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Research Article

Defect engineering of oxygen vacancies and domain configuration for high-performance $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ piezoelectric ceramics

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Abstract: Bismuth-layer-structured ferroelectrics (BLSFs) are promising candidates for high-

temperature piezoelectric applications owing to their intrinsically high Curie temperatures. However, their practical implementation is hindered by the relatively low piezoelectric activity, which is largely associated with oxygen-vacancy-induced pinning of ferroelectric domain walls. Herein, a donor–acceptor defect engineering strategy is proposed to regulate oxygen vacancies and domain structures in $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ through non-equivalent co-doping. The simultaneous introduction of Cr^{3+} and Ta^{5+} into the B-site can effectively increase local lattice distortion, reduce oxygen vacancy concentration, and form defect dipoles to suppress the thermally activated migration of oxygen vacancies, thereby increasing intrinsic polarization contribution, facilitating domain-wall motion, and enhancing the piezoelectric response. As a result, the optimized $\text{CaBi}_4\text{Ti}_{3.96}(\text{Cr}_{1/3}\text{Ta}_{2/3})_{0.04}\text{O}_{15}$ ceramic exhibits a high Curie temperature (T_c) of 792 °C, a DC resistivity of $9.5 \times 10^6 \Omega \cdot \text{cm}$ at 500 °C, and a piezoelectric coefficient (d_{33}) of 25.7 pC/N, while retaining 23.3 pC/N after annealing at 600 °C. Multiscale structural characterization reveals that the enhanced piezoelectric performance originates from the increased intrinsic polarization contribution and the synergistic regulation of oxygen-vacancy behavior coupled with the formation of high-density stripe domain structures. This work provides an effective defect-engineering strategy for developing high-performance BLSFs piezoelectric ceramics for harsh-environment applications.

Keywords: $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$, donor-acceptor non-equivalent doping, oxygen vacancies, domains, piezoelectric properties.

1. Introduction

Piezoelectric materials are widely used in the electronic industry due to their unique electromechanical coupling properties [1]. In recent years, the rapid development of advanced

technologies, such as aerospace, deep-well exploration, and nuclear energy systems, has generated an increasing demand for piezoelectric materials capable of operating at elevated temperatures (above 500 °C) [2,3]. Currently, the most widely used piezoelectric materials are based on perovskite structures. Although these materials exhibit excellent piezoelectric coefficients, the Curie temperatures are generally below 400 °C, which severely limits their applicability in emerging high-temperature environments [4,5].

In contrast, bismuth-layer-structured ferroelectrics have attracted considerable attention as promising candidates for high-temperature piezoelectric applications because of their high Curie temperatures, excellent thermal stability, and superior fatigue resistance [6,7]. BLSFs possess a characteristic layered structure consisting of alternating fluorite-like $(\text{Bi}_2\text{O}_2)^{2+}$ layers and perovskite-like $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ layers stacked along the c -axis, where m denotes the number of oxygen-octahedral layers within the perovskite slabs [8]. Among the various BLSFs compounds, $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ (CBT, $m = 4$) has emerged as a particularly attractive system due to its high T_c of approximately 790 °C. However, its spontaneous polarization is restricted to the a - b direction, resulting in relatively low d_{33} and consequently restricting its practical application [9,10].

To address the limited piezoelectric response of CBT, extensive efforts have been devoted to chemical modification over the past decade. Through various doping strategies, the d_{33} of CBT ceramics has been enhanced from approximately 8 pC/N of pure CBT to over 20 pC/N [11–13]. Despite these improvements, the piezoelectric performance of CBT-based ceramics remains inferior to that of many other piezoelectric systems, indicating substantial room for further optimization. In recent years, increasing attention has been paid to the role of oxygen vacancies because of their profound influence on the electrical and piezoelectric properties of ferroelectric materials [14–16]. For

instance, Na/Pr/Ce co-doping was employed to regulate oxygen-vacancy behavior in CBT ceramics, resulting in an enhanced d_{33} of 22.3 pC/N and a high resistivity of $\sim 10^7 \Omega \cdot \text{cm}$ at 500 °C [17]. Similarly, Nb^{5+} donor doping in $\text{Bi}_3\text{Ti}_{1.5}\text{W}_{0.5}\text{O}_9$ effectively reduced the oxygen vacancy concentration, leading to an order-of-magnitude increase in resistivity at 500 °C, significantly suppressing the dielectric loss, and improving d_{33} from 7.5 pC/N to 13 pC/N [18]. In addition, dopant pairs such as Nb/Mg, Ta/Mn, W/Cr, and Nb/Mn have also been used to improve the properties of CBT [12,19–21]. These findings highlight the critical role of oxygen vacancies as tuneable defect species in determining the functional properties of BLSFs ceramics. However, most reported CBT co-doping strategies have focused on equivalent substitution, whereas the synergistic regulation of oxygen vacancies and domain structures through donor–acceptor non-equivalent co-doping has rarely been investigated in CBT ceramics. More importantly, the underlying relationship between defect chemistry, domain evolution, and piezoelectric enhancement remains insufficiently understood.

Motivated by these considerations, the present work proposes a donor-acceptor non-equivalent co-doping strategy for CBT ceramics through the simultaneous introduction of Cr^{3+} and Ta^{5+} ions, where Ta^{5+} acts as a donor and Cr^{3+} as an acceptor. Firstly, the ionic radii of both ions ($\text{Cr}^{3+} \sim 0.615 \text{ \AA}$, $\text{Ta}^{5+} \sim 0.640 \text{ \AA}$, CN = 6) are highly compatible with those of Ti^{4+} ($\sim 0.605 \text{ \AA}$, CN = 6), ensuring the solid solubility of the doping. Secondly, in the literature on bismuth-layered materials, these two ions have been individually used as dopants, and it has been demonstrated that Cr^{3+} can strongly couple with oxygen vacancies, while Ta^{5+} , with its high polarizability, can effectively tune the local polarization environment [19,20,22]. This defect-engineering approach is designed to reduce the concentration of oxygen vacancies via donor doping while simultaneously constructing defect dipoles through acceptor doping. Such synergistic defect engineering is expected to alleviate the pinning effect of oxygen

vacancies on domain-wall motion and suppress the high-temperature conductivity associated with the directional migration of oxygen vacancies. Consequently, the optimized composition, $\text{CaBi}_4\text{Ti}_{3.96}(\text{Cr}_{1/3}\text{Ta}_{2/3})_{0.04}\text{O}_{15}$, exhibits a high Curie temperature of 792 °C, a resistivity of $9.5 \times 10^6 \Omega\cdot\text{cm}$ at 500 °C, and a d_{33} of 25.7 pC/N. Multiscale structural characterization reveals that the significantly reduced oxygen-vacancy concentration, together with the formation of high-density stripe domain structures, is responsible for the enhanced piezoelectric performance. The present work offers valuable insights into defect engineering in BLSFs materials and provides a promising strategy for the development of high-performance piezoelectric ceramics for harsh-environment applications.

