

## Enhancement of Piezoelectric Properties in $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ -based Ceramics through $\text{Bi}^{3+}$ Self-doping Strategy

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**Abstract:** High-temperature piezoelectric vibration sensors are the preferred choice for structural health monitoring in harsh environments such as high temperatures and complex vibrations. Bismuth layer-structured  $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$  (CBT) high-temperature piezoelectric ceramics, with high Curie temperature ( $T_C$ ), are the key components for piezoelectric vibration sensors operating at temperatures exceeding 500 °C. However, their low piezoelectric coefficient ( $d_{33}$ ) greatly limits their high-temperature applications. In this work, a novel  $\text{Bi}^{3+}$  self-doping strategy was employed to enhance the piezoelectric performance of CBT ceramics. The enhancement is attributed to an increase in the number of grain boundaries, providing more sites for space charge accumulation and promoting formation of space charge polarization. Furthermore, given that space charge polarization predominantly occurs at low frequencies, dielectric temperature spectra at different frequencies were used to elucidate the mechanism by which space charge polarization enhances piezoelectric properties of CBT ceramics. Excellent overall performance was achieved for the CBT-based high-temperature piezoelectric ceramics. Among them,  $T_C$  reached 778 °C,  $d_{33}$  increased by more than 30%, reaching 20.1 pC/N, and the electrical resistivity improved by one order of magnitude (reaching  $6.33 \times 10^6 \Omega \cdot \text{cm}$  at 500 °C). These advancements provide a key functional material with excellent performance for practical applications of piezoelectric vibration sensors at 500 °C and above.

**Key words:** high-temperature piezoelectric ceramic; bismuth layer structure; self-doping; space charge polarization; oxygen vacancy

Piezoelectric materials are a vital category of functional materials<sup>[1-2]</sup>. Among them, high-temperature piezoelectric vibration sensors, which typically use piezoelectric ceramics as their key components, are widely applied in various high-temperature environments. For example, vibration monitoring systems in aero-engines and other critical equipment, operating at 500 °C or higher temperatures, impose stringent requirements on the piezoelectric sensors and ceramics to ensure reliable and long-term performance under such extreme conditions<sup>[3-5]</sup>. CBT, a bismuth layer-structured piezoceramic (BLSP), exhibits high  $T_C$  (780 °C) and low aging rate, positioning it as a promising candidate for high-temperature

piezoelectric vibration sensors operating at 500 °C and above<sup>[6-7]</sup>. However, challenges such as low piezoelectric performance, significant reduction in resistivity at high temperatures, and unclear mechanisms for enhancing piezoelectric activity hinder its practical applications<sup>[8-9]</sup>.

Current research indicates that the enhancement of piezoelectric properties in BLSP is related to intrinsic contributions from lattice distortion and extrinsic contributions from changes of domain walls<sup>[10-12]</sup>. Doping modification can improve piezoelectric performance by altering the magnitude of these contributions. The self-doping strategy, which avoids the introduction of

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foreign ions, is considered a simple and effective method for enhancing piezoelectric properties. Li *et al.*<sup>[13]</sup> successfully constructed a pseudo-tetragonal phase boundary in  $\text{CaBi}_2\text{Nb}_2\text{O}_9$  ceramics through a straightforward A-site  $\text{Bi}^{3+}$  self-doping strategy, resulting in a reduced domain size and an increased  $d_{33}$  to 15.1 pC/N. Additionally, Zhang *et al.*<sup>[14]</sup> achieved an excellent  $d_{33}$  of 11.6 pC/N in  $\text{Bi}_3\text{TiNbO}_9$  by employing self-doping *via* mutual substitution of B-site  $\text{Nb}^{5+}$  with  $\text{Ti}^{4+}$ . The improvement in piezoelectric performance was attributed to the evolution of the crystal structure or domain structure. However, the inherent stability of bismuth-layered structure of BLSP limits the significant impact of ion doping on the crystal and domain structures, thereby restricting the enhancement of piezoelectric properties. This limitation has prompted researchers to explore whether other factors might significantly influence piezoelectric properties.

Space charge polarization (also known as interfacial polarization) is a common microscopic polarization mechanism in dielectrics, caused by space charges in inhomogeneous systems<sup>[15-18]</sup>. It has been widely applied to enhance electric polarization, breakdown field strength, and dielectric constants in various dielectric materials. Recently, charge accumulation and interfacial polarization arising from mismatched dielectric constants between the matrix and filler have been successfully used to boost the piezoelectric properties of nanocomposites<sup>[19]</sup>. This consideration leads to the hypothesis that, in polycrystalline ceramics, space charge polarization may also arise from the differences in dielectric constants, resistivities, and thicknesses of grains and grain boundaries, thereby affecting the piezoelectric performance.

Previous studies have shown that  $\text{Bi}^{3+}$  self-doping can significantly reduce grain size<sup>[13]</sup>. An increased number of grain boundaries facilitates a reduction in the migration distance of space charge and increases the space charge polarization sites, thereby enhancing the space charge polarization effect. Building on this foundation, a simple  $\text{Bi}^{3+}$  self-doping strategy was employed to enhance the overall properties of CBT piezoceramics, with a comprehensive investigation of the mechanisms that underlie the piezoelectric activity enhancement. The significant role of space charge polarization in improving piezoelectric properties was confirmed. Moreover,  $\text{Bi}^{3+}$  self-doping exhibited positive effects on high-temperature resistivity (up to  $6.33 \times 10^6 \Omega \cdot \text{cm}$  at 500 °C) and thermal stability (with a piezoelectric coefficient change rate at 700 °C of less than 10%). This strategy represents a novel approach to designing high-performance piezoelectric ceramics from the perspective of space charge polarization.

