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Lead-Free Metamaterials with Enormous Apparent **Piezoelectric Response**

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Lead-oxide-based piezoelectric materials have been widely used in many applications, such as sensors, actuators, transducers, and energy harvesting devices.^[1] These materials contain more than 60 wt% lead. Because of increasing concern regarding the toxicity of lead, there have been considerable efforts in the past decade to develop high-performance lead-free piezoelectrics.^[2-5] Several lead-free material systems, such as Na_{1/2}Bi_{1/2}TiO₃-based and K_{0.5}Na_{0.5}NbO₃-based materials, have been explored, but their piezoelectric properties are still inferior to those of leadoxide-based materials.^[2-5] Furthermore, it has been observed that an increase of piezoelectric properties through the composition modification of these materials normally leads to a lower temperature stability of the properties and hence a reduction of operating temperature.^[2] Consequently, it is difficult to achieve good piezoelectric properties and a high-temperature stable response comparable to that of lead-oxide-based materials in existing lead-free piezoelectric materials due to the reverse correlation of the two parameters.^[2]

Piezoelectric metamaterials, in which the piezoelectric response of the materials originates from their special geometries or structures and flexoelectricity (or effective flexoelectricity, see the Supporting Information for details), were proposed in recent years and the concept can provide a solution for this issue in conventional piezoelectrics.^[6-13] Generally, piezoelectricity is observed in materials with noncentrosymmetric crystal structures. However, by exploiting flexoelectricity (or effective flexoelectricity), the electromechanical coupling defined as the generation of electric polarization by a strain gradient (direct effect) or stress by an electric field gradient (converse effect) in solid dielectrics, even a centric material can exhibit a piezoelectric-like response if the material has special geometries or structures to convert the applied stress into a strain gradient or

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electric potential into an electric field gradient.^[6-10] Because the piezoelectric response originates not from the intrinsic property but from the gradient-generating structures and geometries, the material can be deemed a metamaterial.^[6-8] In conventional piezoelectric materials, a phase transition between noncentrosymmetric and centrosymmetric phases at certain temperatures causes the disappearance of piezoelectric properties.^[1] However, unlike piezoelectricity, there is no symmetry requirement for a material to have flexoelectricity, and piezoelectric metamaterials can exhibit a high-temperature stable piezoelectric response.^[11]

One key issue that remains unresolved is how to design lead-free piezoelectric metamaterials with a functionality and piezoelectric response comparable to those of lead-oxide-based piezoelectrics. The piezoelectric properties of conventional piezoelectrics are mainly dependent on the compositions of the materials. However, the piezoelectric response of piezoelectric metamaterials is not only related to the compositions of the materials, which determine the magnitude of flexoelectricity or effective flexoelectricity (characterized by the flexoelectric coefficients or apparent flexoelectric coefficients μ_{iikl}), but also dependent on the designs of gradient-generating structures and geometries, which affect the effectiveness of the conversion from the applied stress or electric potential into gradients.^[6,7,14-16] It is not a straightforward task to design such structures and geometries, and at present, only two designs of piezoelectric metamaterials have been realized experimentally.^[7,14-16] Flexure-mode piezoelectric composite metamaterials have part of the functionality of conventional piezoelectrics, exhibiting an intriguing direct piezoelectric response but no converse piezoelectric response because the design can be used to generate only a strain gradient but not an electric field gradient.^[14] Piezoelectric metamaterials with a truncated pyramid geometry exhibit both direct and converse piezoelectric responses, but the piezoelectric response is much weaker than that of lead-oxide-based piezoelectrics.^[7,15,16] Here, we demonstrate that a new design of piezoelectric metamaterials can be created by applying an asymmetric chemical reduction to ferroelectric oxides. Two gradient-generating mechanisms, curvature structure and chemical inhomogeneity, were induced by the reduction. The apparent flexoelectric coefficient of the ceramics was also significantly enhanced after reduction. Consequently, a single piece of reduced ceramic behaves as a real piezoelectric material, exhibiting high effective direct and converse piezoelectric responses (effective piezoelectric coefficient $d_{33} > 3500 \text{ pC}$ N^{-1}) that could be stable at high temperatures (above 400 °C), outperforming existing lead-oxide-based piezoelectrics.

