Supporting informations for

Unusual devisable high performance by engineering in twins,

domains and antiphase boundaries

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Figures and tables



Fig. S1 Scaning electron microscopy (SEM) images of polised and thermal etched surfaces for CTNA ceramics (x=0.65) with different dopants in A-site; a) pure CTNA ceramic, b) $0.65Ca_{0.9}Sr_{0.1}TiO_3-0.35NdAlO_3$ ceramic, c) $0.65Ca_{0.9}Ba_{0.1}TiO_3-0.35NdAlO_3$ ceramic, d) $0.65Ca_{0.95}Sr_{0.05}TiO_3-0.35NdAlO_3$ ceramic, e) $0.65Ca_{0.95}Ba_{0.05}TiO_3-0.35NdAlO_3$ ceramic. The energy dispersive spectrums (EDS) for each ceramics are listed in the space to the right.



Fig. S2 The corresponding energy dispersice spectrometric mapping of CTNA ceramics, the Ca, Ti, Al, Nd, Sr, Ba and O EDS elemental maps for a) 0.65Ca_{0.9}Sr_{0.1}TiO₃-0.35NdAlO₃ ceramic, b) 0.65Ca_{0.9}Ba_{0.1}TiO₃-0.35NdAlO₃ ceramic, respectively.

The FE-SEM micrographs for polished and etched surfaces of xCaTiO₃-(*1-x*)NdAlO₃ (CTNA, x=0.65) ceramic with different dopents in A-site (Sr or Ba elements), i.e., 0.65CaTiO₃-0.35NdAlO₃ ceramic, 0.65Ca_{0.9}Sr_{0.1}TiO₃-0.35NdAlO₃ ceramic and 0.65Ca_{0.9}Ba_{0.1}TiO₃-0.35NdAlO₃ ceramic are exhibited in Fig. S1. The SEM micrographs of CTNA based ceramics are typical for all compostion which exhibit a uniform and compact surface morphology with an average grain size of 2-3 μ m. No obvious composotion dependence of grain size could be detected. Obviously, the elements within the ceramic can be detected in the whole grain, and the elements are homogeneously distrbuted. It's consistent with the discssions in manuscript, such heterogeneity caused by displacements in A-site gives rise to differences in microstructures and then affects the related performances.

Displayed in Fig. S3 are the room temperature XRD patterns of $xCaTiO_3$ -(1x)NdAlO₃ (CTNA, $x = 0.8 \sim 0.4$) ceramics, and no obvious second phases are observed. The perovskite CaTiO₃ phase (PDF #22-0153, PDF #39-0145) and trigonal phase NdAlO₃ (PDF #39-0487) are indexed. The results evidence complete solid solution across the entire compositional range. According to the literatures, for x > 0.85, the structure of the perovskite solid solution exhibits orthorhombic symmetry similar to that of pure CaTiO₃ phase. In the range $0 \le x \le 0.15$, the solid solution has the trigonal.¹ While in 0.2 < x < 0.8, with increasing NdAlO₃ concentration the phase transition occurs. The solid solution is in tetragonal symmetry, for no characteristic peaks of (200) and (040) peaks are found, and the new peaks of both (022) and (202) appear, same as the previous reports.²⁻⁵ These ceramics can reach the sintered densification at 1450 °C. With increasing x, the dielectric properties under microwave frequency are shown in Fig. 3(b). The dielectric permittivity and temperature coefficient of resonant (TCF) decrease while the Q value is enhanced. The ceramic with x=0.65 achieves the best comprehensive dielectric performances. Consequently we can conclude that the enhanced symmetry in microstructure is the important reason for the dependence of properties.



Fig. S3 (a) XRD patterns of *x*CaTiO₃-(*1-x*)NdAlO₃ ceramics as a function of *x* (0.8, 0.7, 0.65, 0.6, 0.5, 0.4). Inset is the corresponding densities of different composition *x*; (b) dielectric parameters of *x*CaTiO₃-(*1-x*)NdAlO₃ ceramics under microwave frequency (3-10 GHz) with different composition *x*. The dielectric permittivity ε' , quality factor Q_f (GHz) and temperature coefficient τ_r (ppm/°C) are depicted with different symbols.