2. Experimental

The piezoelectric ceramics $\text{CaBi}_4\text{Ti}_{4-x}(\text{Cr}_{1/3}\text{Ta}_{2/3})_x\text{O}_{15}$ ($x = 0.00, 0.02, 0.04, 0.06$, abbreviated as CBT- $x\text{CrTa}$) were prepared by the solid-state reaction method. The raw materials included CaCO_3 (99%), Bi_2O_3 (99.99%), TiO_2 (99.8%), Cr_2O_3 (99%), and Ta_2O_5 (99.99%). The powders were weighed according to the stoichiometric ratio, then ball-milled with anhydrous ethanol for 4 hours, and the mixed powders were dried and calcined at 850 °C for 4 hours. The calcined powders were re-ball-milled and dried under the same conditions. Using a concentration of 6 wt% polyvinyl butyral (PVB) as the binder, the powders were mixed evenly and then pressed into discs with a diameter of 10 mm. The discs were slowly heated to 500 °C to remove PVB, and then sintered at 1080 °C for 2 hours. After sintering, the upper and lower surfaces of the samples were polished, and silver paste was applied and then fired at 720 °C for 15 minutes to form silver electrodes.

The XRD patterns of the ceramics were tested using an X-ray diffractometer (D8 ADVANCE, Bruker, Germany). The Raman spectra of the samples were measured using a Raman spectrometer equipped with a 532 nm laser (Horiba Jobin Yvon HR800, France). The microstructure of the sintered

samples was observed using a scanning electron microscope (Hitachi SU-5000 FE-SEM, Japan). The elemental composition and electronic energy levels of the samples were determined using X-ray photoelectron spectroscopy (ESCALAB 250XI, Thermo, USA). The relative concentration of oxygen vacancies in the ceramics was evaluated using an electron paramagnetic resonance (EPR) spectrometer (EMX plus-6/1, Bruker, Germany). The dielectric properties were measured using an impedance analyzer (E4990A, Keysight). The DC resistivity of the samples at 200–700 °C was measured using a high-resistance meter (6517B, KEITHLEY). The ferroelectric properties were measured using a ferroelectric analyzer (Analyzer 2000E, aix-ACCT) at 180 °C and 1 Hz, and the leakage current density–electric field (J – E) characteristics were measured at 180 °C using the same ferroelectric analyzer. The samples were poled in a silicone oil bath at 180 °C under a DC electric field of 10–16 kV·mm⁻¹ for 30 min, and the d_{33} values were subsequently measured at room temperature using a quasi-static d_{33} tester (ZJ-3AN, Institute of Acoustics Academic, China). The samples were held at various temperature from 100–800 °C for 60 min, and then the annealed d_{33} was measured after cooling to room temperature. The domain structure and local piezoelectric response of the samples were observed using piezoresponse force microscopy (Cypher S, Asylum Research, USA).

3. Results and discussion

Figure 1(a) presents the room-temperature XRD patterns of CBT- x CrTa ceramics. The diffraction peaks of all samples can be well indexed to the standard pattern of CaBi₄Ti₄O₁₅ (PDF#52-1640), indicating that the Cr³⁺/Ta⁵⁺ dopants are successfully incorporated into the CBT lattice without altering the crystal structure [23]. The most intense diffraction peak corresponds to the (119) reflection, which is the characteristic ($112m+1$) peak of BLSFs compounds with $m = 4$. A schematic illustration of the crystal structure is shown in Fig. 1(b). Notably, a weak secondary phase identified as Bi_{1.74}Ti₂O_{6.624}

appears adjacent to the (119) peak when $x = 0.06$. This impurity phase is likely induced by excessive dopant incorporation together with Bi_2O_3 volatilization during sintering, resulting in a local deviation from the stoichiometric Bi/Ti ratio [24,25]. Furthermore, we performed Rietveld refinement on the XRD data to obtain more detailed lattice parameters, as shown in Table 1 and Fig. S1 in the Electronic Supplementary Material (ESM). The reliability factors (R_{wp}) for all refined samples are less than 10%, and the goodness of fit (GOF) values are around 2, indicating that the refinement results are reliable. The results show that with increasing doping content, the lattice parameters a , b , and c exhibit an increasing trend, and the unit-cell volume V increases from $1199.734 \text{ \AA}^3$ to $1202.356 \text{ \AA}^3$. This phenomenon can be attributed to the substitution of Ti^{4+} ($\sim 0.605 \text{ \AA}$, CN = 6) by the larger dopant ions ($\text{Cr}^{3+} \sim 0.615 \text{ \AA}$, $\text{Ta}^{5+} \sim 0.640 \text{ \AA}$, CN = 6), which promotes lattice expansion. This increases the degree of distortion of the TiO_6 octahedra, which is beneficial for enhancing the intrinsic polarizability.

To further elucidate the structural influence of $\text{Cr}^{3+}/\text{Ta}^{5+}$ co-doping, Raman spectroscopy was employed, as shown in Fig. 1(c). All samples exhibit similar Raman profiles without detectable impurity-related vibrational modes, further confirming the successful incorporation of Cr and Ta into the CBT lattice. The Raman spectra were deconvoluted into eight characteristic modes (ν_1 – ν_8) using Lorentzian fitting. According to previous reports, these vibrational modes can be divided into low-frequency modes (below 200 cm^{-1}), mainly associated with the vibrations of the $(\text{Bi}_2\text{O}_2)^{2+}$ layers and A-site cations, and high-frequency modes (above 200 cm^{-1}), which are closely related to the distortion of TiO_6 octahedra [26,27]. These vibrational modes have been summarized in Table 2. As illustrated in Figs. 1(d–e), the frequencies of the low-frequency ν_1 and ν_2 modes exhibit only minor fluctuations with increasing dopant concentration, indicating that the $(\text{Bi}_2\text{O}_2)^{2+}$ layers and A-site environments remain essentially unchanged. In contrast, pronounced shifts are observed in the high-frequency ν_4 , ν_6 ,

v_7 , and v_8 modes, indicating changes in the local TiO_6 octahedral environment induced by $\text{Cr}^{3+}/\text{Ta}^{5+}$ co-doping. These structural modifications may alter the local polarization environment and are therefore expected to influence the ferroelectric and piezoelectric responses of the ceramics [28].

