SUPPORTING INFORMATION

Decode internal and external contributions for high piezoelectricity of CBT-based piezoelectric ceramics

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Experiment

$Ca_{0.6}(Na_{0.5}Bi_{0.5})_{0.4}Bi_4Ti_{4-x}(Nb_{2/3}Mg_{1/3})_xO_{15}$ (CBTNM-1000*x*, *x*=0.00, 0.05, 0.075, 0.10, 0.125) ceramics were prepared by the conventional solid-state reaction method. $CaCO_3$ (99.0%), Na_2CO_3 (99.5%), Bi_2O_3 (99.999%), TiO_2 (98.0%), Nb_2O_5 (99.5%), MgO (99.99%) powders were used as raw materials and weighed according to the stoichiometric compositions. After being mixed by ball milling with ethanol for 18 hours, the mixture was calcined at 900 ℃ for 3 hours and then the calcined powders were pressed into pellets by using the 8wt% polyvinyl alcohol (PVA) binder. Finally, the samples with PVA removed were sintered in air at 1010 ℃ for 3 hours.

The crystal structure information was analyzed by the X-ray diffraction (XRD) with a powder X-ray diffractometer (Panalytical B. V. X'Pert Pro) and the Raman scattering spectra with an instrument (LabRAM HR, HORIBA, France). Then the surface images of grains were obtained by the scanning electron microscope (SEM, S-3400N, Hitachi), and the ferro-domain morphologies were observed by the piezoresponse force microscopy (PFM, Asylum Research, MFP-3D, USA). For investigating the electrical properties of samples, a quasi-static d_{33} meter was used to get the piezoelectric constant d_{33}, an LCR analyzer (HP4980A, Agilent, USA) was used to measure the dielectric and impedance performance, an electrometer (Keithley 6517B) was used to obtain dc resistivity, and the *P-E* loops of samples are obtained by an analyzer (TF-2000, Aix ACCT) at 5 Hz and 200 ℃.

Figure S1 shows the Rietveld refinement of the XRD patterns of the CBTNM-1000*x* ceramics.

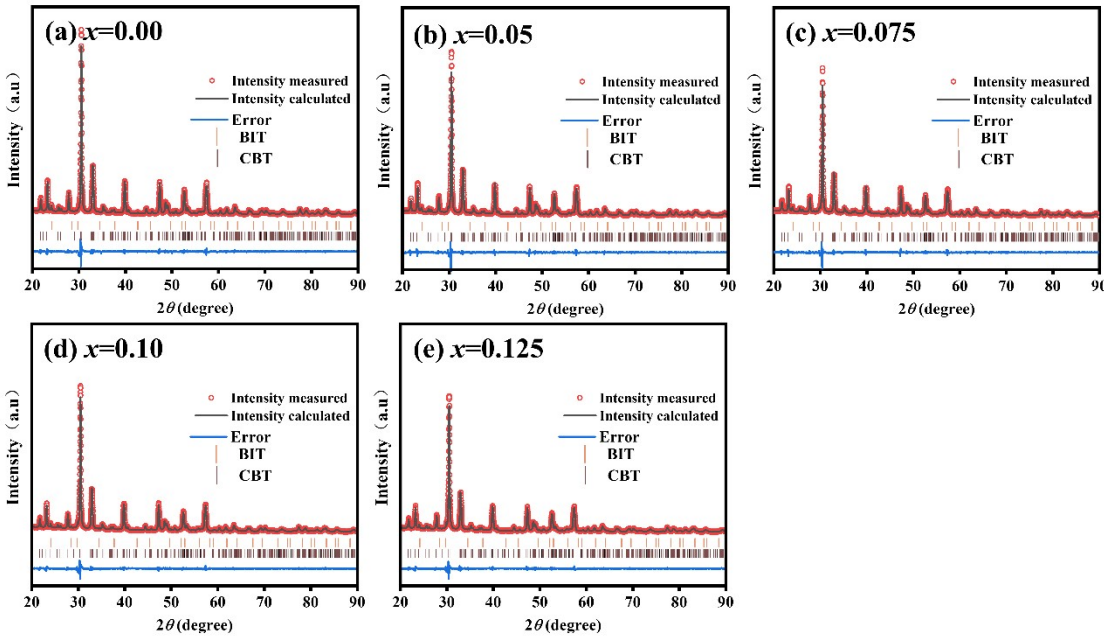

FIGURE S1 (a-e) Rietveld refinement of the XRD patterns of the CBTNM-1000*x*.

