Supporting Information

Recycling hazardous and energy-demanding piezoelectric ceramics using oxide-halide perovskite upside-down composite method

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Details of fabricated ceramic and composite samples

Details of the fabricated samples including amount of sintered crushed filler used to prepare each composite where applicable, weight, and dimensions are listed in Table S1. Pictures of the sintered ceramic pellets and the upside-down composites made with corresponding fillers are shown in Figure S1.

Table S1. Details of the fabricated ceramic pellets and composite samples

Sample ID	Sample description	Amount of filler used in each composite sample (g)	Weight (g)	Thickness (mm)	Diameter (mm)
BT-P	$BaTiO_3$ ceramic pellet	-	0.23	0.738 ± 0.002	8.21 ± 0.00
KNBNNO-P	$(K_{0.52}Na_{0.38}Ba_{0.03})(Nb_{0.985}Ni_{0.015})O_{2.9575}$ ceramic pellet	-	0.22	1.003 ± 0.002	8.29 ± 0.01
H-PZT-P	Hard-type PZT ceramic pellet	-	0.48	0.967 ± 0.003	8.43 ± 0.01
S-PZT-P	Soft-type PZT ceramic pellet	-	0.74 ± 0.02	1.100 ± 0.061	10.92 ± 0.11
BT-C	$BaTiO_3$ composite	0.6	0.63 ± 0.18	1.737 ± 0.384	10.07 ± 0.01
KNBNNO-C	$(K_{0.52}Na_{0.38}Ba_{0.03})(Nb_{0.985}Ni_{0.015})O_{2.9575}$ composite	0.5	0.55 ± 0.06	1.931 ± 0.180	10.06 ± 0.02
H-PZT-C	Hard-type PZT composite	0.8	0.76 ± 0.05	1.616 ± 0.105	10.06 ± 0.02
S-PZT-C	Soft-type PZT composite	0.8	0.82 ± 0.02	1.706 ± 0.043	10.08 ± 0.01

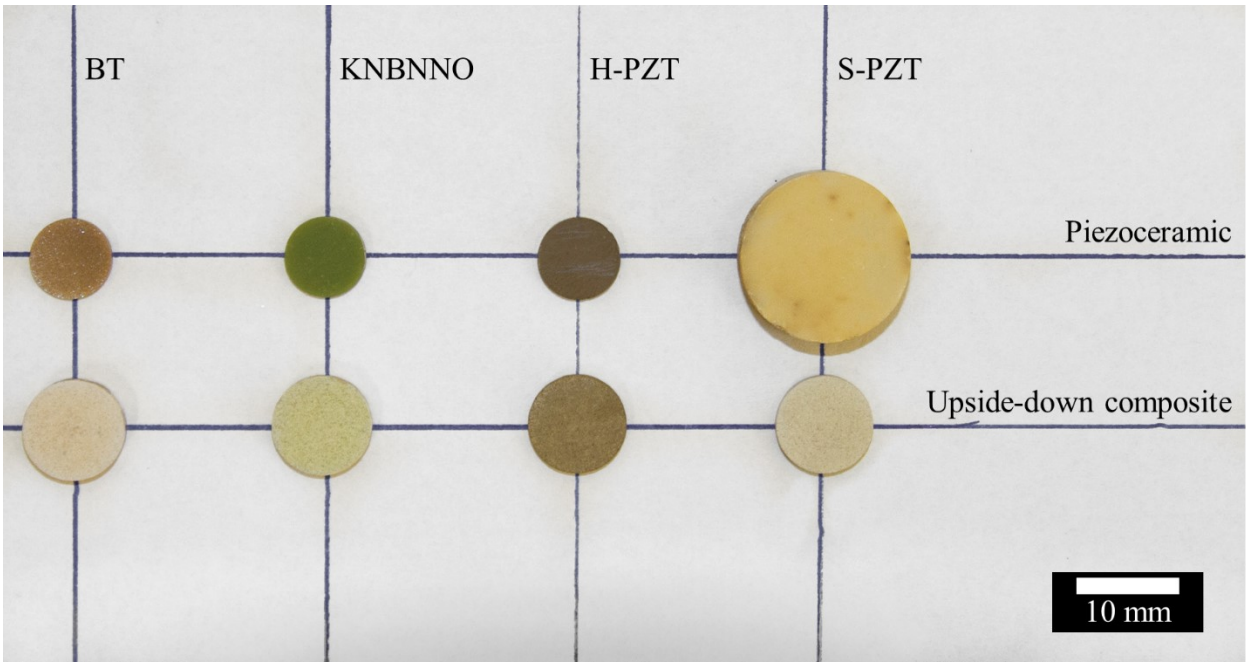

Figure S1. Pictures of sintered ceramic pellets and composite samples fabricated in this work.