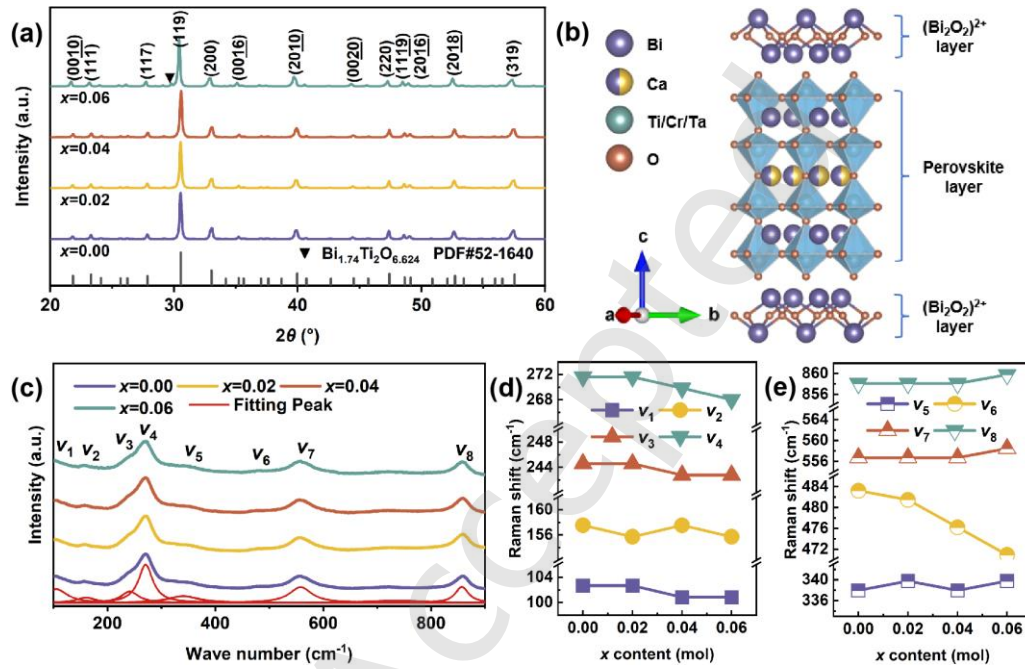


Fig. 1 Structure characterization of CBT-xCrTa ceramics: (a) room-temperature XRD patterns, (b) schematic illustration of the crystal structure, (c) Raman spectra, (d, e) compositional dependence of the Raman vibrational modes.

Table 1 Rietveld refinement results of XRD for CBT-xCrTa ceramics

Sample	a (Å)	b (Å)	c (Å)	V (Å ³)	R_{wp} (%)	GOF
CBT-0.00CrTa	5.43491	5.41622	40.75646	1199.734	8.73	1.97
CBT-0.02CrTa	5.43707	5.41804	40.76723	1200.931	9.22	2.18
CBT-0.04CrTa	5.43771	5.41832	40.77858	1201.470	9.71	2.40

Table 2 Assignments and types of characteristic vibrational modes of Raman peaks for CBT based on references [26,27,29–33].

Peak number	Raman shift (cm ⁻¹)	Symmetry type	Vibration assignment
ν_1	~100	A _{1g}	Vibrations related to the (Bi ₂ O ₂) ²⁺ layer
ν_2	~160	A _{1g}	A-site cation vibration
ν_3	~240	B _{1g}	Torsional vibration of TiO ₆ octahedron
ν_4	~270	B _{2g} and B _{3g}	Bending vibration of O-Ti-O
ν_5	~340	B _{1g}	Bending vibration of TiO ₆ octahedra
ν_6	~480	B _{1g}	Torsional vibration of Ti-O-Ti
ν_7	~560	A _{1g}	Asymmetric deformation vibration of oxygen atoms in TiO ₆ octahedra
ν_8	~860	B _{1g}	Symmetric TiO ₆ stretching

The surface morphologies of CBT-*x*CrTa ceramics are presented in Figs. 2(a–d). Scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) elemental mapping for *x* = 0.04 (Fig. S2 in the ESM) confirms a homogeneous distribution of all constituent elements, indicating that no obvious elemental segregation occurs after Cr³⁺/Ta⁵⁺ co-doping. Consistent with the anisotropic grain-growth characteristics of BLSFs, all samples exhibit a typical plate-like morphology, reflecting the preferential growth of grains along the *a-b* plane [34]. A pronounced evolution in grain morphology is observed with increasing dopant content. As shown in Fig. 2(e) and Fig. S3 in the ESM, the average grain

thickness gradually increases from 0.6 μm to 0.76 μm , while the average length more significantly increases from 2.3 μm to 5.9 μm . To further evaluate the anisotropic growth behavior, the aspect ratio (average length-to-thickness ratio) was calculated, as summarized in Fig. 2(f). The aspect ratio increases continuously from 4.8 to 8.8 with increasing $\text{Cr}^{3+}/\text{Ta}^{5+}$ content, indicating enhanced preferential grain growth along the a - b plane. These results suggest that the lattice distortion induced by the substitution of Ti^{4+} with $\text{Cr}^{3+}/\text{Ta}^{5+}$ ions may weaken local chemical bonds, reduce the activation barrier for atomic diffusion, and thereby facilitate grain boundary migration and grain growth [10,35].

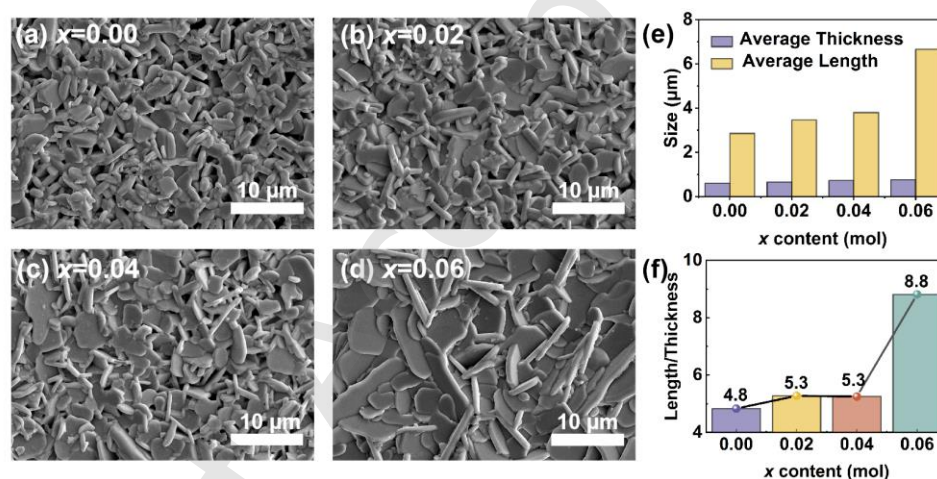
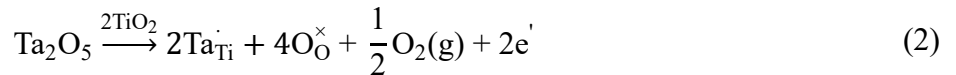
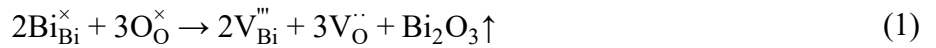


Fig. 2 Microstructural evolution of CBT- x CrTa ceramics: (a–d) SEM micrographs of samples with different Cr/Ta contents, (e) average grain length and thickness, (f) grain aspect ratio (length/thickness).