Figure S2 illustrates the Raman spectra of of the CBTNM-1000*x*.

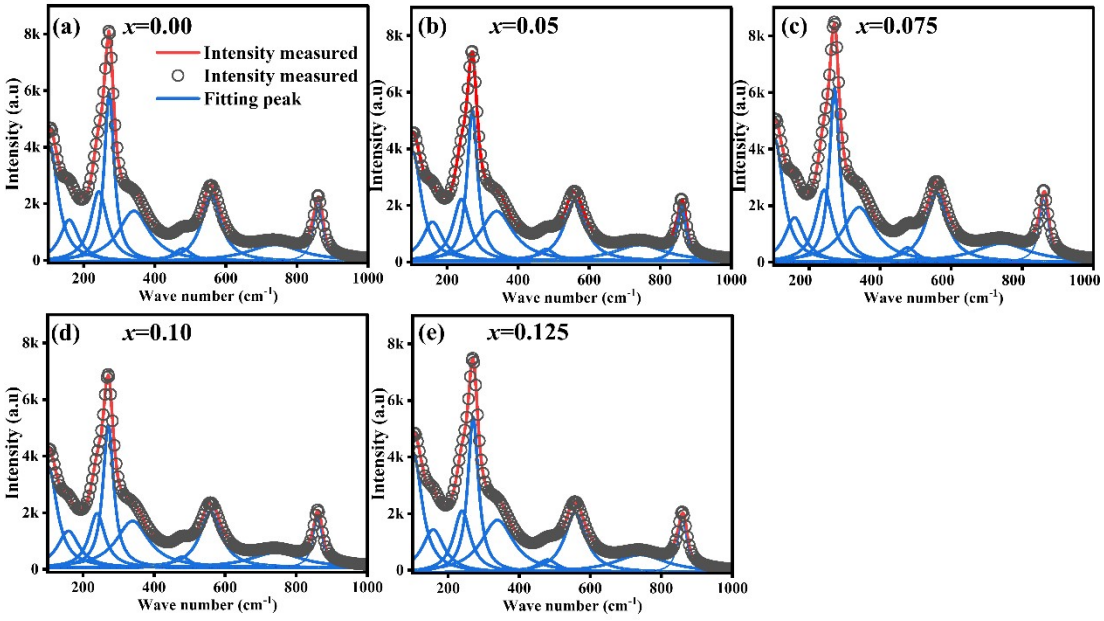

FIGURE S2 (a-e) Raman spectra of the CBTNM-1000*x*.