## 1 Experimental

### 1.1 Sample preparation

$\text{Bi}^{3+}$  self-doping  $\text{Ca}_{1-x}\text{Bi}_{4+x}\text{Ti}_4\text{O}_{15}$  ( $x=0, 0.02, 0.04, 0.06$ , and 0.08, abbreviated as CBT- $x\text{Bi}$ ) ceramics were fabricated *via* conventional solid-state reaction methods. The starting materials of  $\text{CaCO}_3$  (99.0%),  $\text{Bi}_2\text{O}_3$  (99.9%), and  $\text{TiO}_2$  (99.62%) were mixed in a ball mill tank with alcohol as a medium and subjected to wet-milling for 4 h using a planetary ball mill. Post-milling, the mixture was dried and calcined at 850 °C for 2 h. The synthesized block was then mechanically crushed and finely ground again using planetary ball milling. A binder (polyvinyl alcohol) amounting to 6% of the powder mass was added for further grinding and granulation. The resulting powder was then pressed into  $\phi 13$  mm discs using a mold and hydraulic press. The discs were heated to burn off the binder and subsequently sintered at 1150 °C for 2 h. Meantime, during the ceramics sintering process, Bi volatilization was mitigated by adding powder of the same composition as the ceramics into the sintering crucible.

### 1.2 Material characterization

The crystal structures of the CBT- $x\text{Bi}$  samples were analyzed using a Panalytical Aeris X-ray diffractometer (XRD) with  $\text{Cu K}\alpha$  radiation, while *in-situ* XRD measurements were performed using a Bruker X-ray diffractometer. Rietveld refinements of the powder XRD data were conducted using the FullProf software. The microstructure analysis of the ceramics was studied by scanning electron microscope (SEM; Hitachi, Japan). Piezoelectric force microscopy (PFM) was performed on a commercial atomic force microscope (AFM) system (Jupiter XR, Oxford, UK). Transmission electron microscopy (TEM) analysis was carried out using a JEM-2100F electron microscope (JEOL, Japan). X-ray photoelectron spectroscopy (XPS; Escalab 250Xi, ThermoFisher) was used to determine the oxygen vacancy concentration and the valence states of key elements. The dielectric constant and dielectric loss were measured from room temperature to 800 °C using an impedance material analyzer (DMS-1000, Partulab, China) and a meter (Model E4990 A, Keysight, USA). DC resistivity as a function of temperature (100–700 °C) was measured with an HRMS-900 conductivity measuring system (Partulab, China).

## 2 Results and discussion

The surface SEM images of CBT- $x\text{Bi}$  ceramics after thermal etching at 1100 °C for 30 min are displayed in Fig. 1(a-e). All ceramic samples are relatively dense,

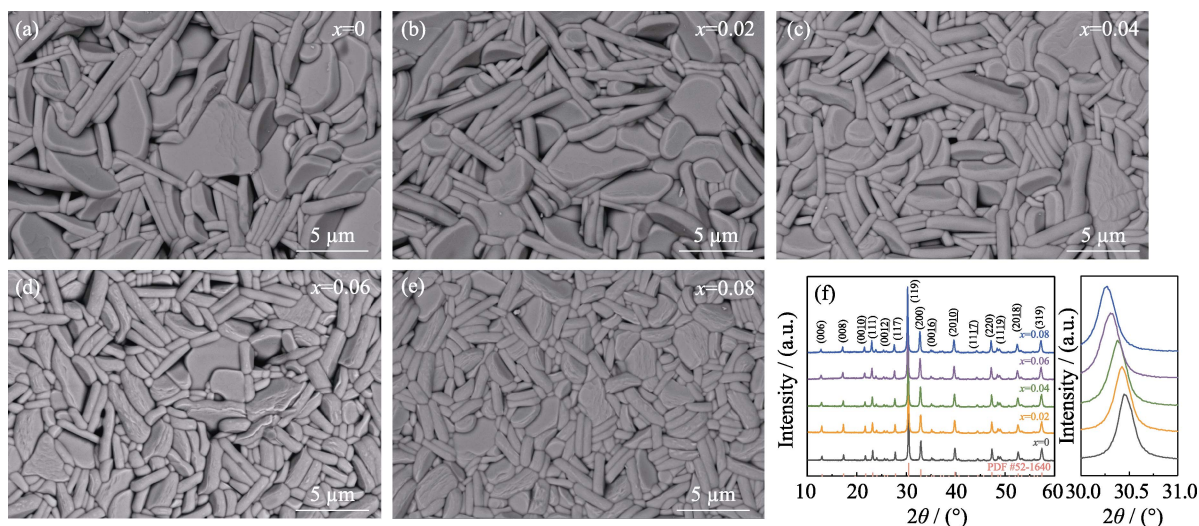


Fig. 1 (a-e) Surface SEM images of CBT- $x$ Bi ceramics after thermal etching; (f) XRD patterns of CBT- $x$ Bi ceramics and corresponding localized enlarged patterns  
(a)  $x=0$ ; (b)  $x=0.02$ ; (c)  $x=0.04$ ; (d)  $x=0.06$ ; (e)  $x=0.08$

with grains exhibiting the characteristic lamellar structure of bismuth layer-structured compounds. This structure is attributed to the significantly higher growth rate of BLSPs along the  $a$ - $b$  plane compared to the  $c$ -axis. Additionally, an increase in the concentration of  $\text{Bi}^{3+}$  self-doping results in a gradual reduction in the grain size, consequently increasing the number of grain boundaries. Fig. 1(f) presents the XRD patterns of CBT- $x$ Bi ceramics along with a magnified section at room temperature. The peak positions correspond well with the standard PDF card (PDF #52-1640), with the strongest peak being the (119) peak, which aligns with the expected strongest peak of BLSP,  $(112m+1)$ . As the  $\text{Bi}^{3+}$  content increases, the (119) peak shifts slightly toward a lower angle, likely due to lattice distortion caused by the introduction of  $\text{Bi}^{3+}$ , which leads to an increase in the lattice parameters.