XRD results of ceramic fillers

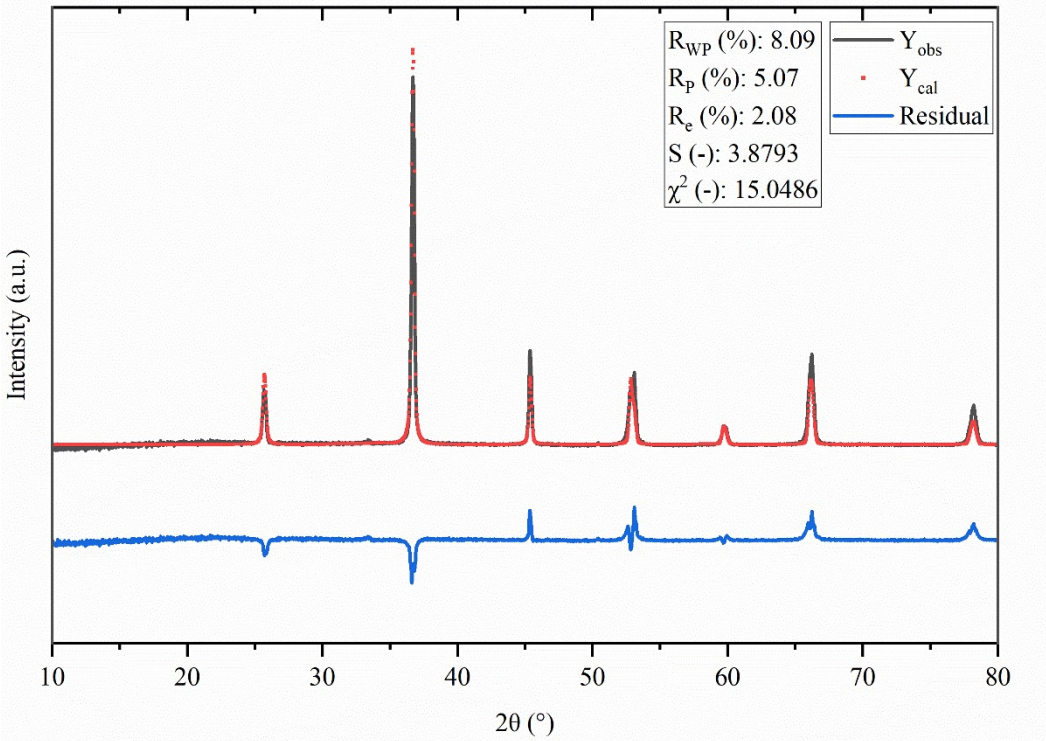

Figure S2. XRD reflections, calculated curve and residual error after Rietveld refinement, and the refinement parameters obtained for the BT filler

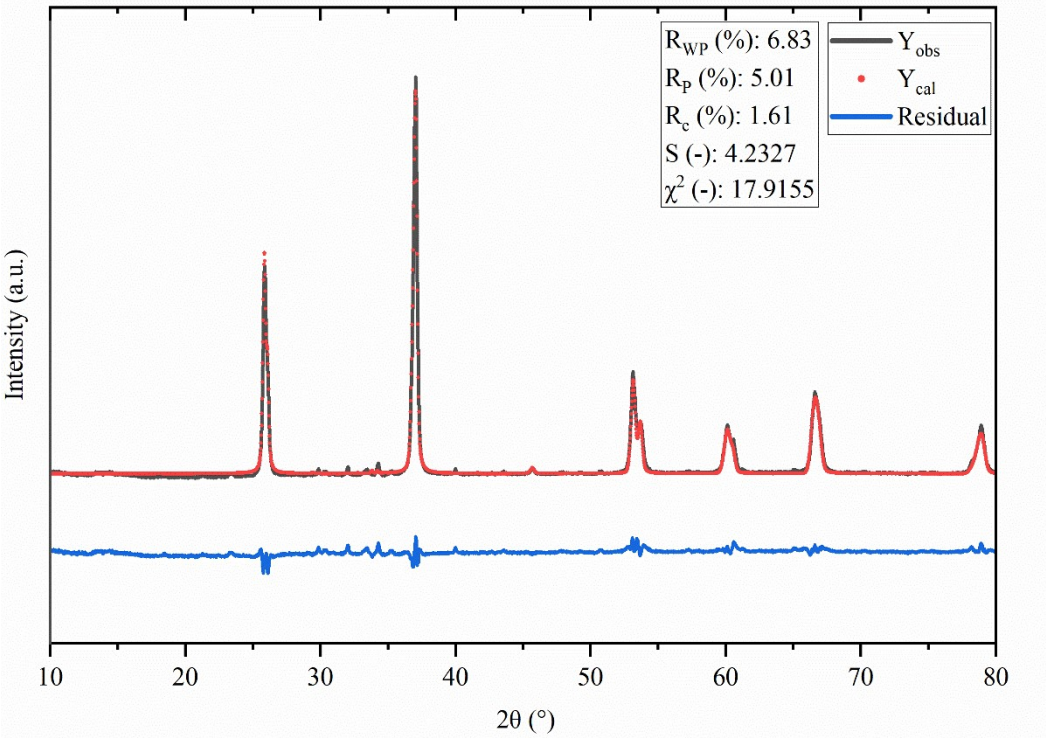

Figure S3. XRD reflections, calculated curve and residual error after Rietveld refinement, and the refinement parameters obtained for the KNBNNO filler