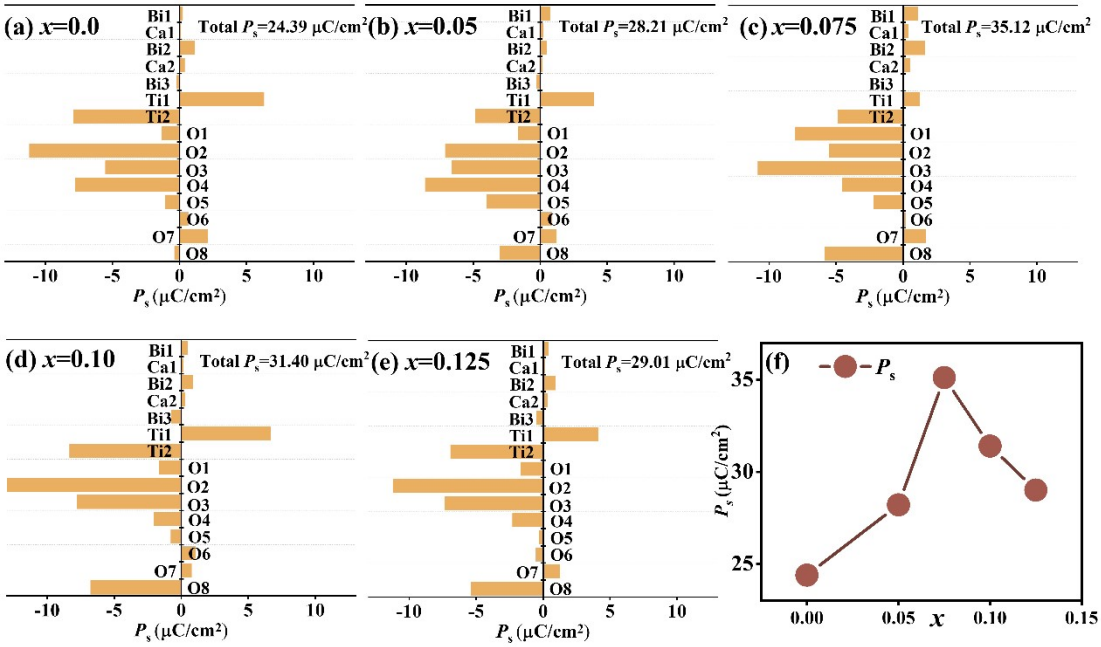

FIGURE S3 (a-e) The contribution to the P_s of each ion of CBTNM-100x ceramics. (f) The total P_s as a function of x = 0.00–0.125.