Temperature dependence of dielectric permittivity ε and dielectric loss *tan* δ at 1 MHz are shown in Fig. S4. The texts are carried out in air followed by rapid heating and slow cooling. The dielectric permittivity of $0.65Ca_{0.9}Ba_{0.1}TiO_3$ - $0.35NdAlO_3$ ceramic are higher compared with the corresponding $0.65Ca_{0.9}Sr_{0.1}TiO_3$ - $0.35NdAlO_3$ ceramic and $0.65CaTiO_3$ - $0.35NdAlO_3$ ceramic. This difference can be attributed to the bigger ion dielectric polarizability of Ba^{2+} to Sr^{2+} and Ca^{2+} ions ($\alpha_{Ba}^{2+}=6.4$ Å³, $\alpha_{Sr}^{2+}=4.24$ Å³, $\alpha_{Ca}^{2+}=3.16$ Å³).⁶ The smooth curve with a section of approximate straight line are observed by the frequency dependence of the dielectric permittivity and dielectric loss indicates the largely reduced defects, which contributes to the

improved microstructure in the manuscript. The dielectric loss are dramatically increased in the range of 350-400 °C, which are directly related to the thermal activation process of the defect carriers. By using rapid heating and slowly cooling, the apparent relaxation of this process are exhibited in Fig. S5.

At room temperature, the $0.65Ca_{0.9}Ba_{0.1}TiO_3$ - $0.35NdAlO_3$ ceramic with Ba dopants has a visible lamellar nanodomains labled with a round lighted-colored regions (Fig. S5). Inset of Fig. S5 dispalyes the selected-area electron diffraction (SAED) pattern of the $0.65Ca_{0.9}Ba_{0.1}TiO_3$ - $0.35NdAlO_3$ ceramic. The lattice indices for SAED are consistent with $<\underline{1}11>$ zone axis, proving a tetragonal structure rather than orthorhombic structure, in agreement with the previous analysis.

Moreover, to further probe the chemical composition and chemical state of CTNA ceramics with or without dopants, X-ray photoelectric spectroscopy was carried out. It could be see the CTNA ceramics were examined for selected elements. And the Ca, Sr, Ba elements can be easily distinguished from the XPS survey spectra. The detailed informations about the XPS spectrums have been carefully discussed in the manuscript.



Fig. S4 Dielectric permittivity ε' and dielectric loss *tan* δ as a function of temperature at 1 MHz for (a) 0.65CaTiO₃-0.35NdAlO₃ ceramic, (b) 0.65Ca_{0.9}Sr_{0.1}TiO₃-0.35NdAlO₃ ceramic, (c) 0.65Ca_{0.9}Ba_{0.1}TiO₃-0.35NdAlO₃ ceramic, respectively. The texts are carried out in air followed by rapid heating and slow cooling.



Fig. S5 TEM image and SAED pattern (inset) for 0.65Ca_{0.9}Ba_{0.1}TiO₃-0.35NdAlO₃ ceramic.



Fig. S6 XPS survey spectra for 0.65CaTiO₃-0.35NdAlO₃ ceramic, 0.65Ca_{0.9}Sr_{0.1}TiO₃-0.35NdAlO₃ ceramic and 0.65Ca_{0.9}Ba_{0.1}TiO₃-0.35NdAlO₃ ceramic, respectively.

The dielectric properties of the CTNA based ceramics under microwave frequency are listed in Table S1. Upon the microwave frequency, the slow polarization mechanisms such as surface charges and polarized dipoles make little contributions to the dielectric performances. Thus defects paly dominant roles. In design of the A-site displacement in perovskite structure, i.e., Sr²⁺, Ba²⁺ substitutes into Ca site, we created a controllable structure of twins and APBs by introducing ferroelectric spontaneous polarization. From Table S1, we can successfully realize controllable enhanced dielectric properties by regulation of the microstructures within its host lattice of the materials. The ultralow loss ($Q \times f > 40000 \text{ GHz}$) and very good temperature stabilities with a near-zero temperature coefficient of resonance frequency (TCF) are observed. It can retain maximum signal intensity as well as frequency resolution and adapting to environmental temperature changes. Finally, the obviously enhanced dielectric performances certificate that it will provide us a new possible way to design the material systems for high performances in scientific researches.

