroelectric polymer thin films.* New Journal of Physics, 2010. **12**(2).023035.
24. Meng, Y., et al., *A cascade electrocaloric cooling device for large temperature lift.* Nature Energy, 2020. **5**(12).996-1002.
25. Zhang, G., et al., *Colossal Room-Temperature Electrocaloric Effect in Ferroelectric Polymer Nanocomposites Using Nanostructured Barium Strontium Titanates.* ACS Nano, 2015. **9**(7).7164-74.
26. Xu, H., et al., *A Metal-Free Molecular Antiferroelectric Material Showing High Phase Transition Temperatures and Large Electrocaloric Effects.* J Am Chem Soc, 2021. **143**(35).14379-14385.