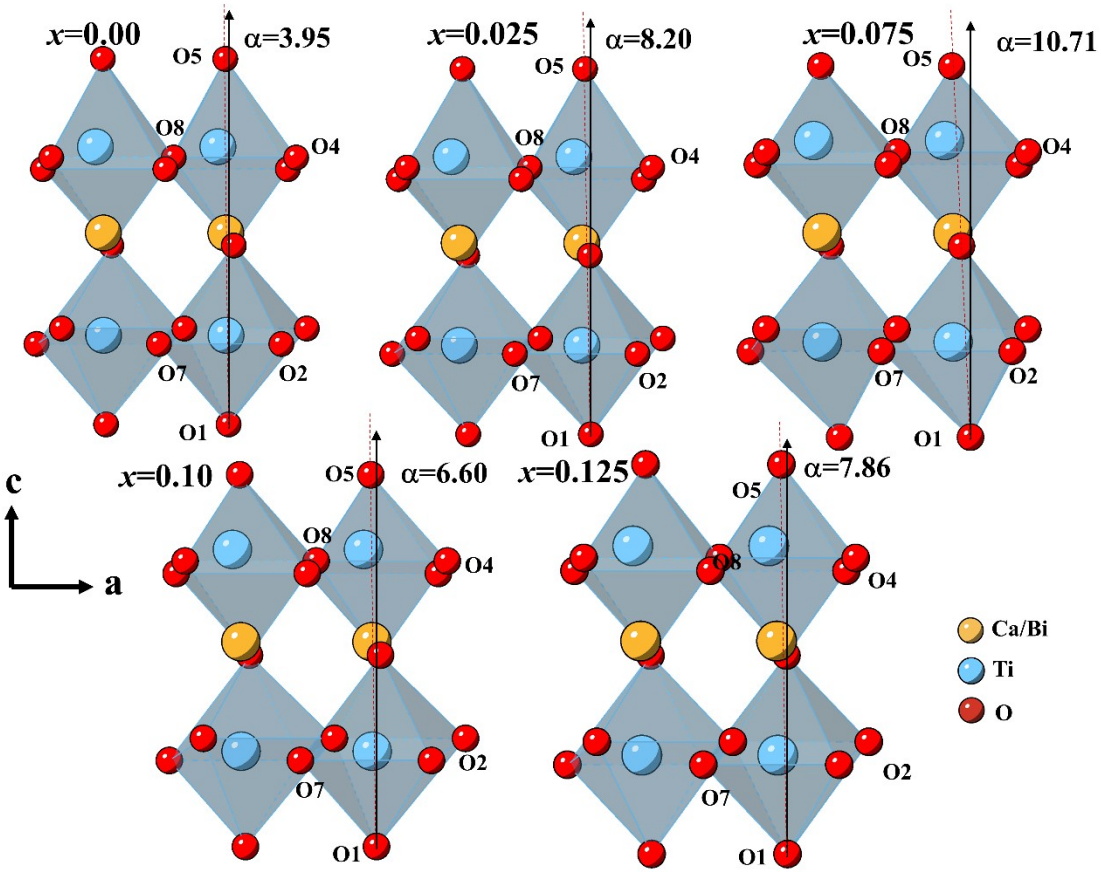

FIGURE S4. Schematic diagram of Ti-O octahedral tilt from the c-axis for the CBTNM-1000x ceramics.