To assess the evolution of defects related to oxygen vacancies, the O 1s XPS spectra were analyzed. As shown in Figs. 3(a–d), the O 1s spectra can be deconvoluted into two components centered at approximately 529 and 531 eV, corresponding to lattice oxygen and defect-associated oxygen species, respectively. The latter is commonly employed as an indicator of the relative oxygen-vacancy concentration in oxide ceramics. The fraction of oxygen-vacancy-related species decreases markedly

from 32.06% for pure CBT to 16.56% at $x = 0.04$, before increasing to 28.20% at $x = 0.06$.

The evolution of oxygen-vacancy concentration can be rationalized on the basis of the defect chemistry described by Eqs. (1–6). During high-temperature sintering, volatilization of Bi_2O_3 inevitably generates bismuth vacancies and charge-compensating oxygen vacancies (Eq. (1)). Upon substitution of Ti^{4+} by Ta^{5+} , donor defects (Ta_{Ti}') are introduced, producing compensating electrons (Eq. (2)). These electrons can annihilate pre-existing oxygen vacancies through the reactions described by Eqs. (3–4), thereby reducing the overall concentration of mobile ionic defects. Simultaneously, acceptor-type (Cr_{Ti}') defects tend to associate with oxygen vacancies owing to electrostatic interactions, forming ($\text{Cr}_{\text{Ti}}'-\text{V}_{\text{O}}''$) defect-dipoles (Eqs. (5–6)). Such defect complexes effectively immobilize oxygen vacancies and suppress their long-range migration under thermal activation. Consequently, the synergistic donor–acceptor co-doping strategy substantially reduces the concentration and mobility of oxygen vacancies at moderate doping levels. When the dopant concentration is further increased to $x = 0.06$, however, a secondary phase emerges, indicating that the solubility limit is being approached. The resulting local compositional imbalance, together with intensified Bi depletion, reconstructs the defect equilibrium and promotes the re-formation of oxygen vacancies, giving rise to the observed increase in oxygen-vacancy concentration.



EPR spectroscopy was used to further evaluate the relative variation in oxygen-vacancy-related defects, as shown in Fig. 3(e). The signals at $g \approx 2.003$ are generally attributed to defects associated with oxygen vacancies [36]. Its intensity decreases with increasing Cr/Ta content, reaches a minimum at $x = 0.04$, and then increases at $x = 0.06$, consistent with the XPS fitting. The J - E curves in Fig. 3(f) provide complementary electrical evidence: the $x = 0.04$ sample shows the lowest leakage current density. In addition, all compositions show similar J - E curve shapes, suggesting that doping changes the magnitude of conduction without introducing an evidently different dominant conduction regime. Together, the XPS, EPR, and J - E results support a minimum in oxygen-vacancy-related defects at $x = 0.04$. The above multiscale characterization demonstrates that Cr/Ta co-doping can effectively tailor oxygen vacancies, thereby improving the overall performance of the samples.

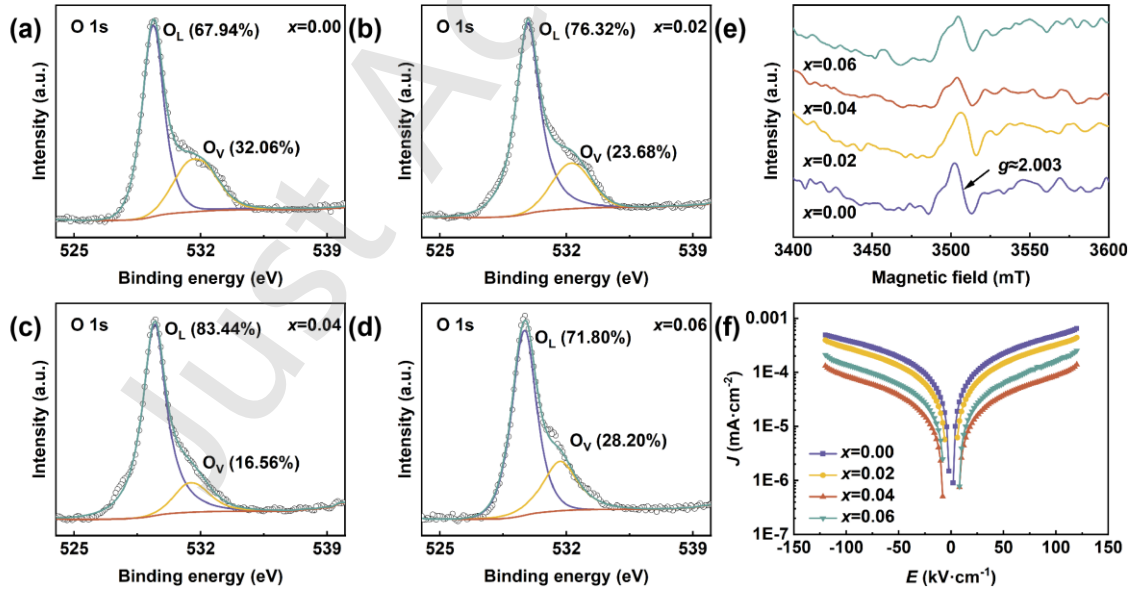


Fig. 3 Oxygen vacancy characterization of the CBT-xCrTa ceramics: (a–d) XPS O 1s spectra with Gaussian fitting, (e) EPR spectra, and (f) J - E curves.

Figures 4(a–b) present the temperature dependence of the relative permittivity (ϵ_r) and dielectric

loss ($\tan\delta$) of CBT- x CrTa ceramics measured at 1 MHz. The permittivity maximum corresponds to the phase transition from the orthorhombic ferroelectric phase to the tetragonal paraelectric phase, and the temperature at which the maximum occurs is defined as the Curie temperature [37]. With increasing $\text{Cr}^{3+}/\text{Ta}^{5+}$ content, the dielectric permittivity gradually increases, which can be attributed to the defect-mediated softening effect associated with donor doping. The reduced concentration of oxygen vacancies weakens defect pinning and facilitates reversible domain-wall motion under an external electric field, thereby enhancing the dielectric response [33]. Furthermore, the substitution of Ti^{4+} by $\text{Cr}^{3+}/\text{Ta}^{5+}$ ions enhances the degree of local lattice distortion, leading to an increase in the intrinsic lattice polarizability, which further contributes to the dielectric response [38]. Therefore, the enhancement of the permittivity in Cr/Ta-doped ceramics is a synergistic consequence of extrinsic pinning release and intrinsic polarization enhancement.