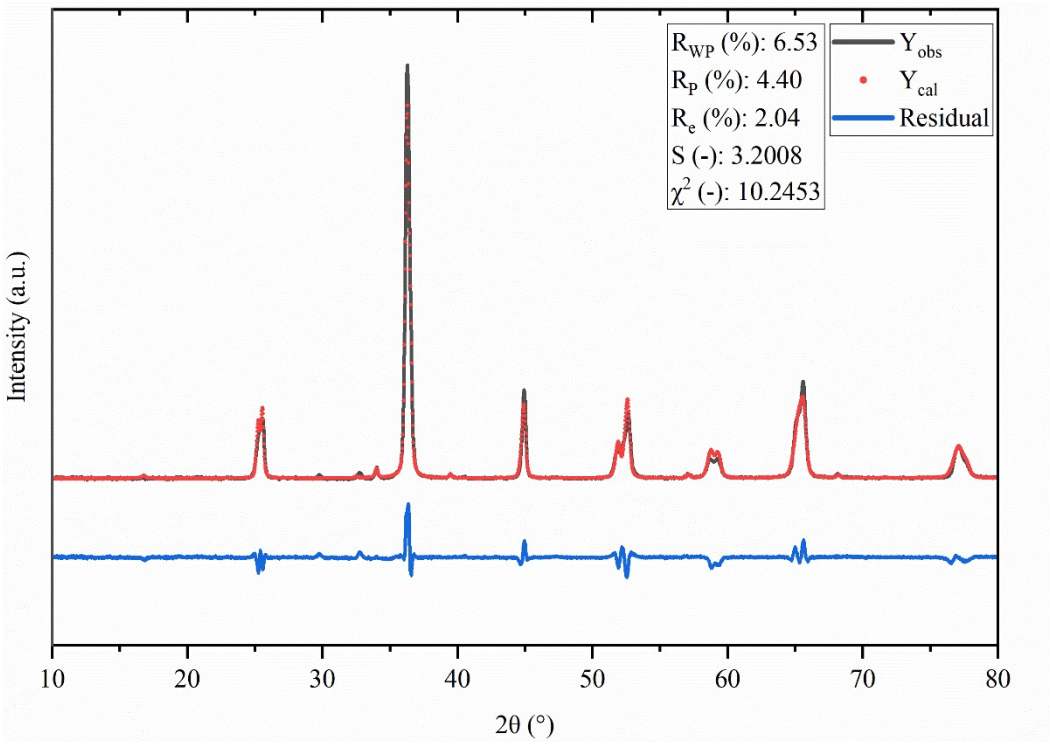

Figure S4. XRD reflections, calculated curve and residual error after Rietveld refinement, and the refinement parameters obtained for the H-PZT filler

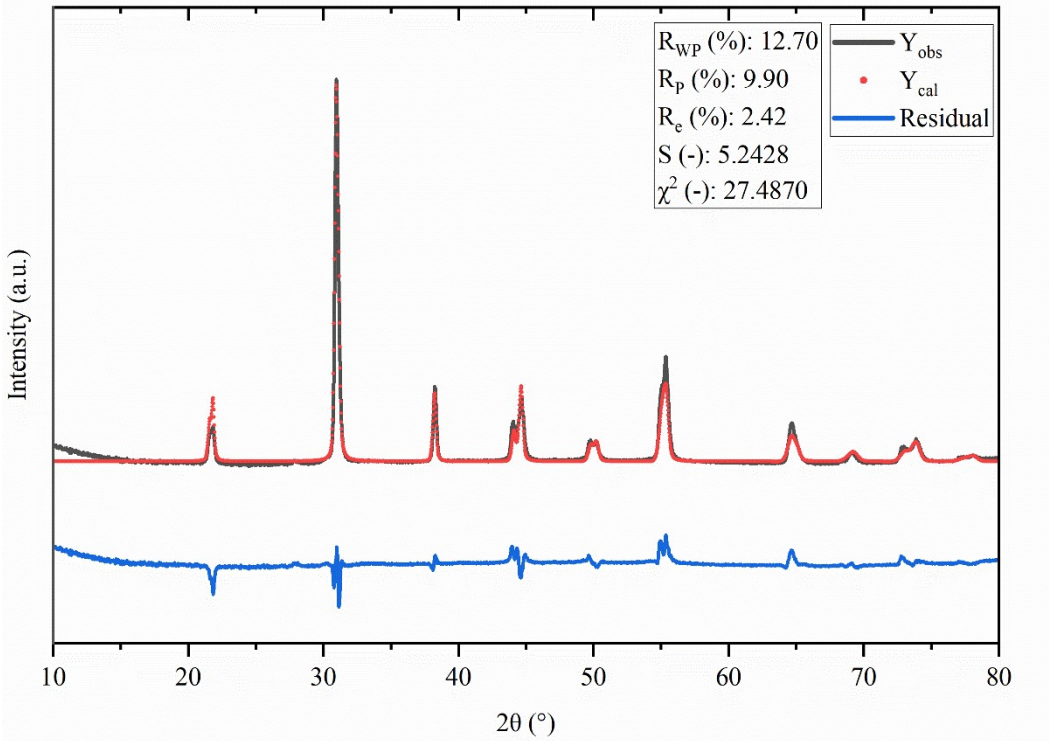

Figure S5. XRD reflections, calculated curve and residual error after Rietveld refinement, and the refinement parameters obtained for the S-PZT filler