Space charge polarization is a common microscopic polarization mechanism that typically occurs at the grain boundaries of ceramic materials. This phenomenon arises from the differences in dielectric constant and resistivity between grains and grain boundaries. These disparities cause a significant accumulation of space charge at the interfaces, which orients in an orderly manner under an external electric field, thereby contributing to the overall polarization of polycrystalline ceramics. Space charge polarization has a limited response to high-frequency electric fields ( $>10^4$  Hz) but contributes significantly to the dielectric constant at lower frequencies. Therefore, the presence of space charge polarization can be assessed by analyzing the dielectric temperature spectra at different frequencies after polarization, as shown in Fig. 2(a-c)<sup>[20]</sup>. At 100 Hz, an anomalous dielectric peak is observed in the range of 400–600 °C, which diminishes and even disappears as the frequency increases, indicating the

occurrence of space charge polarization of CBT- $x$ Bi. Furthermore, by comparing the dielectric temperature spectra of CBT- $x$ Bi before and after polarization at low frequency (100 Hz), the intensity of space charge polarization in each composition can be evaluated, as illustrated in Fig. 2(d-f). It can be seen that  $\text{Bi}^{3+}$  self-doping significantly enhances the space charge polarization in CBT- $x$ Bi, thereby increasing its contribution to the dielectric constant. This directional polarization affects the strength of intrinsic polarization and improves the piezoelectric performance of CBT- $x$ Bi.

Oxygen vacancies are a common form of space charge in BLSP, with a low migration activation energy (0.5–1.0 eV), making them highly mobile within the crystal lattice<sup>[21]</sup>. To investigate the effect of  $\text{Bi}^{3+}$  self-doping on the oxygen vacancy concentration and the valence state of the constituent elements in CBT ceramics, XPS measurements were performed on CBT- $x$ Bi ceramics, as shown in Fig. 3. The O1s peak is observed to split into two peaks: the lower binding energy peak at 530.0 eV corresponds to the lattice oxygen, while the higher binding energy peak at 531.5 eV represents oxygen vacancy. The concentration of oxygen vacancy is typically quantified by the ratio of the oxygen vacancy peak area to the lattice oxygen peak area<sup>[22]</sup>. Fitting analysis reveals that as the  $\text{Bi}^{3+}$  doping content increases, the oxygen vacancy concentration decreases progressively, with the area ratio of oxygen vacancy to lattice oxygen decreasing from 0.24 to 0.18, as summarized in Table 1. Changes in the chemical environment around atoms can induce shifts in the electron binding energies of inner shells, which manifest as peak shifts in the XPS spectrum. Fig. 3(b) shows the  $4f_{5/2}$  and  $4f_{7/2}$  spin-orbit peaks of the Bi element. The peak positions of different  $\text{Bi}^{3+}$  doping

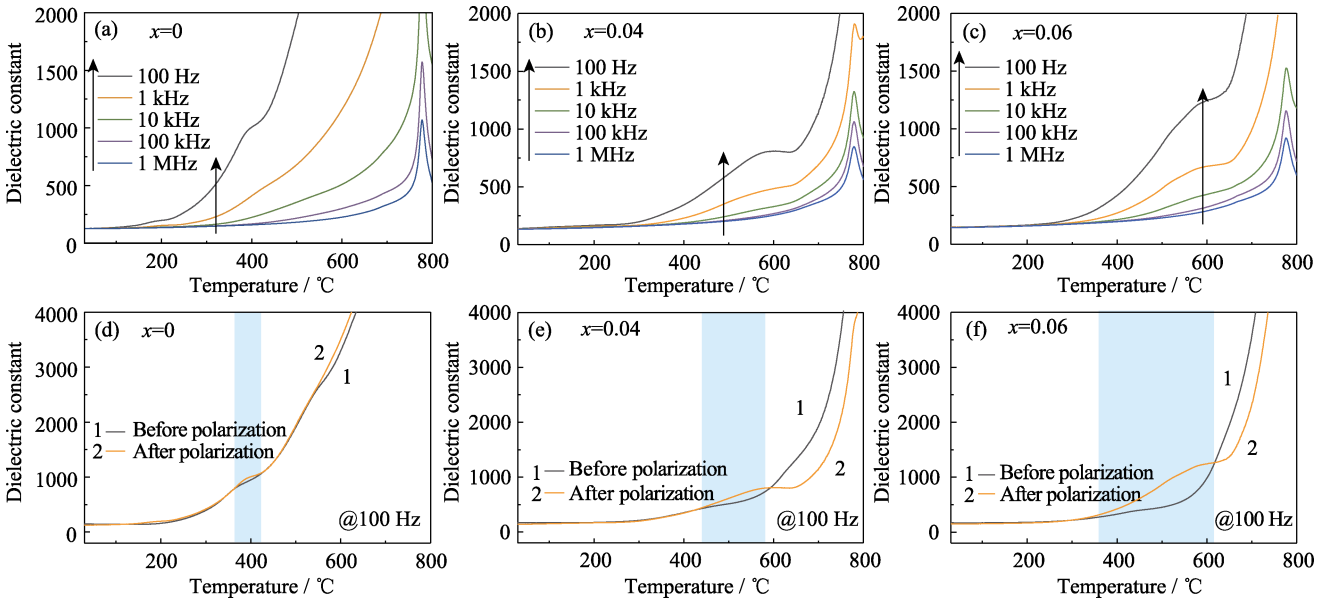


Fig. 2 Dielectric properties of CBT- $x$ Bi ceramics

(a-c) Dielectric constant as a function of temperature at different frequencies after polarization: (a)  $x=0$ , (b)  $x=0.04$  and (c)  $x=0.06$ ; (d-f) Dielectric constant as a function of temperature at 100 Hz before and after polarization: (d)  $x=0$ , (e)  $x=0.04$  and (f)  $x=0.06$