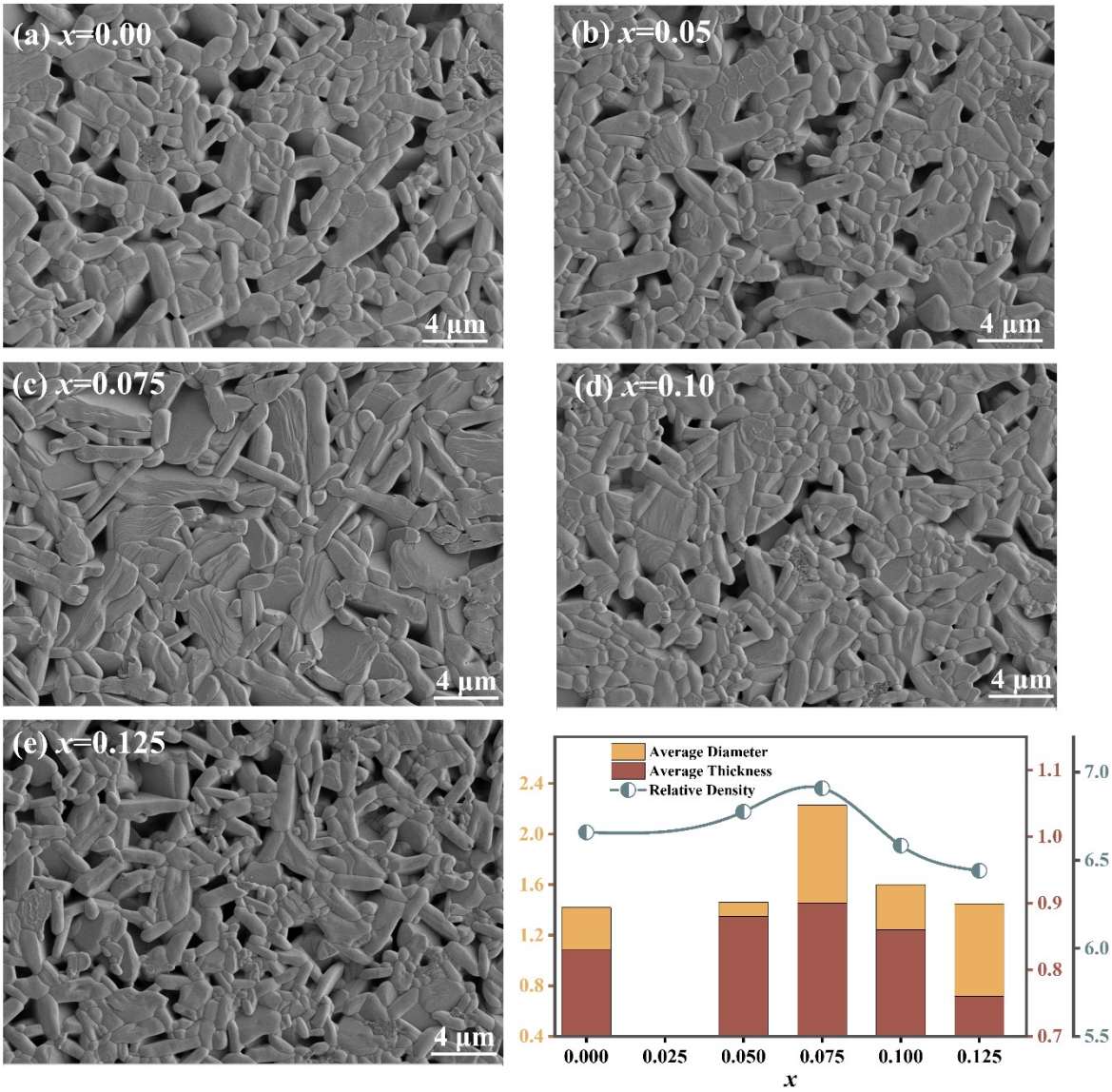

Figure S5 (a-e) The SEM graph and (f) the average grain size of polished and thermal etched CBTNM-100*x* ceramics.

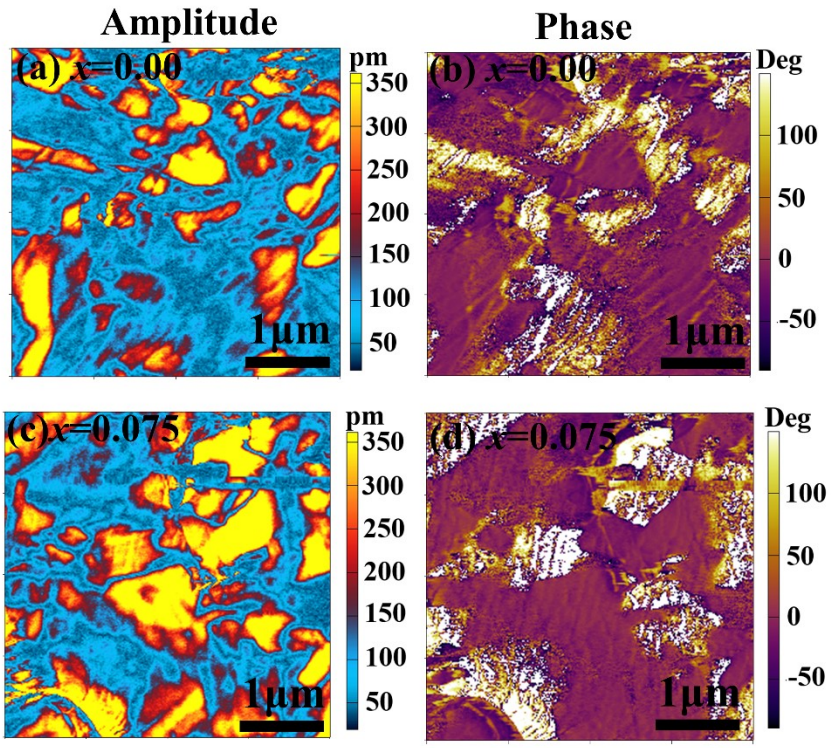

FIGURE S6 (a-d) amplitude patterns and phase patterns of CBTNM-1000*x* ceramics with *x*=0.0, 0.075 at 4 μm×4 μm regions.