Table S2. List of XRD reflections for BT

2θ (°)	**Intensity (normalized)**	**d-space (Å)**	**Diffraction plane**
25.73	16.6	4.0179	Amm2 (0 1 1)
25.85	13.7	3.9995	Amm2 (1 0 0)
31.82	0.3	3.2633	I4/mmm (1 1 0)
33.40	1.0	3.1125	Unidentified
34.07	0.4	3.0530	I4/mmm (1 0 3)
36.70	30.9	2.8412	Amm2 (0 2 0)
36.70	30.6	2.8410	Amm2 (0 0 2)
36.79	100.0	2.8345	Amm2 (1 1 1)
45.43	12.6	2.3162	Amm2 (1 2 0)
45.44	12.9	2.3161	Amm2 (1 0 2)
45.61	0.1	2.3075	I4/mmm (2 0 0)
52.88	24.5	2.0090	Amm2 (0 2 2)
53.14	12.1	1.9997	Amm2 (2 0 0)
58.14	0.1	1.8409	I4/mmm (2 1 3)
59.71	1.3	1.7969	Amm2 (0 3 1)
59.71	1.5	1.7968	Amm2 (0 1 3)
59.77	4.0	1.7952	Amm2 (1 2 2)
59.95	2.5	1.7903	Amm2 (2 1 1)
66.15	10.1	1.6391	Amm2 (1 3 1)
66.15	9.8	1.6390	Amm2 (1 1 3)
66.32	5.8	1.6353	Amm2 (2 2 0)
66.32	5.8	1.6353	Amm2 (2 0 2)
78.05	1.8	1.4206	Amm2 (0 4 0)
78.05	1.8	1.4205	Amm2 (0 0 4)
78.26	7.1	1.4173	Amm2 (2 2 2)

Table S3. Phase information of the assigned phases according to the XRD reflections from the BT filler

Parameter	**Primary phase (¤)**	**Secondary phase (#)**
Chemical formula	$Ba(Ti_{0.95}Zr_{0.05})O_3$	Ba_2ZrO_4
Composition	Ba O_3 $Ti_{0.95}$ $Zr_{0.05}$	Ba O_4 Zr
Z-value	2	2
Concentration (%)	99.5 (4)	0.5 (4)
RIR value	4.654	5.656
DB card no.	00-066-0857	04-005-5869
Reference	0PCOMC	RJICAQ
Crystal system	Orthorhombic	Tetragonal
Space group	38: Amm2	139: I4/mmm
a (ang.)	4.0012	4.1955
b (ang.)	5.6932	4.1955
c (ang.)	5.6840	13.3675
α (ang.)	90	90
β (ang.)	90	90
γ (ang.)	90	90
Calculated density (g/cm^3)	5.6265	6.0675
Mass absorption coefficient (cm^2/g)	365.077	347.2666
Phase reg. method	ICDD (PDF-4+ 2023)	ICDD (PDF-4+ 2023)
Molar ratio (%)	99.7 (2)	0.3 (2)

Table S4. List of XRD reflections for KNBNNO

2θ (°)	**Intensity (normalized)**	**d-space (Å)**	**Diffraction plane**
25.85	64.0	3.9994	Amm2 (0 1 1)
26.09	31.3	3.9633	Amm2 (1 0 0)
29.49	0.2	3.5146	P4bm (3 2 0)
30.36	1.1	3.4162	Unidentified
32.80	0.1	3.1680	P4bm (4 0 0)
33.84	0.9	3.0734	P4bm (4 1 0)
34.23	0.8	3.0391	P4bm (2 1 1)
34.85	0.2	2.9868	P4bm (3 3 0)
36.80	26.2	2.8338	Amm2 (0 0 2)
36.80	1.5	2.8336	P4bm (4 2 0)
36.96	24.9	2.8222	Amm2 (0 2 0)
37.05	100.0	2.8151	Amm2 (1 1 1)
37.17	2.6	2.8066	P4bm (2 2 1)
39.02	1.4	2.6783	P4bm (3 1 1)
41.67	0.1	2.5151	P4bm (3 2 1)
45.66	1.6	2.3052	Amm2 (1 0 2)
45.79	0.3	2.2989	Amm2 (1 2 0)
53.14	29.7	1.9997	Amm2 (0 2 2)
53.66	15.8	1.9816	Amm2 (2 0 0)
59.90	3.8	1.7915	Amm2 (0 1 3)
60.12	3.8	1.7856	Amm2 (0 3 1)
60.13	7.6	1.7853	Amm2 (1 2 2)
60.50	7.3	1.7756	Amm2 (2 1 1)
66.45	12.6	1.6325	Amm2 (1 1 3)
66.65	11.4	1.6280	Amm2 (1 3 1)
66.84	5.6	1.6240	Amm2 (2 0 2)
66.94	5.4	1.6218	Amm2 (2 2 0)
78.29	2.1	1.4169	Amm2 (0 0 4)
78.67	3.0	1.4111	Amm2 (0 4 0)
78.91	10.7	1.4076	Amm2 (2 2 2)

Table S5. Phase information of the assigned phases according to the XRD reflections from the KNBNNO filler