The corresponding T_c values and dielectric losses measured at 500 °C are summarized in Fig. 4(c). Although substitution of Ti^{4+} by $\text{Cr}^{3+}/\text{Ta}^{5+}$ may modify the local TiO_6 octahedral environment, the Curie temperature of CBT is predominantly governed by the Aurivillius layered framework and the stereochemically active $\text{Bi}^{3+} 6s^2$ lone pair. Consequently, only slight variations in T_c (from 791 to 792 °C) are observed after $\text{Cr}^{3+}/\text{Ta}^{5+}$ co-doping. In addition, all $\text{Cr}^{3+}/\text{Ta}^{5+}$ -doped samples maintain low dielectric losses at 500 °C, with $\tan\delta$ values below 0.025. This behavior is mainly attributed to the synergistic defect-regulation effect of donor–acceptor co-doping. On the one hand, donor doping suppresses the formation of oxygen vacancies, thereby reducing charge-carrier concentration. On the other hand, acceptor-induced defect dipoles can hinder the long-range migration of oxygen vacancies at elevated temperatures. As a result, the dielectric losses of the doped ceramics are lower than those of pure CBT [22]. When the dopant concentration is further increased, however, a slight increase in

dielectric loss is observed. This behavior is likely associated with the pronounced grain growth and the emergence of a secondary phase, which may introduce additional leakage pathways and partially deteriorate the insulating characteristics of the ceramics [39].

To further elucidate the influence of $\text{Cr}^{3+}/\text{Ta}^{5+}$ co-doping on the dielectric response of CBT ceramics, the relationship between $1000/\varepsilon_r$ and temperature is plotted in Fig. 4(d). The deviation from the Curie-Weiss law can be quantified by $\Delta T_m = T_{\text{cw}} - T_m$, where T_m denotes the temperature corresponding to the maximum dielectric permittivity, and T_{cw} is the temperature above which the dielectric behavior follows the Curie-Weiss law [26,40]. As shown in Fig. 4(d), ΔT_m increases progressively from 4 °C for pure CBT to 9 °C for the doped compositions. Furthermore, Fig. S4 in the ESM presents the temperature-dependent dielectric spectra measured at several frequencies. Frequency dispersion becomes more pronounced as the Cr/Ta content increases. T_m is nearly frequency independent for $x = 0.00$, whereas it shifts to higher temperature by approximately 4 °C for $x = 0.06$ across the measured frequency range, indicating a gradual enhancement of the diffuse phase-transition behavior. To further evaluate the relaxor characteristics, the modified Curie-Weiss law was employed, and the corresponding diffuseness coefficient (γ) is summarized in Fig. 4(e). With increasing $\text{Cr}^{3+}/\text{Ta}^{5+}$ content, γ increases from 1.23 to 1.45, revealing a progressively stronger deviation from a normal ferroelectric phase transition. The simultaneous increase in both ΔT_m and γ suggests that the local compositional fluctuations and lattice distortions at the B-site induced by the substitution of Ti^{4+} with Cr^{3+} and Ta^{5+} ions of different ionic radii broaden the phase-transition region and promote relaxor-like dielectric behavior, which is consistent with the XRD and Raman results.

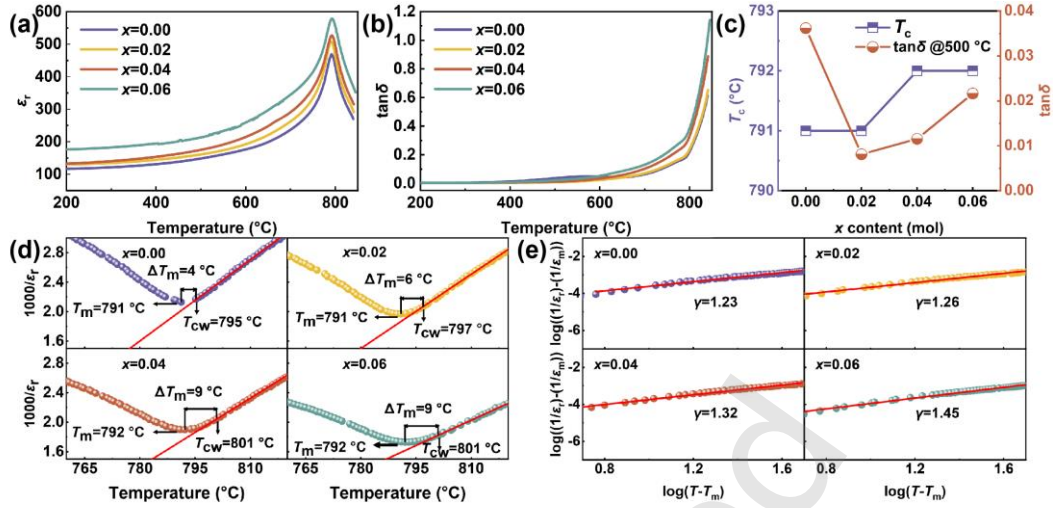


Fig. 4 Dielectric properties of CBT- x CrTa ceramics measured at 1 MHz: (a) Temperature dependence of relative permittivity, (b) Temperature dependence of dielectric loss, (c) T_c and $\tan\delta$ values at 500 °C as a function of dopant content, (d) Relationship between $1000/\epsilon_r$ and temperature, (e) Relationship between $\log(1/\epsilon_r - 1/\epsilon_m)$ and $\log(T - T_m)$.

The temperature dependence of the DC resistivity (ρ_{dc}) of CBT- x CrTa ceramics measured from 200 to 700 °C is presented in Fig. 5(a). For all compositions, the resistivity decreases monotonically with increasing temperature, exhibiting a typical negative temperature coefficient behavior. This trend can be attributed to thermally activated charge transport, whereby increasing thermal energy enables charge carriers, particularly oxygen-vacancy-related defects, to overcome migration barriers and contribute more effectively to electrical conduction [41,42]. At 500 °C, the resistivity initially increases from $6.9 \times 10^6 \Omega \cdot \text{cm}$ for $x = 0.00$ to $9.5 \times 10^6 \Omega \cdot \text{cm}$ for $x = 0.04$, and subsequently decreases to $8.4 \times 10^6 \Omega \cdot \text{cm}$ for $x = 0.06$. Notably, all samples maintain resistivities on the order of $10^6 \Omega \cdot \text{cm}$ at 500 °C, demonstrating good high-temperature insulating characteristics.

To gain further insight into the conduction behavior of CBT- x CrTa ceramics, the activation energy (E_a) was determined using the Arrhenius relationship (7) [43]:

$$\rho = \rho_0 \exp \left(-\frac{E_a}{K_B T} \right) \quad (7)$$

where ρ is the DC resistivity, ρ_0 is the pre-exponential factor, K_B is the Boltzmann constant, and T is the absolute temperature. Accordingly, E_a can be extracted from the slope of the $\ln \rho$ versus $1000/T$ plots. As shown in Fig. 5(b), two distinct conduction regimes can be identified, separated by a transition temperature of approximately 350 °C. The corresponding activation energies obtained from linear fitting are summarized in Fig. 5(c) and Table S1 in the ESM. In the low-temperature region (below 350 °C), the E_a values range from 0.72 to 0.83 eV, suggesting that electrical conduction is primarily associated with defect-related electronic transport, such as carrier hopping mediated by impurity states or localized defects within the lattice [44]. In contrast, the activation energies in the high-temperature region (above 350 °C) are significantly higher, varying from 1.26 eV for pure CBT to 1.30 eV for $x = 0.04$, followed by a slight decrease to 1.25 eV for $x = 0.06$. Such values are characteristic of oxygen-vacancy-mediated ionic conduction and are consistent with the thermally activated migration of oxygen vacancies at elevated temperatures [45]. The increase in E_a from $x = 0$ to $x = 0.04$ indicates a higher migration barrier for ionic transport, which is likely associated with the suppression of oxygen-vacancy defects induced by Cr/Ta co-doping.