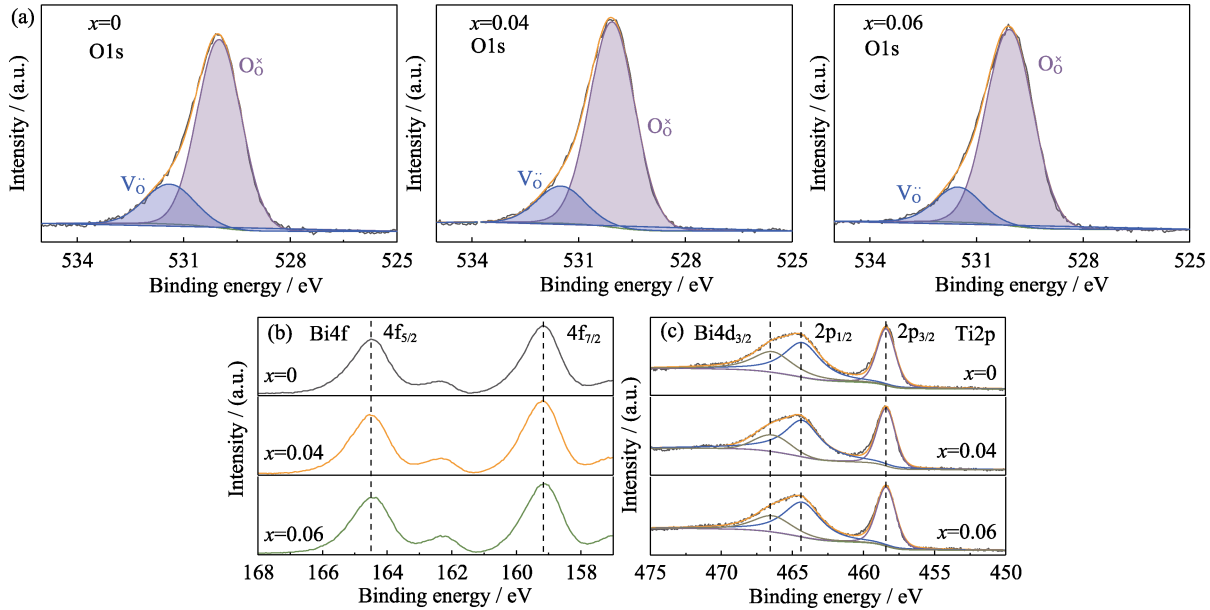


Fig. 3 XPS core-level spectra of CBT- $x$ Bi ceramics

(a) O1s; (b) Bi4f; (c) Bi4 $d_{3/2}$  and Ti2p

Table 1 Results of CBT- $x$ Bi ceramics O1s XPS peak fitting analysis

| $x$                     | $S_1$ (Oxygen vacancy area) | $S_2$ (Lattice oxygen area) | $S$ (Total area, $S_1+S_2$ ) | $S_1/S_2$ | $S_1/S$ |
|-------------------------|-----------------------------|-----------------------------|------------------------------|-----------|---------|
| 0                       | 5581.86                     | 23546.90                    | 29128.76                     | 0.24      | 0.19    |
| 0.04                    | 5635.40                     | 28758.79                    | 34394.19                     | 0.20      | 0.16    |
| 0.06                    | 5078.49                     | 27836.63                    | 32915.12                     | 0.18      | 0.15    |
| 0.06 (Oxygen sintering) | 3969.83                     | 24463.16                    | 28432.99                     | 0.16      | 0.14    |

contents remain consistent, with the energy difference between the two peaks unchanged at 5.3 eV, indicating that the valence state of Bi ions remains +3<sup>[23]</sup>. Similarly, the peaks of Ti2 $p_{1/2}$  and Ti2 $p_{3/2}$  are always maintained at 464.4 and 458.5 eV, respectively, with a binding energy

difference of 5.9 eV, corresponding to the typical Ti<sup>4+</sup>-O bond in TiO<sub>2</sub><sup>[24]</sup>.

To confirm whether the space charge in the CBT- $x$ Bi ceramics is indeed due to oxygen vacancies, raw billets with an  $x=0.06$  composition were sintered in a flowing

oxygen atmosphere. As shown in Fig. 4(a, b), the phase composition, grain morphology, and size of the oxygen-sintered samples are not significantly different from those of the samples sintered in air. However, a decrease in oxygen vacancy concentration in the oxygen-sintered samples was observed compared to the air-sintered samples. XPS measurements of the oxygen-sintered samples reveal a reduction in oxygen vacancy content, with the area ratio of oxygen vacancy to lattice oxygen decreasing from 0.18 to 0.16, as detailed in Table 1. Additionally, as shown in Fig. 4(d), the dielectric temperature spectrum at 100 Hz for the oxygen-sintered samples demonstrates a reduction in space charge polarization intensity. The piezoelectric coefficient of the oxygen-sintered samples decreased to 18.8 pC/N, which is due to the decrease of the charge concentration that forms the space charge polarization. This finding indicates that the space charge in this experiment is indeed associated with oxygen vacancy.

$T_C$  is a critical parameter for piezoelectric ceramics as it defines the maximum operational temperature for practical applications. High value  $T_C$  is essential for the use of CBT ceramics in high-temperature piezoelectric vibration sensors, especially for applications exceeding 500 °C. The dielectric temperature spectrum of CBT- $x$ Bi ceramics at 1 MHz, as shown in Fig. 5(a), exhibits a sharp phase transition peak near  $T_C$ , indicative of typical

ferroelectric behavior. After  $\text{Bi}^{3+}$  doping, there is a slight decrease (about 5 °C) in  $T_C$ , which is attributed to the substitution of  $\text{Ca}^{2+}$  (ionic radius: 1.34 Å) by  $\text{Bi}^{3+}$  (ionic radius: 1.36 Å). This substitution increases the tolerance factor, which is inversely related to  $T_C$ <sup>[25]</sup>. Nevertheless,  $T_C$  remains above 775 °C after  $\text{Bi}^{3+}$  doping, rendering the material suitable for high-temperature applications. Additionally, the dielectric constant remains stable up to 600 °C, demonstrating outstanding thermal stability in dielectric properties.

High electrical resistivity is crucial for maintaining reliable device signal output. Fig. 5(b) presents the variation in DC resistivity ( $\rho$ ) of CBT- $x$ Bi ceramics with temperature. The resistivity significantly improves after  $\text{Bi}^{3+}$  doping, and the CBT-0.06Bi ceramic exhibits a DC resistivity of  $6.33 \times 10^6 \Omega \cdot \text{cm}$  at 500 °C, which is an order of magnitude higher than the undoped component, as shown in the inset. The low resistivity in CBT ceramics is generally attributed to oxygen vacancies formed by the volatilization of  $\text{Bi}_2\text{O}_3$ . Donor doping with high-valent  $\text{Bi}^{3+}$  reduces the formation of oxygen vacancies, leading to an increase in resistivity<sup>[26]</sup>.