Parameter	**Primary phase (¤)**	**Secondary phase (#)**
Chemical formula	$(K_{0.49}Na_{0.49}Ba_{0.02})(Nb_{0.99}Ni_{0.01})O_3$	$Ba_3Nb_{4.67}Ni_{0.33}O_{15}$
Composition	$Ba_{0.02}\,K_{0.49}\,Na_{0.49}\,Nb_{0.99}\,Ni_{0.01}\,O_3$	$Ba_3\,Nb_{4.67}\,Ni_{0.33}\,O_{15}$
Z-value	2	2
Concentration (%)	99.2	0.8
RIR value	3.664	2.802
DB card no.	01-087-7260	04-006-0584
Reference	432352	550973
Crystal system	Orthorhombic	Tetragonal
Space group	38: Amm2	100: P4bm
a (ang.)	3.9633	12.6721
b (ang.)	5.6444	12.6721
c (ang.)	5.6676	3.6006
α (ang.)	90	90
β (ang.)	90	90
γ (ang.)	90	90
Calculated density (g/cm^3)	4.5486	6.413
Mass absorption coefficient (cm^2/g)	150.1362	266.2282
Phase reg. method	ICDD (PDF-4+ 2023)	ICDD (PDF-4+ 2023)
Molar ratio (%)	99.9	0.1

Table S6. List of XRD reflections for H-PZT

2θ (°)	**Intensity (normalized)**	**d-space (Å)**	**Diffraction plane**
16.84	0.8	6.1094	Fd-3m (1 1 1)
25.28	15.4	4.0869	P4mm (0 0 1)
25.60	20.4	4.0374	P4mm (1 0 0)
29.75	1.1	3.4838	Unidentified
32.56	0.6	3.1906	Fd-3m (3 1 1)
34.05	3.0	3.0547	Fd-3m (2 2 2)
36.29	100.0	2.8722	P4mm (1 0 1)
36.52	51.8	2.8549	P4mm (1 1 0)
39.52	1.3	2.6455	Fd-3m (4 0 0)
43.24	0.2	2.4276	Fd-3m (3 3 1)
44.94	23.4	2.3404	P4mm (1 1 1)
51.92	10.8	2.0435	P4mm (0 0 2)
52.11	0.1	2.0365	Fd-3m (3 3 3)
52.60	25.0	2.0187	P4mm (2 0 0)
57.13	1.3	1.8706	Fd-3m (4 4 0)
58.76	8.0	1.8232	P4mm (1 0 2)
59.23	4.9	1.8100	P4mm (2 0 1)
59.39	3.6	1.8056	P4mm (2 1 0)
60.01	0.2	1.7887	Fd-3m (5 3 1)
65.14	11.5	1.6617	P4mm (1 1 2)
65.58	24.8	1.6516	P4mm (2 1 1)
68.21	1.0	1.5953	Fd-3m (6 2 2)
71.69	0.2	1.5274	Fd-3m (4 4 4)
77.05	8.8	1.4361	P4mm (2 0 2)
77.60	5.3	1.4274	P4mm (2 2 0)

Table S7. Phase information of the assigned phases according to the XRD reflections from the H-PZT filler

Parameter	**Primary phase (¤)**	**Secondary phase (#)**
Chemical formula	$Pb(Ti_{0.45}Zr_{0.45}Sb_{0.05}Mn_{0.05})O_3$	$Pb(Ti_{0.5}Zr_{0.5})O_3$
Composition	$Mn_{0.05}\,O_3\,Pb\,Sb_{0.05}\,Ti_{0.45}\,Zr_{0.45}$	$O_3\,Pb\,Ti_{0.5}\,Zr_{0.5}$
Z-value	1	16
Concentration (%)	98.99 (9)	1.01 (9)
RIR value	4.216	11.136
DB card no.	00-067-0380	04-014-5162
Reference	-	1217491
Crystal system	Tetragonal	Cubic
Space group	99: P4mm	227: Fd-3m, choice-2
a (ang.)	4.0374	10.5819
b (ang.)	4.0374	10.5819
c (ang.)	4.0869	10.5819
α (ang.)	90	90
β (ang.)	90	90
γ (ang.)	90	90
Calculated density (g/cm^3)	8.1414	7.2816
Mass absorption coefficient (cm^2/g)	256.0721	252.0801
Phase reg. method	ICDD (PDF-4+ 2023)	ICDD (PDF-4+ 2023)
Molar ratio (%)	98.98 (9)	1.02 (9)

Table S8. List of XRD reflections for S-PZT

2θ (°)	**Intensity (normalized)**	**d-space (Å)**	**Diffraction plane**
21.69	9.9	4.0948	P4mm (0 0 1)
21.94	17.6	4.0484	P4mm (1 0 0)
31.04	100.0	2.8789	P4mm (1 0 1)
31.22	51.8	2.8627	P4mm (1 1 0)
38.33	21.1	2.3462	P4mm (1 1 1)
44.20	9.0	2.0474	P4mm (0 0 2)
44.73	22.9	2.0242	P4mm (2 0 0)
49.70	4.5	1.8330	Unidentified
49.87	4.3	1.8271	P4mm (1 0 2)
50.24	2.9	1.8146	P4mm (2 0 1)
50.36	2.7	1.8105	P4mm (2 1 0)
55.10	10.7	1.6653	P4mm (1 1 2)
55.44	21.4	1.6559	P4mm (2 1 1)
64.70	6.1	1.4395	P4mm (2 0 2)
65.12	3.7	1.4313	P4mm (2 2 0)
69.21	1.8	1.3563	P4mm (2 1 2)
69.51	0.4	1.3512	P4mm (2 2 1)
73.10	2.6	1.2934	P4mm (1 0 3)
73.88	2.5	1.2817	P4mm (3 0 1)
73.98	2.7	1.2802	P4mm (3 1 0)
77.40	0.4	1.2321	P4mm (1 1 3)
78.16	1.3	1.2219	P4mm (3 1 1)

