Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Tunable thermal expansion and high hardness of $(0.9\text{-}x)PbTiO_3\text{-}xCaTiO_3\text{-}0.1Bi(Zn_{2/3}Ta_{1/3})O_3$ ceramics

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1. **Experimental section**

A series of $(0.9-x)PbTiO_3$-$xCaTiO_3$-$0.1Bi(Zn_{2/3}Ta_{1/3})O_3$ (x = 0~0.45) ceramics prepared by simple solid state reaction method using analytic reagent grade raw materials, PbO, TiO_2, CaO, Bi_2O_3, ZnO, Ta_2O_5. To avoid the moisture in the samples, necessary materials were dried at 375 K in air for 12h. raw materials at stoichiometric ratio were ball-milled with ethanol for 24h. Dried powders were put into alumina crucible for calcining at 800^{o}C for 5h. Then grind the powders fully and add suitable binder, get the pellets from tableting machine, sintered at 550^{o}C for 2h to remove the binder and sintered at 1100^{o}C for 2h to get hard ceramics. Before sintered, some powders should be covered the pellets to avoid volatilization from the samples. To remove the mechanical strain during the sintering and grinding procedures, the pellets were sintered again at 800^{o}C for 2h.

The crystal structure and properties of thermal expansion were conducted using the X-ray diffraction (XRD) technique on a diffractometer (model X'pert PRO, PANalytical, Netherlands). To get X-ray diffraction peaks accurately, silicon standard was used to rectify the system and sample error. In order to get better data of diffraction, synchrotron XRD patterns of the powder were collected at the beamline BL44B2 in Japan Spring-8. The data of Raman spectroscopy were collected at high-precision modular tertiary Raman spectrometer (JYT64000). Structure refinement were adopted to Rietveld full spectrum fitting by software of FullProf. The linear

thermal expansion ($\Delta l/l_0$) were obtained from a thermo-dilatometer (NETZSCH DIL 402). Micrographs of the samples were measured on a field-emission scanning electron microscope (FE-SEM, LEO1530). The hardness of the material was characterized by Digital Vickers tester with 200g loads for 10s dwell time. Charge dentist were calculated by VASP using the method of first principle calculate.

First principle calculation was performed based on density functional using VASP package. Exchange correlation function adopt Generalized Gradient Approximation (GGA), exchange correlation potential adopt PBE pseudo potential method. The calculating parameters were optimized at the beginning. The plane-wave energy cutoff selected at 400eV. The integrations of the Brillouin-zone use the method of Monkhorst-Pack special k point sampling, Brillouin-zone integrations were using 4×4×4 k-point mesh. To get the proper proportions approach the practical situation, 3×3×3 supercell were established. The theoretical model $Pb_{15}Ti_{15}O_{45}$-$Bi_3Zn_2Ta_1O_9$-$Ca_9Ti_9O_{27}$ pretty close to the actual model $0.55PbTiO_3$-$0.35CaTiO_3$-0.1Bi $(Zn_{2/3}Ta_{1/3})O_3$, which exhibit the feature of ZTE. Structural optimization were carried out for the theoretical model, and then got the structure and electron density. In contrast, the related calculation of $PbTiO_3$ do the same options to find the difference to the doping system.