The piezoelectric coefficient  $d_{33}$  of CBT ceramics was successfully enhanced by 31% through space charge polarization, reaching 20.1 pC/N for the  $x=0.06$  composition ( $T_C=778$  °C), as shown in Fig. 5(c). The trend of  $d_{33}$

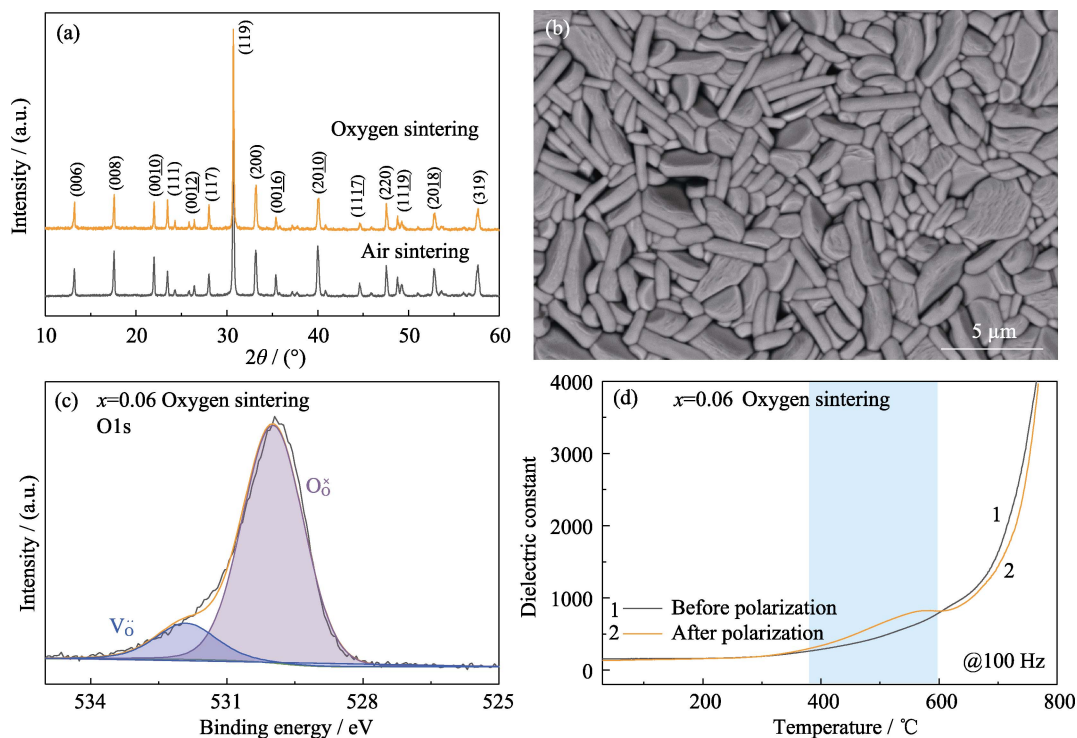


Fig. 4 Characterization of CBT-0.06Bi ceramic sintered in a flowing oxygen atmosphere  
(a) XRD patterns; (b) SEM image of the thermal etching surface; (c) O1s XPS spectrum;  
(d) Dielectric temperature spectra at 100 Hz before and after polarization

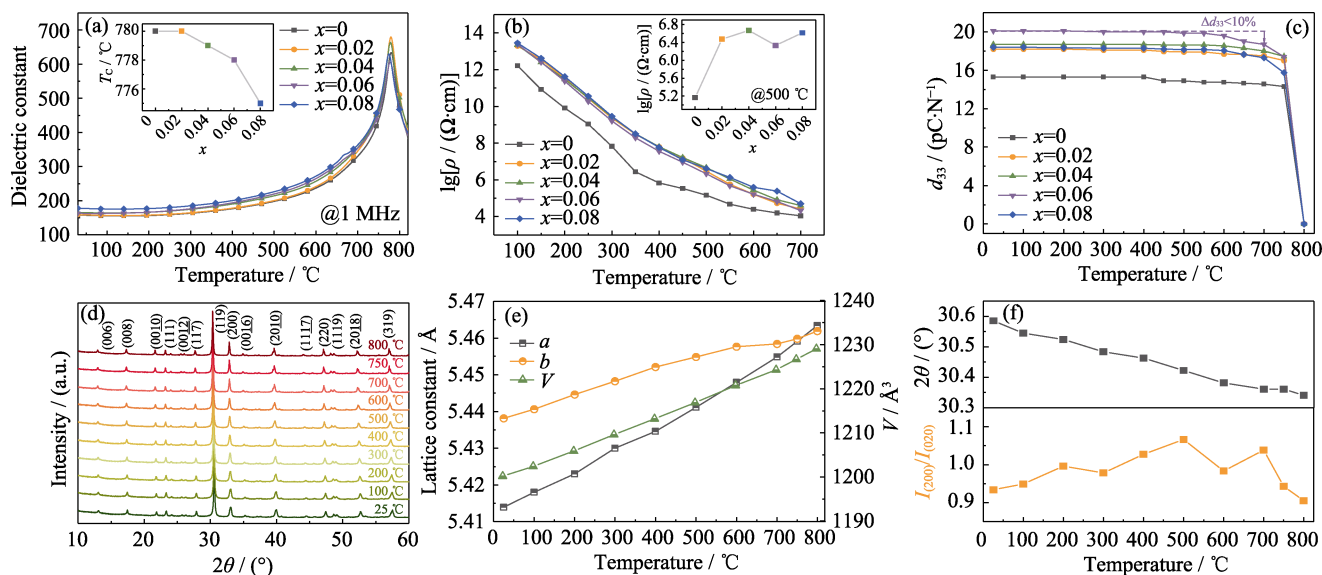


Fig. 5 (a) Dielectric temperature spectra of CBT-xBi ceramics; (b) Temperature dependence of DC resistivity of CBT-xBi ceramics; (c) Effect of heat treatment on the piezoelectric constants of CBT-xBi ceramics (set temperature annealing 2 h); (d) *In-situ* XRD patterns of CBT-0.06Bi ceramic; (e) Relationship between lattice constants and unit cell volume with temperature; (f) (119) peak position and  $I_{(200)}/I_{(020)}$  changed with temperature

firstly increasing and then decreasing with rising  $\text{Bi}^{3+}$  content can be attributed to the synergistic effects of oxygen vacancy concentration and grain size. Space charge polarization is influenced by both space charge concentration and space charge migration. On one hand, as  $\text{Bi}^{3+}$  doping increases, the concentration of oxygen vacancy decreases, which leads to a reduction in available space charges. On the other hand, the reduction in grain size increases the grain boundary content, shortens the migration distance of space charges, and creates more sites for polarization to accumulate. This interaction between the reduction in oxygen vacancies and the increased grain boundary density contributes to the initial rise in  $d_{33}$ , followed by a subsequent decline, reflecting the complex relationship between these factors.