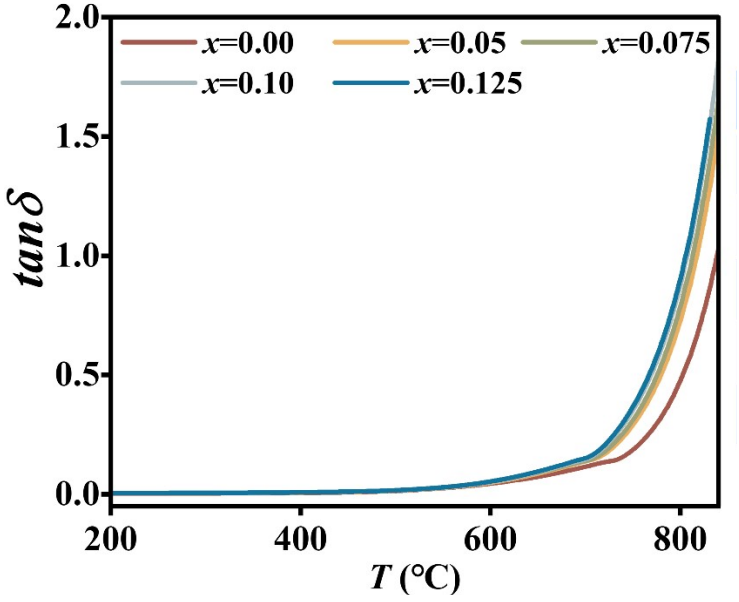

Figure S7 Temperature dependence the dielectric loss for CBTNM-100*x* ceramics.

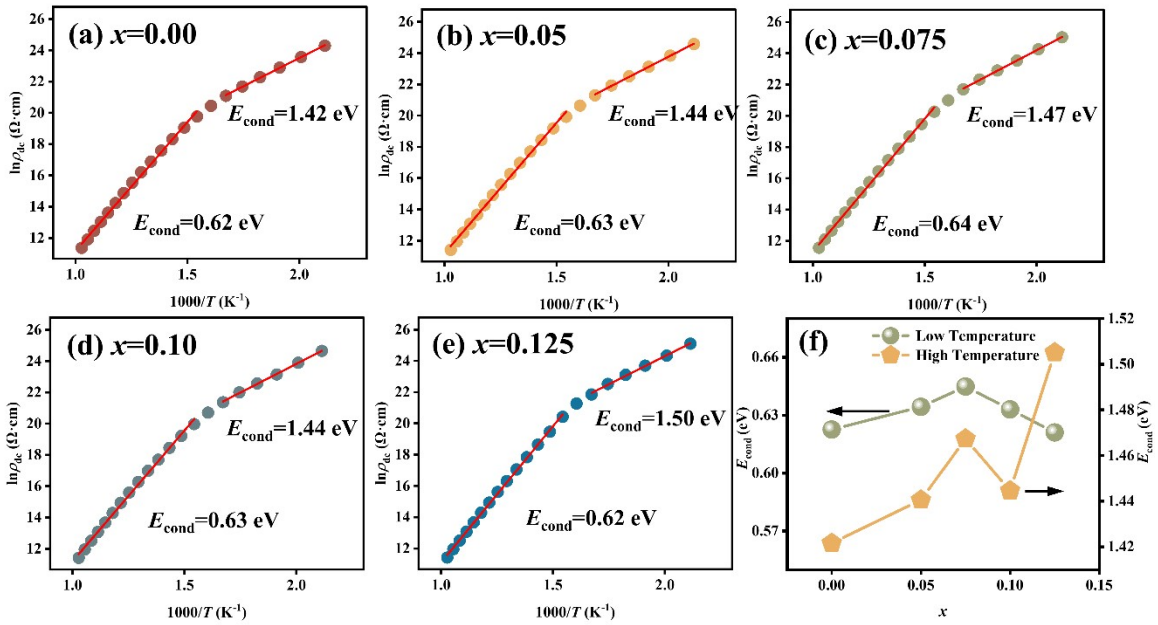

Figure S8 (a)The relationship between temperature and ρ fitted by Arrehenius equation. (b) The activation energy (E_a) of two temperature regions for CBTNM-1000x samples.