2. **Results and discussion**

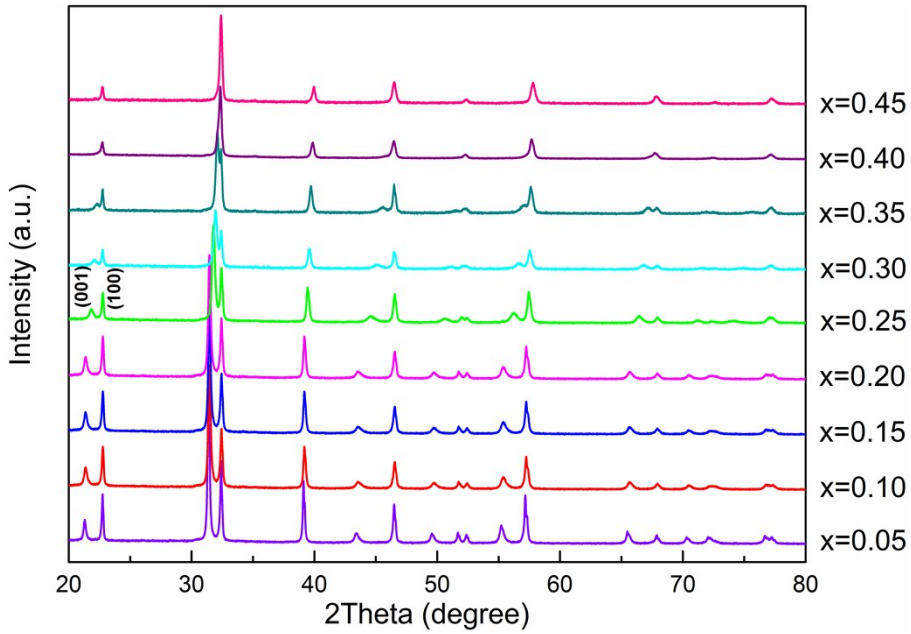

Figure S1 The XRD patterns of (0.9-x)$PbTiO_3$-$x$$CaTiO_3-0.1Bi(Zn_{2/3}Ta_{1/3})O_3$ (x = 0~0.45) at room temperature.

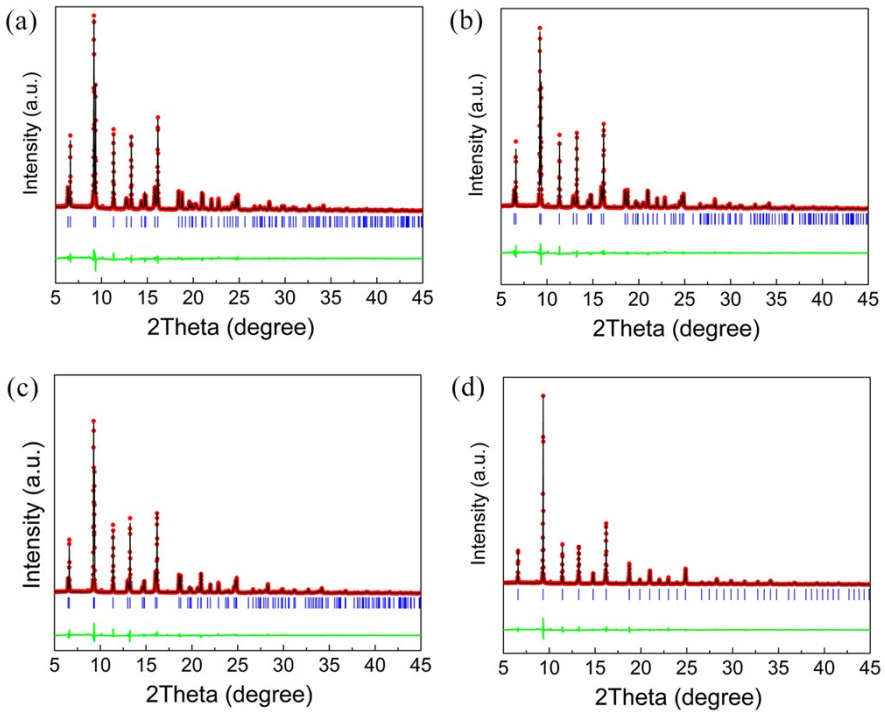

Figure S2 Rietveld refinement of the synchrotron XRD patterns of (0.9-*x*)$PbTiO_3$-*x*$CaTiO_3$-0.1$Bi(Zn_{2/3}Ta_{1/3})O_3$ ((a): x = 0.25; (b): x = 0.30; (c): x = 0.35; (d): x = 0.40;) at room temperature.