Ferroelectrics normally have much stronger flexoelectricity than common dielectrics because of their high dielectric properties.^[7,10] Here, we use lead-free $(1 - x)Na_{1/2}Bi_{1/2}TiO_3-x$ BaTiO₃ (0 < x < 0.9) (NBBT or NBBT*x*, where *x* denotes the

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molar percentage of BaTiO₃) ferroelectric ceramics as a model system to demonstrate the feasibility of our approach to achieve high-performance flexoelectric piezoelectric metamaterials.^[2] NBBT ceramics were fabricated using the conventional solidstate reaction method, and one-surface asymmetric chemical reduction was applied to the ceramic wafers.^[17] Unless otherwise specified, the dimensions of the ceramic wafers used in this work were ≈ 20 mm in diameter and 0.5 mm in thickness, and the materials were reduced at 825 °C for 2 h. After the reduction, the reduced surfaces of the ceramic wafers turned black in color (Figure 1a). From the cross-section of the reduced samples, a gradual change in color between the reduced and unreduced surfaces can be discerned by eye, indicating a possible chemical inhomogeneity between the two surfaces. Figure 1b presents the X-ray diffraction (XRD) patterns of an NBBT8 ceramic wafer. Before reduction, the NBBT8 ceramic has a tetragonal perovskite structure.^[18] After reduction, the reduced surface of the NBBT8 ceramic exhibits complex diffraction patterns, which are from NBBT8, Bi, and Na₂Ti₆O₁₃. After one layer that was $\approx 60 \ \mu m$ thick was removed from the reduced surface, the material exhibited a structure close to that of the unreduced NBBT8, and no obvious structural change was observed after the material was further polished. Although no obvious structure change can be observed by XRD after the bismuth-containing surface layer is removed, the continuous shifting of X-ray photoelectron spectroscopic (XPS) peaks for Ti2p toward a higher binding energy after the reduced sample was polished toward the unreduced surface, which is corresponding to a valence change from Ti³⁺ to Ti⁴⁺, indicates a chemical inhomogeneity across the thickness of the ceramic wafer (Figure 1c). A progressive decrease of the polarization response (Figure 1d) under high electric field and weak field dielectric constant (Figure S1, Supporting Information) after the reduced sample was polished toward the unreduced surface further supports the existence of the chemical inhomogeneity in the thickness direction. Figure 1e shows that the reduced sample has a smaller thermal expansion than the unreduced sample, indicating that the thermal expansion of the highly reduced portion in the reduced sample is smaller than that of the unreduced or slightly reduced portion of the sample. The chemical inhomogeneity and variation of thermal shrinkage from the reduction lead to a small curvature of less than 15 um toward the reduced surface of the ceramic wafer after the ceramic wafers are reduced and cooled down from the high temperature (Figure 1f; the measurement method is described in the Supporting Information and Figure S2). These results suggest a curvature structure can be formed due to the reduction-induced chemical inhomogeneity in the reduced NBBT ceramics.

The curvature formation may induce a static strain gradient across the thickness, which could polarize the ferroelectric materials, as observed in nanoscale ferroelectrics in which the flexoelectric effect is enhanced due to the size effect of flexoelectricity.^[19–24] Recent study has also shown that chemical inhomogeneity could possibly cause a polar structure and weak piezo-electric response in ferroelectrics.^[25] However, the experimental results of impedance spectra indicate that the reduced ceramics were in a nonpiezoelectric state. As shown in **Figure 2a** and Figure S3 (Supporting Information), abrupt changes in



impedance and phase angle at resonance and antiresonance frequencies due to the piezoelectric effect can be observed on the impedance spectra measured in the poled unreduced and reduced NBBT8 ceramic wafers, but such anomalies cannot be observed in reduced ceramic wafers without poling, indicating that the reduced materials are not polarized by the static strain gradient or chemical inhomogeneity.