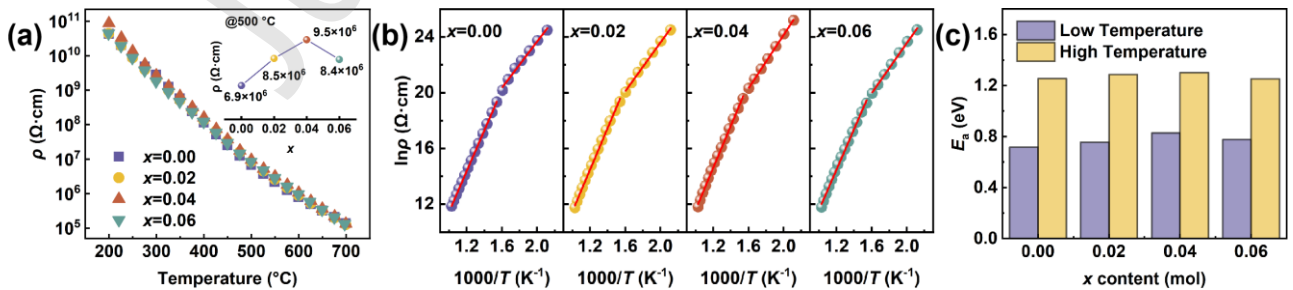


Fig. 5 Electrical transport properties in CBT- x CrTa ceramics: (a) temperature dependence of DC resistivity measured from 200 to 700 °C, (b) Arrhenius plots of DC resistivity, (c) composition dependence of the activation energy in different temperature regions.

The ferroelectric properties of the CBT- x CrTa ceramics are presented in Figs. 6(a–e). All samples exhibit well-saturated polarization–electric field (P – E) hysteresis loops accompanied by distinct current–electric field (I – E) responses, confirming robust ferroelectric switching behavior. A slight horizontal offset of the P – E loops can be observed for all compositions, indicating the presence of an internal bias field. Such behavior is commonly associated with defect-related pinning effects, particularly the interaction between oxygen-vacancy-associated defect complexes and ferroelectric domain walls, which partially restrict domain switching under an applied electric field [46].

To quantitatively evaluate the influence of Cr/Ta co-doping on the ferroelectric response, the coercive field ($2E_c$) and remanent polarization ($2P_r$) were extracted from the hysteresis loops and are summarized in Fig. 6(f). With increasing $\text{Cr}^{3+}/\text{Ta}^{5+}$ content, $2E_c$ decreases progressively, whereas $2P_r$ increases continuously, reaching a maximum value of $19.3 \mu\text{C}\cdot\text{cm}^{-2}$ at $x = 0.06$. These results indicate a gradual softening of the ferroelectric behavior induced by Cr/Ta co-doping.

The evolution of the ferroelectric properties can be understood from the combined effects of defect regulation and microstructural development. At moderate doping levels, donor-induced suppression of oxygen vacancies reduces defect-related pinning centers, thereby facilitating domain-wall motion and polarization reversal under an external electric field. This interpretation is consistent with the XPS results, which reveal a pronounced decrease in oxygen-vacancy concentration from $x = 0.00$ to $x = 0.04$. In addition, Cr/Ta co-doping promotes anisotropic grain growth, leading to larger plate-like grains with reduced grain-boundary density. Since grain boundaries act as obstacles to domain-wall propagation, the enlarged grain size lowers the switching barrier and contributes to the observed decrease in coercive field.

Although the oxygen-vacancy concentration increases slightly at $x = 0.06$, the remanent polarization continues to increase. This behavior suggests that the beneficial effect of grain growth on domain switching outweighs the adverse influence of the increased defect concentration. The significantly enlarged grains provide a more favorable environment for domain reorientation and polarization development, resulting in the highest $2P_r$ value for the $x = 0.06$ composition. Consequently, the enhanced ferroelectric performance of the Cr/Ta-doped ceramics originates from the synergistic interplay between defect engineering and microstructural evolution.

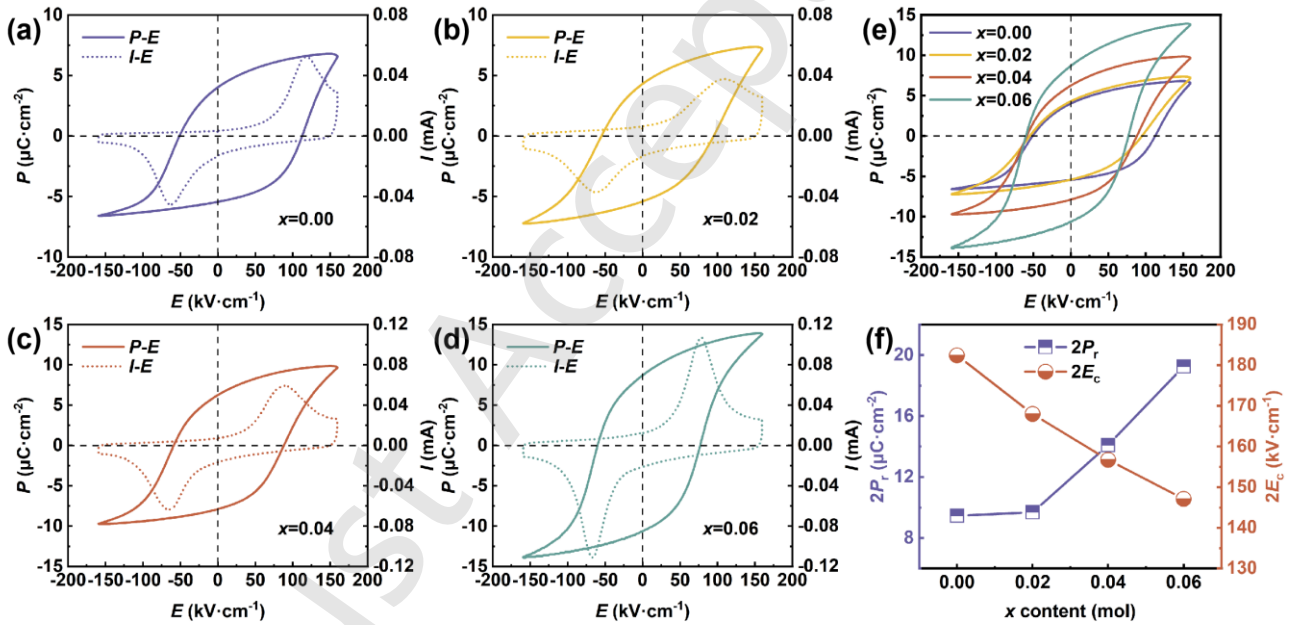


Fig. 6 Ferroelectric behavior of CBT- x CrTa ceramics: (a–d) P – E hysteresis loops and corresponding I – E curves for $x = 0.00$, 0.02 , 0.04 , and 0.06 , (e) Comparison of the P – E loops, (f) Composition dependence of $2P_r$ and $2E_c$.