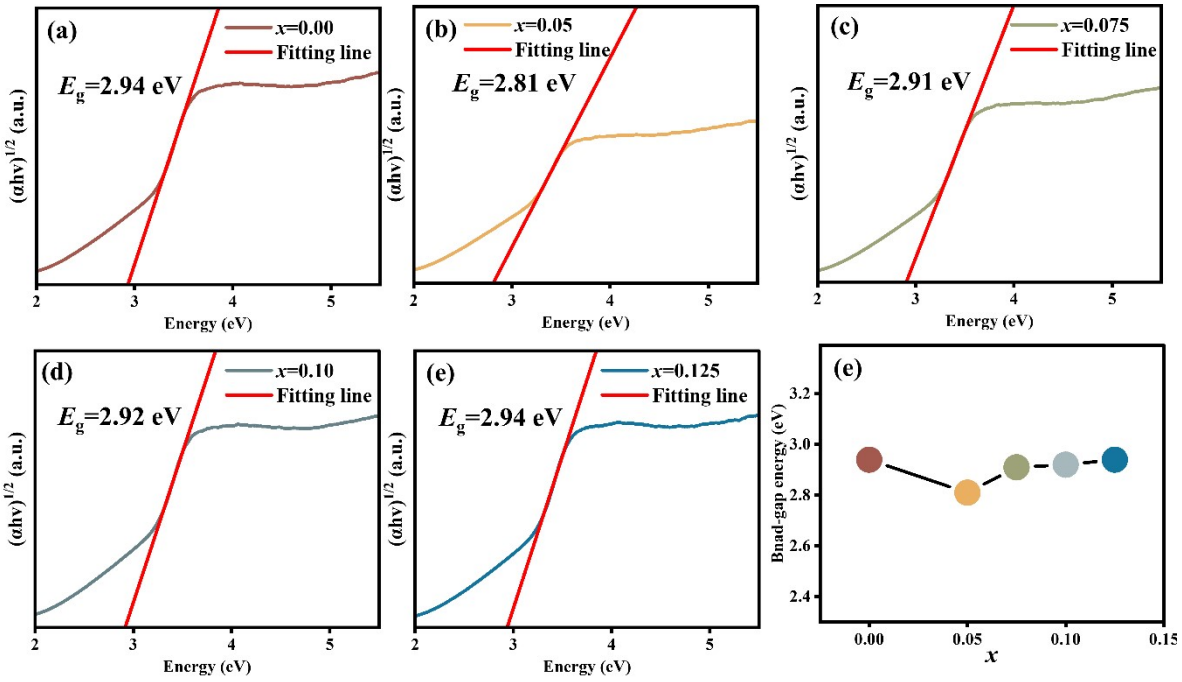

FIGURE S9 (a) The relationship between $(\alpha hv)^{1/2}$ and photon energy; (g) The band-gap energy (E_g) of CBTNM-1000x ceramics.

Table S1

Crystal structure parameters of CBTNM-1000*x* ceramics derived from the Rietveld structure refinement program.

	x=0.00	*x*=0.05	*x*=0.075	*x*=0.10	*x*=0.125
R_w (%)	5.29	5.35	5.17	4.98	4.97
Sig	1.85	1.87	1.79	1.73	1.67
$CaBi_4Ti_4O_{15}$ (%) (volume proportion)	96.58	96.00	99.52	97.08	98.73
$Bi_{1.74}Ti_2O_{6.624}$ (%) (volume proportion)	3.42	4.00	0.48	2.92	1.27
a_{CBT} (Å)	5.4350	5.4348	5.4347	5.4402	5.4411
b_{CBT} (Å)	5.4106	5.4115	5.4119	5.4176	5.4180
c_{CBT} (Å)	40.7204	40.7154	40.7198	40.7657	40.7703
a/b_{CBT}	1.0045	1.0043	1.0042	1.0042	1.0043
V_{CBT} (Å^3)	1197.45	1197.49	1197.64	1201.49	1201.89

Table S2 Atomic coordinates of CBTNM-1000*x* ceramics with *x*=0.0, 0.025, 0.075.