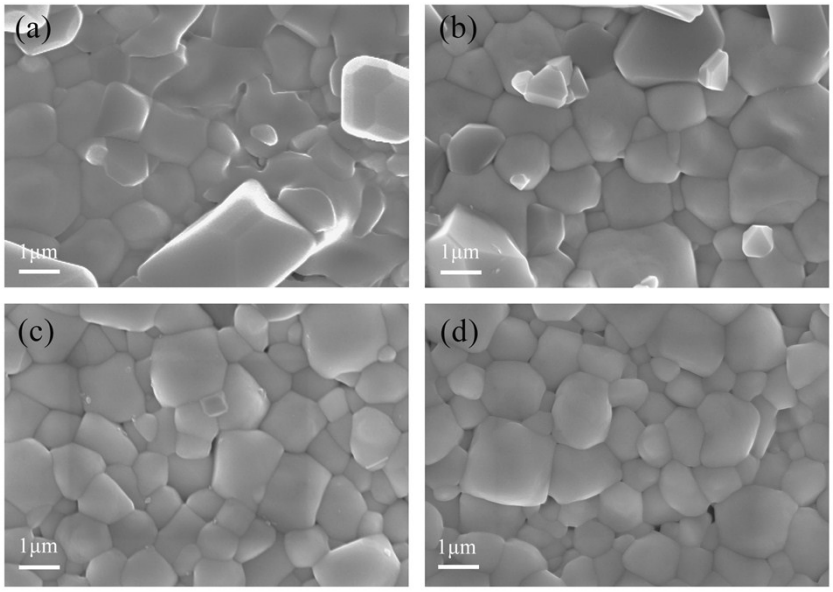

Figure S3 Surface FE-SEM micrographs of samples of solubility x = 0.25(a), 0.30(b), 0.35(c), 0.40(d).

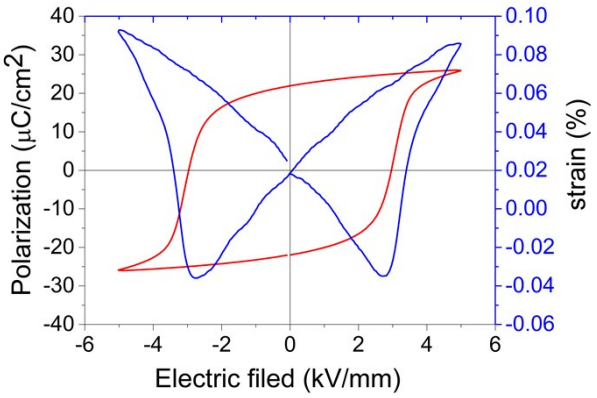

Figure S4 Polarization-field hysteresis loop and the corresponding strain-field butterfly loop of the $0.55PbTiO_3$-$0.35CaTiO_3$-$0.1Bi(Zn_{2/3}Ta_{1/3})O_3$ ceramic at 1Hz.

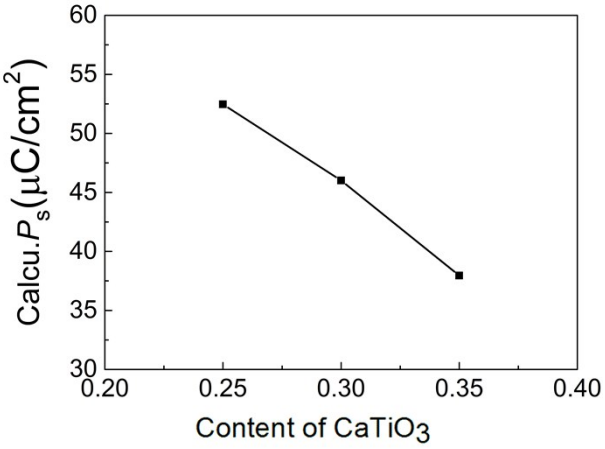

Figure S5 Spontaneous polarization (P_S) of $(0.9\text{-}x)PbTiO_3$-$xCaTiO_3$-$0.1Bi(Zn_{2/3}Ta_{1/3})O_3$ ($x = 0.25 \sim 0.35$), determined by the structural refinement.