The room-temperature piezoelectric coefficients of the poled CBT- x CrTa ceramics are summarized in Fig. 7(a). All doped samples exhibit enhanced piezoelectric responses compared with pure CBT, demonstrating the effectiveness of Cr/Ta co-doping in improving the electromechanical performance

of the ceramics. The d_{33} value increases initially with increasing dopant concentration, reaching a maximum of 25.7 pC/N at $x = 0.04$, and then decreases slightly at $x = 0.06$.

The enhanced piezoelectric response may arise from two contributions. First, Cr/Ta-induced local lattice distortion can increase lattice polarizability and strengthen the intrinsic piezoelectric response [47]. Second, the lower concentration of oxygen-vacancy-related defects at moderate doping levels reduces domain-wall pinning and facilitates field-induced domain-wall motion. The combined intrinsic and extrinsic contributions account for the improved electromechanical response. Although the remanent polarization continues to increase at $x = 0.06$, the piezoelectric coefficient decreases slightly, suggesting that piezoelectric activity is governed not only by polarization magnitude but also by defects and domain-wall mobility. The increase in oxygen-vacancy concentration and the emergence of a secondary phase at high doping levels are therefore likely responsible for the slight deterioration of the piezoelectric response.

The thermal stability of the piezoelectric properties was further evaluated through thermal depolarization measurements, as shown in Fig. 7(b). For all compositions, the d_{33} value decreases gradually with increasing temperature. Notably, the $x = 0.04$ sample retains a d_{33} value of 23.3 pC/N after annealing at 600 °C, corresponding to only a 9.4% reduction relative to its room-temperature value, indicative of excellent thermal stability. This superior stability can be attributed to the reduced concentration and mobility of oxygen vacancies, which suppress thermally activated defect migration and mitigate the degradation of domain alignment at elevated temperatures. As the temperature increases further, intensified lattice vibrations and migration of oxygen vacancies progressively destabilize the domain structure, leading to a continuous decrease in piezoelectric response. Once the temperature approaches the T_c , the ferroelectric-to-paraelectric phase transition occurs, resulting in the

disappearance of spontaneous polarization and, consequently, the complete loss of piezoelectricity [48,49]. Furthermore, CBT-0.04CrTa was repeatedly heated to 500 °C, held for 1 h, and cooled before d_{33} was measured, as shown in Fig. 7(c). After the initial decrease, d_{33} remained approximately 25.2 pC/N over the subsequent cycles, indicating stable post-cycle piezoelectric retention under this test protocol. The initial decrease may reflect partial domain reversal during the first high-temperature cycle.

Figure 7(d) and Table S2 in the ESM compare the piezoelectric coefficient and Curie temperature of the optimized CBT-0.04CrTa ceramic with those reported for other modified CBT-based ceramics [12,13,19–21,24,25,27,50–53]. The CBT-0.04CrTa composition exhibits a competitive d_{33} value while maintaining an exceptionally high T_c of 792 °C, highlighting the effectiveness of the donor–acceptor co-doping strategy in simultaneously enhancing piezoelectric activity and high-temperature stability. These results demonstrate that defect engineering through synergistic Cr/Ta co-doping provides an effective route for developing high-performance Aurivillius piezoelectric ceramics for harsh-environment applications.

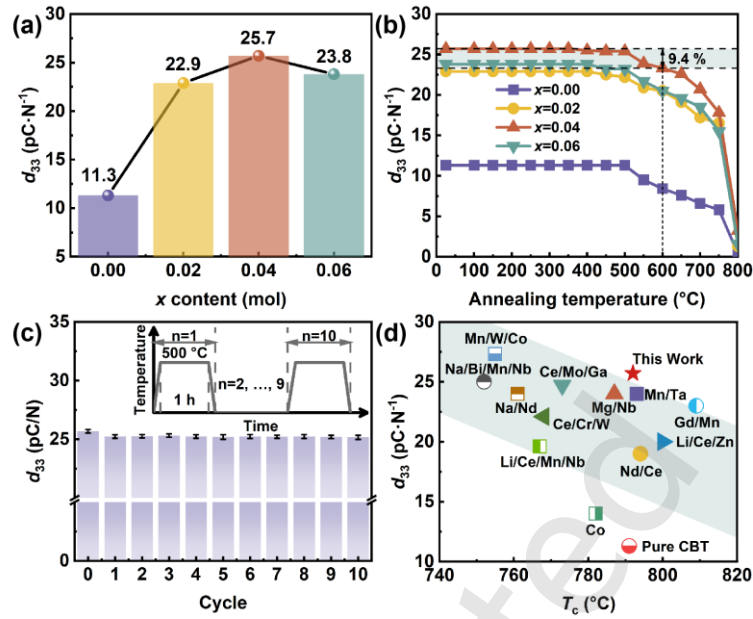


Fig. 7 Piezoelectric performance and thermal stability of CBT-xCrTa ceramics: (a) Composition dependence of the piezoelectric coefficient, (b) Thermal depolarization behavior of d_{33} , (c) Cyclic annealing of CBT-0.04CrTa at 500 °C for 1 h, (d) Comparison of d_{33} and T_c values between CBT-0.04CrTa and representative modified CBT-based ceramics reported in the literature.

To further elucidate the origin of the enhanced piezoelectric performance, the domain structures of the $x = 0.00$ and $x = 0.04$ samples were characterized by piezoresponse force microscopy (PFM), as shown in Fig. 8(a). The CBT-0.04CrTa ceramic exhibits a noticeably stronger PFM amplitude response than the pure CBT sample, indicating an enhanced local electromechanical activity. Moreover, well-developed high-density stripe domains are observed in the doped ceramic, and adjacent domains display a phase contrast of approximately 180°. The introduction of Cr³⁺/Ta⁵⁺ ions into the B-site disrupts the long-range ferroelectric order and introduces local lattice distortions and compositional fluctuations [54]. Together with the altered oxygen-vacancy-related defect landscape, these local perturbations may favor the formation of high-density stripe domains. Creating additional domain walls can help accommodate elastic and defect-related energies associated with local lattice mismatch

[3,55]. The formation of these densely distributed stripe domains is expected to increase the density of switchable domain walls, thereby facilitating polarization reorientation under an external electric field and contributing to the enhanced piezoelectric response [56]. In contrast, the pure CBT ceramic exhibits a weaker phase contrast and less pronounced domain features. Considering the significantly higher oxygen-vacancy concentration revealed by XPS analysis, this behavior is likely associated with stronger defect-induced pinning of domain walls, which hinders domain-wall motion and limits the electromechanical response. In addition to defect regulation, Cr/Ta co-doping markedly promotes anisotropic grain growth. The enlarged plate-like grains can accommodate more extensive domain structures and reduce the constraint imposed by grain boundaries. As a result, the density of mobile domain walls is increased, while intergranular stresses and domain-wall migration barriers are reduced. These factors collectively facilitate domain-wall motion under an applied electric field and contribute to the enhanced piezoelectric performance of the CBT–0.04CrTa ceramic.