Table S9. Phase information of the assigned phases according to the XRD reflections from the S-PZT filler

Parameter	**Primary phase (¤)**
Chemical formula	$(Pb_{0.91}Sr_{0.06})(Ti_{0.5}Zr_{0.5})O_3$
Composition	$O_3\ Pb_{0.91}\ Sr_{0.06}\ Ti_{0.5}\ Zr_{0.5}$
Z-value	1
Concentration (%)	100
RIR value	11.202
DB card no.	01-070-6380
Reference	91813
Crystal system	Tetragonal
Space group	99: P4mm
a (ang.)	4.0484
b (ang.)	4.0484
c (ang.)	4.0948
α (ang.)	90
β (ang.)	90
γ (ang.)	90
Calculated density (g/cm^3)	7.7035
Mass absorption coefficient (cm^2/g)	167.9128
Phase reg. method	ICDD (PDF-4+ 2023)
Molar ratio (%)	100

EPMA results

Table S10. Summary of theoretical molecular weights and nominal chemical formulas calculated from EPMA results for the fabricated ceramics

Ceramic material	Constituent element	Theoretical molecular weight (g/mol)	Nominal chemical formula
BT	Ba, Sr, Ti, Zr, O	229.33 ± 2.41	$(Ba_{0.96\pm0.02}Sr_{0.005\pm0.001})(Ti_{0.97\pm0.00}Zr_{0.03\pm0.00})O_{2.97\pm0.02}$
KNBNNO	K, Na, Ba, Nb, Ni, O	172.73 ± 2.75	$(K_{0.52\pm0.06}Na_{0.30\pm0.05}Ba_{0.04\pm0.03})(Nb_{0.99\pm0.00}Ni_{0.01\pm0.00})O_{2.94\pm0.04}$
H-PZT	Pb, Zr, Ti, Sb, Mn, O	314.98 ± 5.63	$(Pb_{0.95\pm0.02})(Sb_{0.06\pm0.03}Zr_{0.44\pm0.02}Ti_{0.48\pm0.04}Mn_{0.01\pm0.00})O_{2.95\pm0.02}$
S-PZT	Pb, Zr, Ti, Sr, O	307.09 ± 4.05	$(Pb_{0.88\pm0.02}Sr_{0.07\pm0.003})(Zr_{0.54\pm0.01}Ti_{0.46\pm0.01})O_{2.95\pm0.02}$

Microstructure of upside-down composites

Microstructure of the BT composite is provided in Figure 1. FESEM (field-emission scanning electron microscope) micrographs and EDS (energy dispersive X-ray spectroscopy) maps for composites of KNBNNO, H-PZT, and S-PZT are shown in Figures S6-S8 below.