	CBTNM-0 (*x*=0.0)			CBTNM-25 (*x*=0.025)			CBTNM-75 (*x*=0.075)		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Bi1	0.2542	0.2420	0.0000	0.2623	0.2314	0.0000	0.2688	0.2747	0.0000
Ca1	0.2542	0.2420	0.0000	0.2623	0.2314	0.0000	0.2688	0.2747	0.0000
Bi2	0.2600	0.2419	0.1045	0.2542	0.2399	0.1036	0.2641	0.2780	0.1298
Ca2	0.2600	0.2419	0.1045	0.2542	0.2399	0.1036	0.2641	0.2780	0.1298
Bi3	0.2487	0.2686	0.2190	0.2486	0.2689	0.2168	0.2496	0.3057	0.2538
Ti1	0.2771	0.2453	0.5481	0.2674	0.2526	0.5441	0.2554	0.2763	0.5847
Ti2	0.2161	0.2538	0.3465	0.2292	0.2646	0.3428	0.2290	0.2909	0.3821
O1	0.2724	0.2097	0.5000	0.2981	0.2470	0.5000	0.3283	0.2916	0.5000
O2	0.5963	0.5215	0.0400	0.5610	0.5549	0.0387	0.5474	0.5666	0.0551
O3	0.2975	0.3174	0.4050	0.3067	0.3131	0.4020	0.3432	0.3400	0.4392
O4	0.5668	0.4720	0.1378	0.5737	0.4294	0.1374	0.5392	0.4878	0.1680
O5	0.2592	0.1862	0.3091	0.2744	0.1880	0.3044	0.2990	0.2431	0.3451
O6	0.4944	0.5173	0.2536	0.4923	0.5301	0.2513	0.4984	0.5452	0.2899
O7	-0.0180	-0.0006	0.0434	0.0106	0.0170	0.0423	-0.0148	-0.0258	0.0545
O8	0.0032	0.0477	0.1410	0.0259	0.0432	0.1391	0.0502	0.0397	0.1727

Table S3 Atomic coordinates of CBTNM-1000*x* ceramics with *x*=0.100, 0.125.

	CBTNM-100 (*x*=0.100)			CBTNM-125 (*x*=0.125)		
	x	*y*	*z*	*x*	*y*	*z*
Bi1	0.2585	0.2446	0.0000	0.2571	0.2431	0.0000
Ca1	0.2585	0.2446	0.0000	0.2571	0.2431	0.0000
Bi2	0.2575	0.2407	0.1046	0.2578	0.2436	0.1045
Ca2	0.2575	0.2407	0.1046	0.2578	0.2436	0.1045
Bi3	0.2458	0.2648	0.2192	0.2472	0.2680	0.2189
Ti1	0.2787	0.2501	0.5478	0.2677	0.2375	0.5481
Ti2	0.2141	0.2563	0.3471	0.2202	0.2529	0.3472
O1	0.2786	0.1904	0.5000	0.2980	0.1904	0.5000
O2	0.6180	0.5121	0.0406	0.5967	0.5195	0.0412
O3	0.3170	0.3285	0.4045	0.3131	0.3267	0.4042
O4	0.5176	0.4970	0.1425	0.5197	0.4940	0.1393
O5	0.2567	0.2115	0.3108	0.2756	0.1838	0.3088
O6	0.4907	0.5363	0.2425	0.5047	0.5249	0.2521
O7	-0.0067	0.0120	0.0444	-0.0108	-0.0124	0.0424
O8	0.0583	0.0267	0.1396	0.0464	-0.0038	0.1401

Table S4 tanδ for CBTNM-100*x* ceramics with different temperature.

x	tanδ (RT)	tanδ (250°C)	tanδ (350°C)	tanδ (450°C)	tanδ (550°C)	tanδ (650°C)
0.0	0.0033	0.0037	0.0047	0.0082	0.0252	0.0733
0.05	0.0040	0.0047	0.0062	0.0101	0.0266	0.0864
0.075	0.0041	0.0049	0.0064	0.0107	0.0291	0.0907
0.10	0.0039	0.0049	0.0065	0.0107	0.0278	0.0918
0.125	0.0044	0.0053	0.0067	0.0107	0.0290	0.0957