	methods	\mathcal{E}_r	Qf(GHz)	$\tau_f(\text{ppm/oc})$	Ref.
CaTiO ₃	Solid state	170	3600	800	[7].
Ca _{0.9} Sr _{0.1} TiO ₃	Solid state	170	5900	931	[8].
CTNA <i>(x=0.7)</i>	Solid state	45	45000	0	[1].
CTNA <i>(x=0.7)</i>	Solid state	43.5	30000	-2.1	[4]
CTNA <i>(x=0.7)</i>	Solid state	45	44000	3	[9].
CTNA(<i>x</i> =0.65)	Sol-Gel	39	50000	-7.1	[10].
CTNA(<i>x</i> =0.65)	Solid state	48	49022	1.8	This work
CTNA(<i>x</i> =0.65,Sr)	Solid state	49.6	53088	5.4	This work
CTNA(<i>x</i> =0.65,Ba)	Solid state	54	55992	6.5	This work

Table S1. The dielectric properties of the CTNA based ceramics under microwave frequency

Experimental Sections

The *x*CaTiO₃-(*1-x*)NdAIO₃ (CTNA) solid-solution system across the entire compositional range were prepared by solid-state reaction¹² from dried high-purity chemical powders (\geq 99.8 wt%; Sinopharm Chemical Reagent Co., Ltd, CN). To remove moisture retains, the TiO₂ powder were calcined at 600 °C for 2 h and cooled in dry. The stoichiometric quantities of CaO, TiO₂ powders were mixed and ground under ethanol medium for 10 h in a ball mill with zirconia balls. The mixture were dried at 100 °C for 10 h, and then calcined at 1200-1300 °C for 3 h, as precursor powders. After sieved through a 200 µm sieve, the calcined powders were remilled with zirconia balls for 10 h in ethanol and dried. Afterwards, the final powders grounded and pressed into disk pellets with a diameter of 12 mm and thickness of 2 or 6 mm at a pressure of 300 MPa by a cold isostatic press. Finally, the samples were sintered at 1300-1450 °C for 2-5h in air. In the second procedure, CTNA ceramics are synthesized with Ba and Sr dopants. The final pellets were sintered at 1450 °C-1650 °C for 3 h according to the composition.

Densities of the sintered ceramics were measured by Archimedes method with distilled water. The crystalline phase of ceramics was examined with Powder X-ray diffraction data by using an automated diffractometer at room temperature (X'Pert PRO MPD, Philips, Eindhoven, The Netherlands). The microstructure and surface morphologies of ceramics was examined by scanning electron microscopy (SEM; JSM-5610, Japan Electron Co., Tokyo, Japan) with an applied voltage of 15 kV. Lattice images were observed by using high-resolution transmission electron microscopy (HRTEM; Tecnai F30G², FEI, Hillsboro, OR, USA) operated at 300 kV accelerating voltage. Raman scattering experiments were performed with an instrument (LabRAM HR800, Horiba JobinYvon, Lyon, France) in a backward scattering geometry (the exciting source was the 514.5 nm line from an argon ion laser). Chemical compositions and valence states of the samples were analyzed using X-ray photoelectron spectroscopy (XPS, VG ESCALAB 220i-XL, Thermo Scientific, Waltham, MA, USA) with an AL Kα source (E=1486.6 eV). All binding energies were referenced to the C

1s peak (284.6 eV) arising from adventitious carbon. Piezoelectric force microscopy (PFM) was measured using a scanning probe microscopy system (AFM; SPI3800N&SPA400, Seiko, Tokyo, Japan). The oxygen vacancies were directly proofed by electron spin resonance analysis (ESR; FA-200, JEOL, Japan).

For the electrical property measurements, silver paste was painted on pellets as the electrodes and fired at 550 °C for 30 min. The dielectric properties were measured by using a precision impedance analyzer (4294A, Agilent, Santa Clara, CA, USA) in the frequency ranging from 100 Hz to 1MHz with a heating rate of 2 °C·min⁻¹. The dielectric properties in the frequency range of 3-10 GHz were measured using network analyzer (8720ES, Agilent, Santa Clara, CA, USA) with the Hakki-Coleman dielectric resonator method. The temperature coefficient of resonant frequency (τ_f) is defined as follow¹¹:

$$\tau_f = \frac{f_{80} - f_{20}}{60 \times f_{20}} \quad (ppm / {}^{o}C) \tag{1}$$

where f_{20} and f_{80} represent the resonant frequencies at 20 °C and 80 °C, respectively.

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