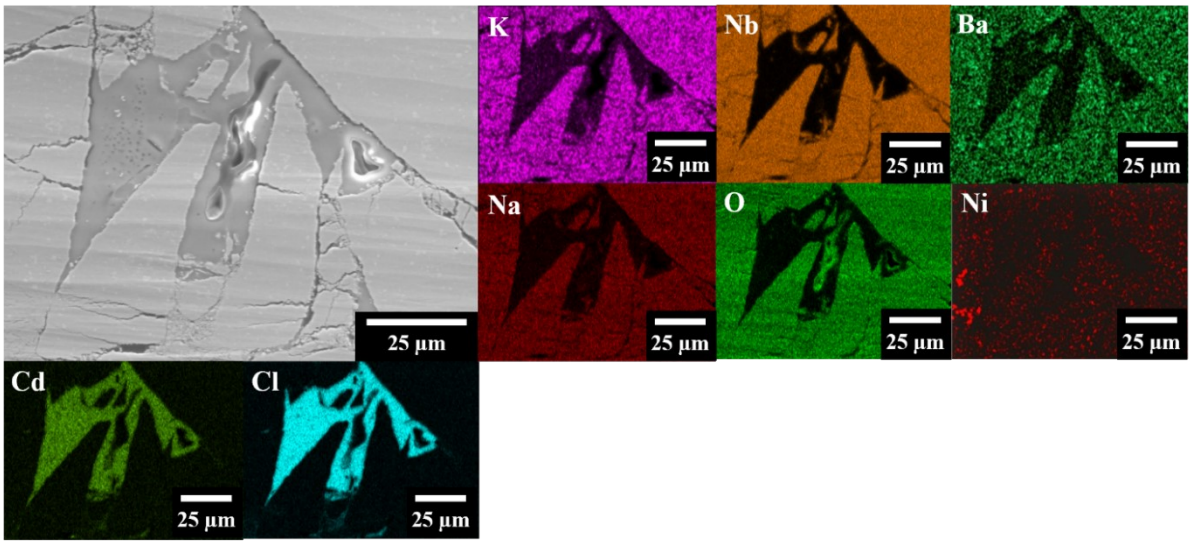

Figure S6. FESEM micrograph and EDS maps of upside-down composite KNBNNO-C

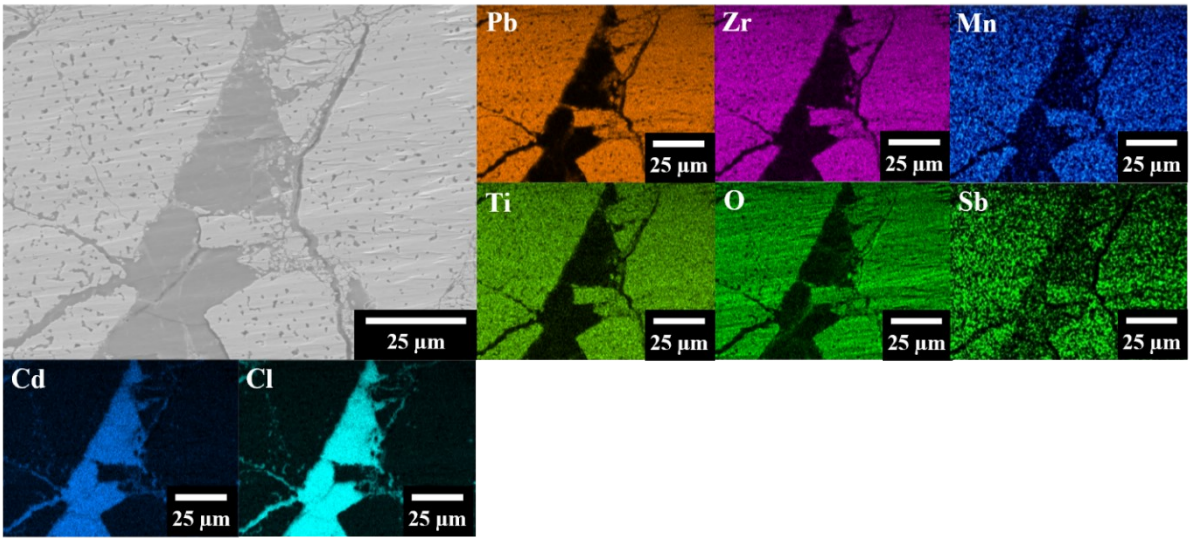

Figure S7. FESEM micrograph and EDS maps of upside-down composite H-PZT-C

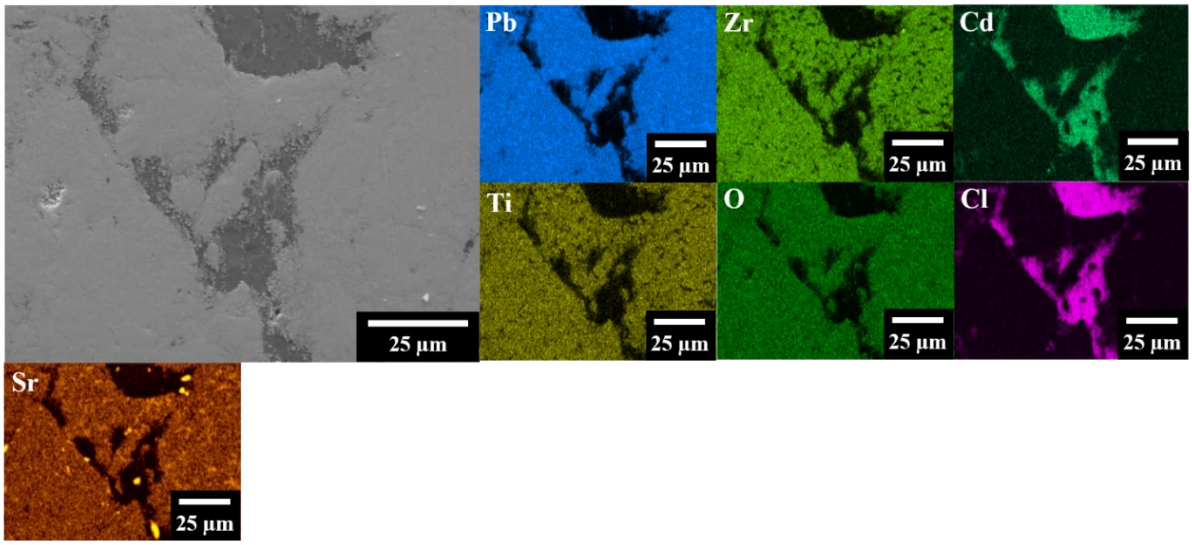

Figure S8. FESEM micrographs and EDS maps of upside-down composite S-PZT-C

Frequency-dependent dielectric properties for the ceramic samples and upside-down composite samples made with corresponding ceramic fillers