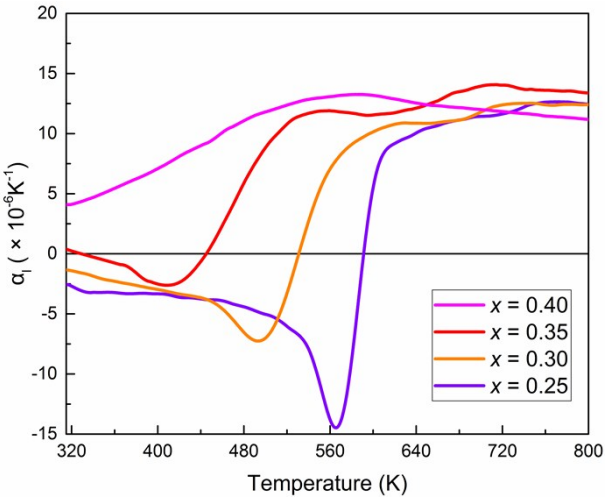

Figure S6 The temperature dependent linear CTE for different contents in (0.9-*x*)$PbTiO_3$- *x*$CaTiO_3$-0.1$Bi(Zn_{2/3}Ta_{1/3})O_3$ system (*x* = 0.25 ~ 0.40).

Table S1 Average linear and volumetric CTE of (0.9-*x*)$PbTiO_3$-*x*$CaTiO_3$-0.1$Bi(Zn_{2/3}Ta_{1/3})O_3$ (*x* = 0.25~0.40). α_v: volumetric CTE, measured by XRD; α_l: linear CTE, measured with a dilatometer.

Solubility *x*	Temperature Range (K)	α_l	Temperature Range (K)	α_v
x = 0.25	300~585	-0.520×10^{-5}/K	300~600	-2.16×10^{-5}/K
x = 0.30	300~530	-0.353×10^{-5}/K	300~530	-1.64×10^{-5}/K
x = 0.35	125~465	-0.099×10^{-5}/K	125~470	-0.29×10^{-5}/K
x = 0.40	300~800	1.001×10^{-5}/K	300~800	3.32×10^{-5}/K

Table S2 Theory, actual density and relative density of (0.9-x)$PbTiO_3$-$x$$CaTiO_3-0.1Bi(Zn_{2/3}Ta_{1/3})O_3$ (x = 0.25 ~ 0.40) system.

Solubility x	Theory density (g/cm^3)	Actual density (g/cm^3)	Relative density
x = 0.25	7.472	6.942	0.929
x = 0.30	7.301	6.866	0.940
x = 0.35	7.116	6.639	0.932
x = 0.40	6.935	6.622	0.955

Table S3 Zero thermal expansion properties of related materials.

Materials	α_v ($\times 10^{-5}$/K)	Temperature Range (K)
0.55$PbTiO_3$-0.35$CaTiO_3$-0.1$Bi(Zn_{2/3}Ta_{1/3})O_3$	-0.29	125~470
$Pb(Fe_{1/2}Nb_{1/2})O_3$	0.6	300~393
$Pb(Fe_{2/3}W_{1/3})O_3$	0.45	<300
0.6$PbTiO_3$-0.3$Bi(Zn_{1/2}Ti_{1/2})O_3$-0.1$BiFeO_3$	-0.31	298~773
$SrRuO_3$	0.16	12~160
Y_2Fe_{17}	-0.56	5~320
$Nb_2Fe_{14}B$	-1.0	300~600
$Y_2Fe_{17}C_{0.6}$	0.24	5~460