Good temperature stability is critical for the long-term, reliable operation of CBT ceramics. As shown in Fig. 5(c),  $d_{33}$  of CBT-xBi ceramics retains over 90% of its room temperature value even at elevated temperatures. This demonstrates that CBT-xBi ceramics not only possess excellent piezoelectric properties but also exhibit strong thermal stability, making them highly promising for high-temperature applications. To gain deeper insight into the origins of this temperature stability, *in-situ* XRD measurements conducted on the CBT-0.06Bi ceramic sample demonstrate the best overall properties, as shown in Fig. 5(d-f). As the temperature rises, lattice expansion causes a leftward shift in peak positions, such as the strongest diffraction peak (119), indicating an increase in cell parameters ( $a$  and  $b$ ) and cell volume ( $V$ ). Ferroelectric domain reversal can be inferred through

X-ray intensity measurements<sup>[27-28]</sup>, and recent studies have determined this reversal in bismuth layer-structured ceramics like  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  by analyzing the intensity ratio of (200) to (020) peaks ( $I_{(200)}/I_{(020)}$ )<sup>[29]</sup>. Fig. 5(f) shows the  $I_{(200)}/I_{(020)}$  for CBT-xBi ceramics from 25 to 800 °C. It can be seen that the ratio remains stable at around 1, even with increasing temperature, suggesting that the oriented ferroelectric domains maintain their stability, which is key to the material's excellent temperature stability.

The improvement of piezoelectric properties is often linked to intrinsic lattice distortion and extrinsic changes in domains or domain walls. In the case of BLSP, lattice distortion can be represented by the tilt of the  $[\text{TiO}_6]$  octahedron along the  $c$ -axis and the rotation in the  $a$ - $b$  plane, both of which directly impact spontaneous polarization ( $P_s$ )<sup>[30]</sup>. To investigate these effects in CBT-xBi ceramics, further Rietveld refinements of powder XRD data were performed using FullProf software, with the space group A21am set as the initial model (Fig. 6(a)). The refinement process showed that the reliability factors  $R_p$  and  $R_{wp}$  fell within reasonable limits, thereby confirming the validity of the results. Fig. 6(b) presents a visualized crystal structure based on the Rietveld refinement. In this structure,  $\angle\alpha$  is the angle between the Ti-O bond and the  $c$ -axis, representing the tilt of the  $[\text{TiO}_6]$  octahedron, while  $\angle\beta$  represents its rotation in the  $a$ - $b$  plane. The data reveal that, with increasing  $\text{Bi}^{3+}$  doping content, the tilt and rotation of the  $[\text{TiO}_6]$  octahedron gradually increase (with a maximum change of  $0.003^\circ$ ). However, the overall degree of

structural distortion remains considerably smaller compared to the large lattice distortions reported by Chen *et al.*<sup>[11]</sup> and Nie *et al.*<sup>[31]</sup>, where  $\angle\alpha$  changes by  $7.45^\circ$  and  $6.76^\circ$ , respectively. This suggests that, while the introduction of  $\text{Bi}^{3+}$  increases lattice distortion to some extent, the effect remains relatively modest. Thus, intrinsic lattice distortion has a limited impact on enhancing the piezoelectric properties of CBT- $x\text{Bi}$  ceramics.

Studies have identified two primary phonon vibration modes in CBT. One is the Raman peak with a wavenumber greater than  $200\text{ cm}^{-1}$ , related to the vibration of the  $[\text{TiO}_6]$  octahedron, the other is the Raman peak with a wavenumber less than  $200\text{ cm}^{-1}$ , which is in connection with ion vibration at A-sites of  $(\text{Bi}_2\text{O}_2)^{2+}$  and within the pseudo-perovskite layer. Raman spectroscopy serves as an effective tool to assess the degree of structural

distortion in materials. As shown in Fig. 6(c), the Raman spectra of CBT ceramics reveal peaks at  $270$ ,  $555$ , and  $855\text{ cm}^{-1}$ , consistent with previous studies<sup>[32]</sup>. The Raman peak at  $270\text{ cm}^{-1}$  corresponds to the  $\text{B}_{2g}$  and  $\text{B}_{3g}$  modes, which are related to the vibration of  $\text{O-Ti-O}$ . The Raman peak at  $555\text{ cm}^{-1}$ , attributed to the  $\text{A}_{1g}$  mode, is related to the relative displacement of oxygen atoms in the  $[\text{TiO}_6]$  octahedron, whereas the  $\text{B}_{1g}$  mode at  $855\text{ cm}^{-1}$  is related to the stretching of the  $[\text{TiO}_6]$  octahedron. As illustrated in Fig. 6(d), the shifts in these three modal peak positions are minimal with varying  $\text{Bi}^{3+}$  doping levels, indicating a limited influence of the doping on lattice distortion. This finding is consistent with the XRD refinement results, further confirming that lattice distortion has a minimal impact on enhancing the piezoelectric properties of CBT- $x\text{Bi}$  ceramics.