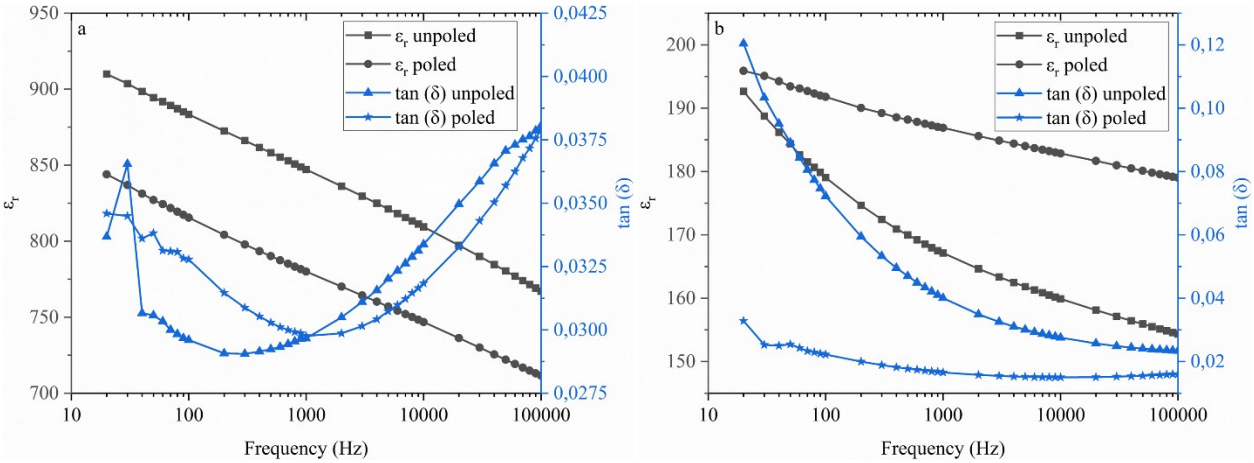

Figure S9. Dependence of relative permittivity (ε_r) and dielectric loss (tan (δ)) on frequency for unpoled and poled (a) KNBNNO-P and (b) KNBNNO-C measured at room temperature in the dark

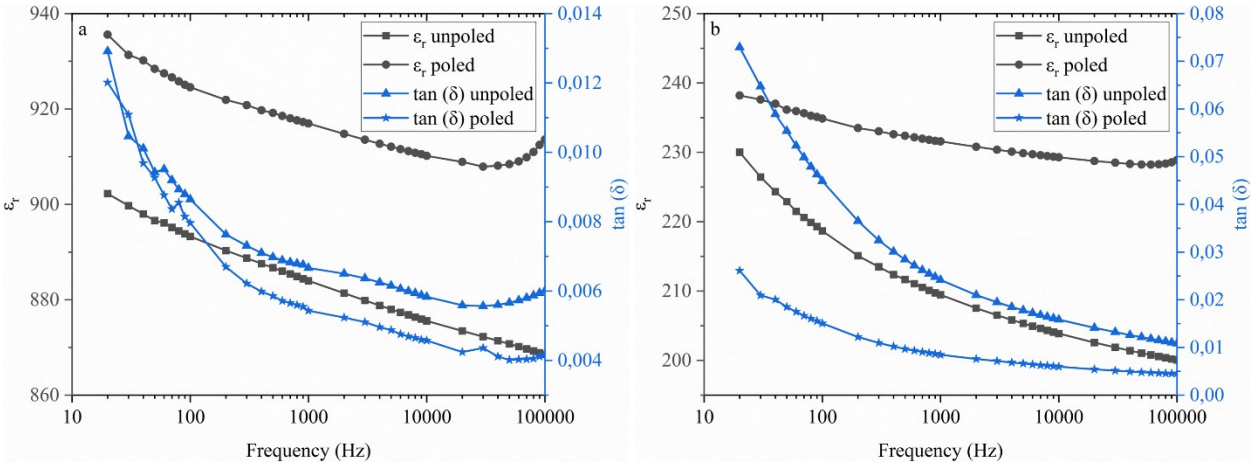

Figure S10. Dependence of ε_r and tan (δ) on frequency for unpoled and poled (a) H-PZT-P and (b) H-PZT-C measured at room temperature in the dark

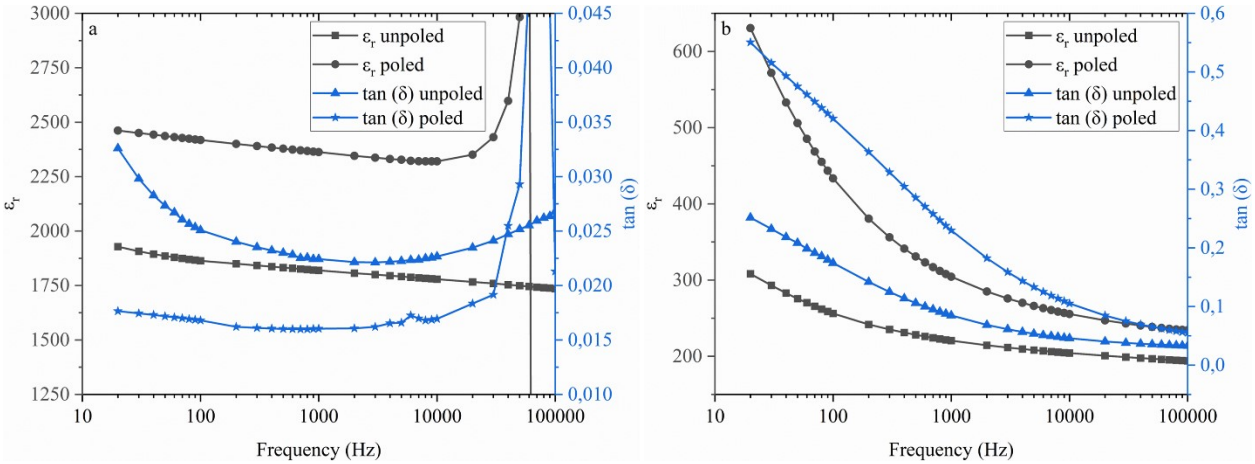

Figure S11. Dependence of ε_r and tan (δ) on frequency for unpoled and poled (a) S-PZT-P and (b) S-PZT-C measured at room temperature in the dark