Figure 8(b) compares the domain wall evolution behaviors of CBT and CBT-0.04CrTa during the poling process. After sintering, the ferroelectric domains with spontaneous polarization and the defect dipoles formed by acceptor doping via trapping oxygen vacancies are randomly oriented in the piezoelectric ceramics. After poling, the high-density stripe domains in CBT-0.04CrTa, which possess a lower domain wall migration barrier, can rapidly switch and rearrange along the electric field direction, thus contributing to excellent piezoelectric performance [57]. However, for CBT, the insufficient ferroelectric domain activity together with the excessively high concentration of oxygen vacancies leads to strong pinning of domain wall motion, making it difficult for the domains to respond to the external electric field and ultimately resulting in relatively low piezoelectric activity. This interpretation is consistent with the switching spectroscopy PFM results (Fig. S5 in the ESM). Under

a DC bias of ± 100 V, a larger fraction of domains switched in CBT-0.04CrTa than in pristine CBT. This comparison supports the greater field-induced switchability of the high-density stripe-domain structure in the doped ceramic. Together with the lower concentration of oxygen-vacancy-related defects, this behavior contributes to the enhanced piezoelectric response of CBT-0.04CrTa.

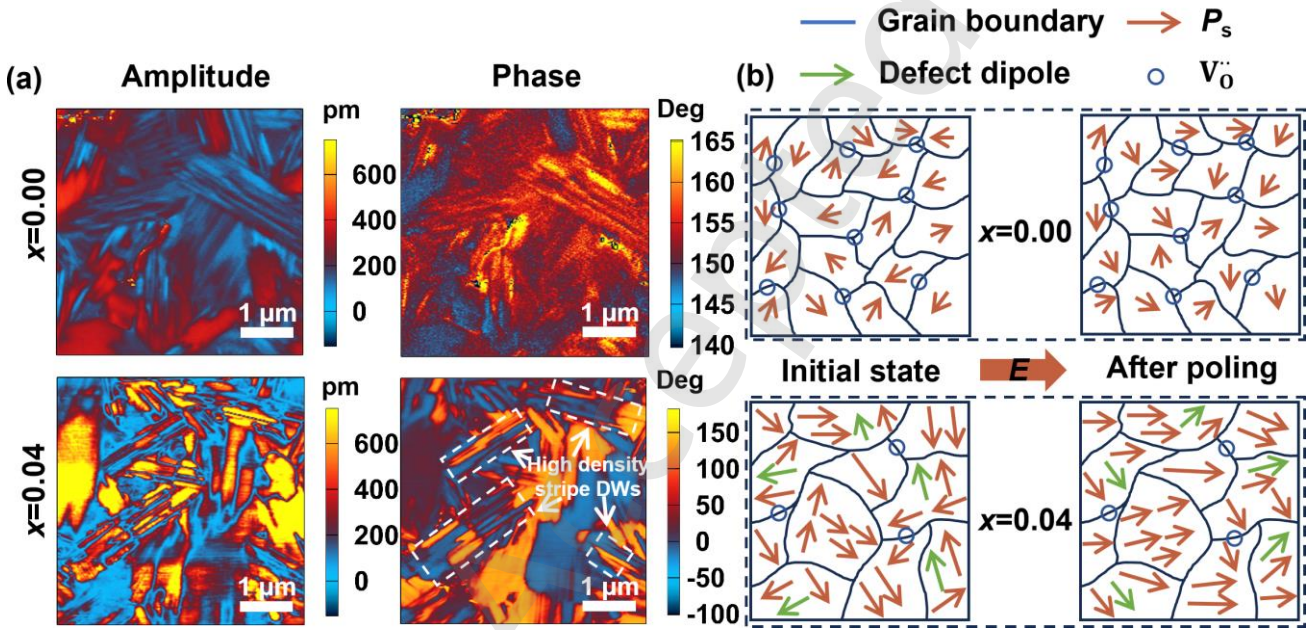


Fig. 8 Domain evolution and defect-engineering mechanism: (a) PFM amplitude and phase images of the $x = 0.00$ and $x = 0.04$ samples, (b) Schematic illustration showing how oxygen-vacancy regulation and domain-structure optimization contribute to the enhanced piezoelectric performance.

4. Conclusions

A donor–acceptor defect engineering strategy was developed to optimize the piezoelectric performance of $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ -based ceramics through $\text{Cr}^{3+}/\text{Ta}^{5+}$ co-doping. Structural analyses confirmed the successful incorporation of the dopants into the CBT lattice, enhancing the local lattice distortion of the TiO_6 octahedron and increasing the intrinsic polarization contribution of the material.

Meanwhile, the defect characterization revealed that the co-doping effectively regulated the oxygen-vacancy concentration and suppressed oxygen-vacancy migration. Consequently, the ceramics exhibited enhanced electrical resistivity, reduced dielectric loss, improved ferroelectric polarization, and a significantly increased piezoelectric coefficient without compromising the intrinsically high Curie temperature. PFM observations further demonstrated that the enhanced piezoelectric response is closely associated with the formation of high-density stripe domain structures and the reduced pinning effect of oxygen vacancies on domain-wall motion. These results demonstrate that rational defect engineering provides an effective route to simultaneously regulate oxygen-vacancy behavior and domain configuration, thereby achieving balanced piezoelectric and high-temperature electrical properties in BLSFs ceramics. This work offers valuable guidance for the design of high-performance high-temperature piezoelectric materials for harsh-environment applications.

Electronic Supplementary Material

Supplementary material is available in the online version of this article.

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Author contributions

Junhui Tan: investigation, methodology, data curation, validation, formal analysis, conceptualization, writing—original draft. Xuanyu Chen: investigation, methodology, formal analysis. Yuxing Dai: investigation, methodology, formal analysis. Yi Cheng: methodology, formal analysis. Xiqi Chen: methodology, formal analysis. Bao Ou: methodology, formal analysis. Guanfu Liu: methodology, formal analysis. Bin Li: funding acquisition, resources, supervision, project administration. Yejing Dai: methodology, formal analysis, writing—review & editing, conceptualization, funding acquisition, resources, supervision, project administration.

Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

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