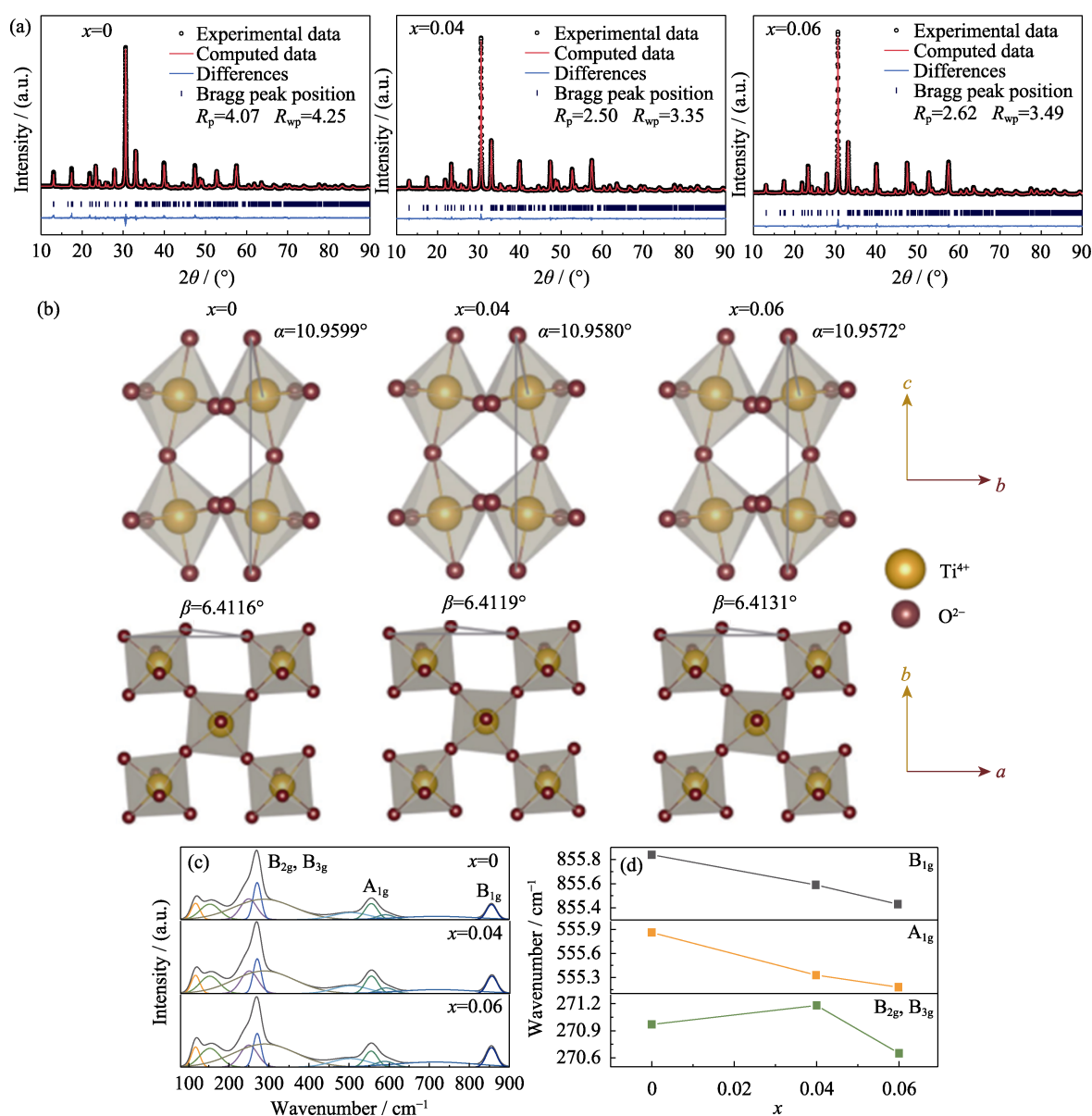


Fig. 6 (a) XRD refinement results of CBT- $x\text{Bi}$  ceramics; (b) Visual crystal structures of CBT- $x\text{Bi}$  ceramics; (c) Raman scattering spectra in the range of  $80\text{--}900\text{ cm}^{-1}$ ; (d) Wavenumber displacements of  $\text{B}_{2g}$ ,  $\text{B}_{3g}$ ,  $\text{A}_{1g}$ , and  $\text{B}_{1g}$  modes