Even if the reduced NBBT8 ceramics are nonpiezoelectric, a strong piezoelectric response can be measured if the materials are placed on a plate with the concave surface facing the plate (the point–plane method, Figure S4a, Supporting Information). With this measurement method, the force applied to the reduced surface can cause a bending-like deformation, and a strain gradient can be generated.^[14,17] Consequently, an effective d_{33} of 110–170 pC N⁻¹ was measured in the reduced NBBT8 wafers due to the flexoelectric (or effective flexoelectric) effect. If the samples were measured using the point–ring test (Figure S4b, Supporting Information), d_{33} was close to the value measured using the point–plane test. Therefore, with the reduction-induced curvature, a single NBBT8 ceramic wafer becomes a piezoelectric metamaterial when it is supported by a substrate, such as a plate or ring.

The temperature stability of the piezoelectric properties is always a concern for piezoelectrics.^[1,26,27] To characterize the temperature stability of the metamaterials, the reduced NBBT8 and NBBT10 ceramic wafers were treated at temperatures between 300 and 650 °C for 5 h in air, and after each treatment, d_{33} was measured at room temperature. As observed in Figure 2b, the piezoelectric response of the materials can be sustained after heat treatment at 450 °C. The effective d_{33} of a reduced NBBT8 ceramic wafer was also directly measured at 400 °C. The effective d_{33} is ≈ 117 pC N⁻¹ at 400 °C, which is close to the value measured at room temperature (\approx 121 pC N⁻¹), as shown in Table S1 (Supporting Information). These results indicate that the metamaterials could have a high-temperature stable (>400 °C) piezoelectric response. In contrast, most commercial lead-oxide-based piezoelectrics lose piezoelectricity well below 400 °C.^[1,2,28] The disappearance of the piezoelectric response above 450 °C is due to the destruction of the reduction-induced structures at high temperatures in the air because we found the black color of the reduced samples turned into gray if they were heat treated at a high temperature close to 650 °C, and it is unrelated to the phase transition between a ferroelectric phase and a nonpolar phase in NBBT ceramics, which occurs at a temperature below 200 °C.^[2,18]

The aforementioned tests used a silver electrode that was fabricated at 650 °C for 0.5 h. To avoid exposure to high temperatures, a low-temperature electrode fabrication technique, DC sputtering, was used to prepare the electrode for the piezoelectric tests. As expected, the effective d_{33} of the NBBT8 metamaterials was greatly improved to 340–600 pC N⁻¹ when using sputtered gold as the electrode. Although the piezoelectric response can be improved using the gold electrode, one drawback of the gold electrode is that the adhesion between the ceramic sample and the sputtered gold electrode seems to not be strong, especially above 300 °C. When the piezoelectric response was measured in the samples with a gold electrode after heat treatments, the gold electrode was reprepared after each heat treatment. As shown in Figure 2b, the piezoelectric

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Figure 1. Effect of the chemical reduction on the microstructure and properties of NBBT8 ceramics. a) Reduction induced color change in NBBT ceramics. b) XRD patterns before and after the reduction. 1, Perovskite structure; 2, Bi; and 3, $Na_2Ti_6O_{13}$. c) Ti2p XPS spectra of NBBT8 before and after the reduction. Two vertical dash lines mark the peak positions of Ti2p spectra obtained from the surface after a layer that is $\approx 80 \,\mu$ m is removed. The peak positions for each curve are also marked on the curves. d) *P*–*E* hysteresis loops before and after the reduction. In (b–d), the reduced sample was polished from the reduced surface by the thickness indicated in the plots. e) Temperature dependence of the thermal expansion of the ceramic before reduction (black curve) and after (blue curve). f) Change of the distance relative to a flat marble surface of the points on the surfaces of an NBBT ceramic wafer after it was reduced. These points are on four diametral lines. Two perpendicular lines are on the reduced surface (solid square and circle symbols), which are parallel to the other two on the opposite surface (solid upward and downward triangle symbols).

response of the metamaterials with the gold electrode can also be sustained after the heat treatment at 450 $^{\circ}{\rm C}$ for 5 h.

