SUPPORTING INFORMATION

A-site Ordered Double Perovskite $CaMnTi_2O_6$ as a Multifunctional Piezoelectric and Ferroelectric-Photovoltaic Material

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Predicted crystal structures of $CaMnTi_2O_6$

Table S1: Comparison between the calculated and measured crystallographic parameters for ferroelectric $P4_2mc$ $CaMnTi_2O_6$ phase. Experimental results are obtained from Ref.[1]

PBEsol: a = b = 7.47 Å, c = 7.59 Å, V = 423.59 Å^3 Exp: a = b = 7.54 Å, c = 7.60 Å, V = 431.81 Å^3						
	Exp			PBEsol		
Atom	x	y	z	x	y	z
Ca (2a)	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0052
Ca (2b)	0.5000	0.5000	0.0494	0.5000	0.5000	0.0501
Mn1 (2c)	0.0000	0.5000	0.5209	0.0000	0.5000	0.5183
Mn2 (2c)	0.0000	0.5000	0.0740	0.0000	0.5000	0.0633
Ti (8f)	0.2565	0.2452	0.2821	0.2567	0.2457	0.2810
O (4e)	0.3025	0.5000	0.3015	0.3096	0.5000	0.3048
O (4d)	0.2952	0.0000	0.8246	0.2996	0.0000	0.8372
O (4d)	0.1976	0.0000	0.2318	0.1906	0.0000	0.2332
O (4e)	0.2111	0.5000	0.7040	0.2049	0.5000	0.6921
O (8f)	0.2005	0.2992	0.0158	0.1905	0.3101	0.0187

Table S2: Calculated crystallographic parameters for paraelectric $P4_2/nmc$ $CaMnTi_2O_6$ phase.

PBEsol: a = b = 7.48 Å, c = 7.55 Å, V = 422.56 Å^3 Exp: a = b = 7.59 Å, c = 7.60 Å, V = 438.19 Å^3			
Atom	x	y	z
Ca (4d)	0.2500	0.2500	0.2218
Mn (2a)	0.2500	0.7500	0.2500
Mn (2b)	0.7500	0.2500	0.2500
Ti (8e)	0.0000	0.0000	0.0000
O (8g)	0.2500	0.4410	0.9634
O (8g)	0.2500	0.5458	0.5741
O (8f)	0.0611	0.9389	0.2500

Table S3: Calculated Born effective charge tensors (Z^*) of each ion and the cation polar displacement amplitudes respective to the center of the oxygen cages (along the polar axis) for ground-state $P4_2mc$ $CaMnTi_2O_6$ phase. Ca_1 and Ca_2 cations are from the neighboring Ca-Ca columns. Mn cations refer to the planar coordinated ones. Note: there are 8 Ti cations, 2 Ca_1, Ca_2 and planar-coordinated Mn cations respectively in one $CaMnTi_2O_6$ unit cell.

	Z^*_{11}	Z^*_{22}	Z^*_{33}	displacement (Å)
$Ca_1\times2$	2.34	2.50	2.59	0.34
$Ca_2\times2$	2.50	2.34	2.59	-0.26
Planar Mn×2	2.41	2.38	2.66	0.35
Ti×8	6.45	7.04	5.83	0.10
O×24	-2.38	-2.34	-2.40	–

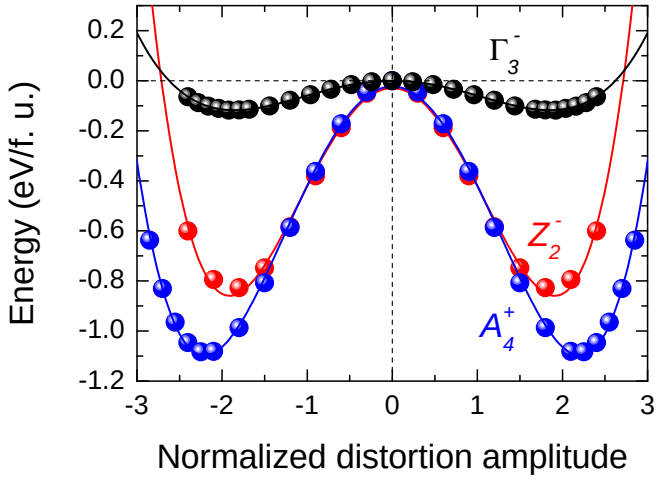

Figure S1: The calculated energy evolution of $CaMnTi_2O_6$ as a function of the distortion magnitude by freezing in the displacements of each structural distortion mode into the high-symmetry $P4/mmm$ phase.

References

(1) Aimi, A.; Mori, D.; Hiraki, K.-i.; Takahashi, T.; Shan, Y. J.; Shirako, Y.; Zhou, J.; Inaguma, Y. High-Pressure Synthesis of A-Site Ordered Double Perovskite $CaMnTi_2O_6$ and Ferroelectricity Driven by Coupling of A-Site Ordering and the Second-Order Jahn-Teller Effect. *Chem. Mater.* **2014**, *26*, 2601–2608.