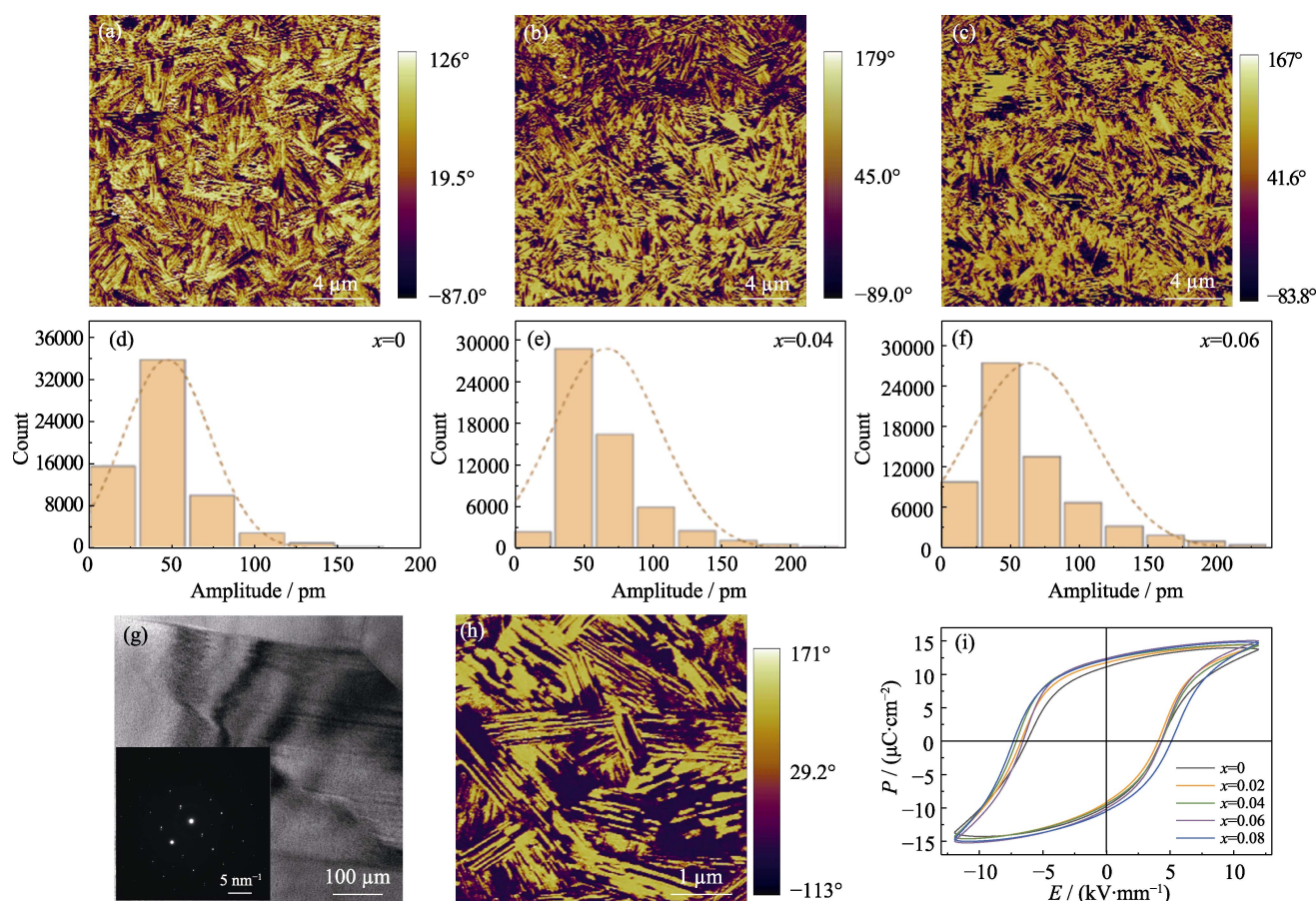


Fig. 7 PFM characterization of CBT- $x$ Bi ceramics

(a-c) PFM phase images for (a)  $x=0$ , (b)  $x=0.04$ , and (c)  $x=0.06$ ; (d-f) PFM amplitude distribution histograms for (d)  $x=0$ , (e)  $x=0.04$ , and (f)  $x=0.06$ ; (g) TEM image of CBT-0.06Bi; (h)  $5\ \mu\text{m} \times 5\ \mu\text{m}$  PFM phase image of CBT-0.06Bi; (i) Hysteresis loops of CBT- $x$ Bi ceramics after polarizing at  $180\ ^\circ\text{C}$  and 1 Hz. Colorful figures are available on website

The effect of ferroelectric domains on piezoelectric properties was further analyzed using PFM and TEM. PFM images (Fig. 7(a-c)) of the CBT- $x$ Bi ceramics, taken over a  $20\ \mu\text{m} \times 20\ \mu\text{m}$  area, reveal that the morphology and dimension of the domains across different components are quite similar. The amplitude distribution ranges from 50 to 75 pm, remaining largely unchanged with varying levels of  $\text{Bi}^{3+}$  doping (Fig. 7(d-f)). TEM images of the CBT-0.06Bi ceramic also revealed a strip domain structure<sup>[33-34]</sup>, aligning with the PFM results (Fig. 7(g, h)) and confirming that  $\text{Bi}^{3+}$  doping has a negligible impact on the domain structure. These findings suggest that domain structure (extrinsic) does not significantly contribute to the enhanced piezoelectric properties in CBT- $x$ Bi ceramics. Instead, the improvement can be primarily attributed to space charge polarization, as evidenced by the changes in crystal structure and domain configuration. Further evidence of space charge polarization is demonstrated by the hysteresis loops (Fig. 7(i)), which show greater polarization intensity with  $\text{Bi}^{3+}$  doping under the same temperature, frequency, and voltage conditions. Given the minimal difference between the crystal structure and domain structure of

each component, the excess polarization intensity should be attributed to space charge polarization<sup>[19]</sup>.

### 3 Conclusions

In summary, this study successfully prepared a series of CBT- $x$ Bi compositions using a self-doping strategy through solid-state synthesis. The presence of space charge polarization was confirmed through low-frequency (100 Hz) dielectric temperature spectra, which significantly enhanced the piezoelectric properties of CBT ceramics. Space charge polarization arises from the mismatch in dielectric constants between the grains and grain boundaries, leading to the accumulation of space charge at the interfaces. The accumulated charges contribute additional polarization under the application of an external electric field, thereby improving the piezoelectric properties. This research deepens the understanding of the mechanism underlying the enhancement of piezoelectric activity. CBT-0.06Bi ceramic exhibited excellent performance through self-doping, maintaining a high Curie temperature while increasing the piezoelectric coefficient to  $20.1\ \text{pC/N}$ . The electrical

resistivity also improved significantly, increasing by one order of magnitude, reaching  $6.33 \times 10^6 \Omega \cdot \text{cm}$  at 500 °C. This study highlights space charge polarization as a promising strategy for designing high-performance piezoelectric ceramics and paves a way for advancements in ceramic materials suitable for high-temperature applications.

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# 通过 $\text{Bi}^{3+}$ 自掺杂增强 $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ 基陶瓷压电性能

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**摘要:** 高温压电振动传感器是高温、复杂振动等严苛环境下用于结构健康监测的首选传感器。具有高居里温度( $T_C$ )的铋层状结构  $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ (CBT)高温压电陶瓷是 500 °C 及以上压电振动传感器的核心元件, 但其压电系数  $d_{33}$  低, 极大限制了其高温应用。本研究采用独特的  $\text{Bi}^{3+}$  自掺杂策略, 提高了 CBT 压电陶瓷内部晶界数量, 增加了空间电荷的聚集位点, 促进了空间电荷极化的形成。进一步地, 基于空间电荷极化主要在低频下产生的特性, 利用不同频率介电温谱阐明了空间电荷极化提升 CBT 压电陶瓷压电性能的重要机制。最终获得了综合性能优异的 CBT 基高温压电陶瓷:  $T_C$  高达 778 °C;  $d_{33}$  提高了 30% 以上, 达到 20.1 pC/N; 电阻率提高了 1 个数量级(在 500 °C 下达到  $6.33 \times 10^6 \Omega \cdot \text{cm}$ )。本工作为 500 °C 及以上压电振动传感器的实际应用提供了性能优异的关键功能材料。

**关键词:** 高温压电陶瓷; 铋层状结构; 自掺杂; 空间电荷极化; 氧空位

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