The effective d_{33} of the piezoelectric metamaterials can be tuned by various factors. As shown in Figure 2c, with the same dimensions, reduction conditions and a sputtered gold electrode, the effective d_{33} can be greatly enhanced by changing the compositions of NBBT ceramics. A maximum effective d_{33} of \approx 3500 pC N⁻¹ was measured in the reduced NBBT20 ceramics. This value is higher than that of piezoelectric single crystals ($d_{33} \approx$ 2500 pC N⁻¹), the piezoelectric materials with



or effective d., (pC/N)

ц Ч



Figure 2. Piezoelectric response of NBBT piezoelectric metamaterials. a) The impedance spectra of unreduced and reduced NBBT8 ceramics before and after the materials were poled under a DC electric field. The measurement frequency range is from 90 to 210 kHz, which is corresponding to the first resonance/antiresonance mode (radial vibration) of the poled unreduced ceramic in Figure S3a (Supporting Information). b) The effective d₁₃ of NBBT8 and NBBT10 metamaterials after heat treatment at different temperatures. The d_{33} at the lowest temperature is from the samples without heat treatment. c) Dependence of the effective d₃₃ of the metamaterials (unpoled reduced ceramic wafers) and d₃₃ of poled unreduced ceramic wafers on the composition of the NBBT ceramics. d) Dependence of d_{33} of the reduced NBBT8 ceramic on the reduction temperature. The reduction time is 2 h. In (c) and (d), the average of the d_{33} values of four to five samples is shown for each data point and the error bar shows the standard deviation. e) Thickness dependence of the effective d_{33} of the reduced NBBT8 ceramic after the curvature was removed. The effective d_{33} was measured by the plane-plane test (squares) and point-plane test (circles) with a gold electrode. f) Electric field-induced displacement of a reduced NBBT8 ceramic wafer measured when the concave surface (squares) or convex surface (circles) was facing the flat plate.

the best piezoelectric properties.^[1,26,28] The effective d_{33} of the metamaterials is also much higher than the intrinsic d_{33} measured in poled NBBT ceramics (Figure 2c), which is typically below 160 pC N^{-1} . The piezoelectric response of the metamaterials is size dependent due to the size-dependent effect of flexoelectricity.^[7,11,23,24] For example, as shown in Table 1, for the same diameter (20 mm), reducing the thickness of the NBBT8 ceramic wafer from 0.5 mm (reduced at 825 °C for 2 h) to 0.3 mm (reduced at 825 °C for 45 min) could enhance the d_{33} value of the materials from below 170 to \approx 320 pC N⁻¹ (with the silver electrode); for the same thickness (0.5 mm) and the same reduction conditions, reducing the diameter to 10 mm could reduce d_{33} to less than 40 pC N⁻¹. The effective d_{33} is also dependent on the reduction conditions, and reduction at 825 °C for 2 h is nearly the optimum reduction condition for NBBT8 ceramics (with the silver electrode) to achieve the highest d_{33} (Figure 2d).

Because the mechanical properties of NBBT ceramics can be enhanced by the reduction (Figure S5, Supporting Information) and there is a chemical inhomogeneity in the

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Table 1. Effect of the sample size on the effective d_{33} of the reduced NBBT8 ceramics.

Diameter [mm]	Thickness [mm]	Reduction conditions	Effective d ₃₃ [pC N ⁻¹]	Electrode
20	0.5	825 °C/2 h	110–170 ^{a)}	Fired-on silver
20	0.3	825 °C/45 min	321 ^{b)}	Fired-on silver
10	0.5	825 °C/2 h	18-40 ^{a)}	Fired-on silver

^{a)}Measured in at least four samples; ^{b)}Measured in one sample.

materials, a variation of mechanical properties across the thickness is expected. As a result, even if the curvature of the reduced ceramic wafer is removed by polishing to eliminate the bending-like deformation under a stress, when a force is applied on the polished flat samples by using plane-plane test method (Figure S4c, Supporting Information), an inhomogeneous deformation in the materials could be generated because of the variation of mechanical properties in the materials, leading to a flexoelectric (or effective flexoelectric) response and an apparent piezoelectric response. Therefore, the chemical inhomogeneity combined with variations in the mechanical properties (Figure S5, Supporting Information) caused by the reduction could be another strain gradient-generating mechanism in the reduced materials. For example, after one reduced NBBT8 plate (9.50 mm long, 9.40 mm wide, and 1.25 mm thick, reduced at 825 °C for 5 h) was polished down to various thicknesses to remove the curvature, a thickness-dependent effective d_{33} (Figure 2e) could be measured using the plane-plane test method (Figure S4c, Supporting Information). When the thickness was reduced to 0.26 mm, d_{33} increased to ≈ 300 pC N⁻¹, much larger than the intrinsic piezoelectric response of NBBT8 ceramics (Figure 2c).

Because the reduced NBBT ceramics exhibit a progressive variation in the dielectric property (Figures 1d and S1, Supporting Information) across the thickness, when an electric voltage is applied on the reduced sample, an electric field gradient (the electric field in each component is inversely proportional to the dielectric constant in dielectric composite materials) can be generated, leading to a converse flexoelectric (or effective flexoelectric) response. Consequently, the reduced ceramic materials also exhibit a large electric field-induced strain, which is equivalent to a converse piezoelectric response in conventional piezoelectrics. Figure 2f shows the electric field-induced displacement of an NBBT8 ceramic wafer with a gold electrode measured by placing the material on a flat surface (Figure S4d, Supporting Information). A displacement of \approx 1.2 µm was obtained under a low voltage of 29 V when the concave surface of the reduced sample was facing the plate, equivalent to an effective $d_{33} > 4 \times 10^4$ pm V⁻¹. However, if the convex surface faces the plate, the displacement under a similar voltage is less than 0.1 μ m. In the latter case, the contribution from the bending deformation of the curvature structure to the measured displacement is eliminated and the material exhibits a smaller displacement, indicating that the curvature could amplify the displacement from the converse flexoelectric effect.^[17]

We demonstrate that two types of gradient-generating mechanisms can be induced by the chemical reduction. We further find that the reduction can also greatly enhance the apparent flexoelectric coefficient in NBBT ceramics, which is the reason for the enormous piezoelectric response observed in this study. During the point-plane or point-ring tests, the applied force causes the bending-like deformation of the ceramic wafers, and the flexoelectric coefficient (or apparent flexoelectric coefficient) with the largest contribution to the piezoelectric response is μ_{12} .^[7,14] The apparent μ_{12} was measured by bending a ceramic beam (see the Supporting Information for details).^[7,29] The flexoelectric current versus tip displacement curves of reduced and unreduced NBBT20 ceramic beams are shown in **Figure 3**a, and the apparent μ_{12} was calculated from the slopes of the curves. The apparent μ_{12} of NBBT20 ceramics increased from ${\approx}2.4~\mu C~m^{-1},$ which is close to the values measured in many ferroelectrics,^[7,30,31] to $\approx 100 \ \mu C \ m^{-1}$ (with the gold electrode) after reduction; however, after the fabrication of the silver electrode under a high temperature, the μ_{12} of the reduced sample was $\approx 13 \ \mu C \ m^{-1}$. With the measured apparent μ_{12} of $\approx 100 \ \mu C \ m^{-1}$, the effective d_{33} measured by point-ring test (Figure S4b, Supporting Information) can be estimated at \approx 3500 pC N⁻¹ (see the Supporting Information for details) and the experiment results (Figure 2c) are close to this value.^[12] Those results could explain the observed high piezoelectric response in the metamaterials and why the piezoelectric response was reduced after the fabrication of the silver electrode. The mechanisms for the enhancement of the apparent flexoelectric coefficient after reduction are unknown and the enhancement might mainly originate from the extrinsic contributions of the effective flexoelectric response (see the Supporting Information for details). We also observed that the phase transition temperature between the ferroelectric and nonpolar phases shifted to a lower temperature, manifested by a decrease in the depolarization temperature (Figure 3b) after reduction.^[18] A sharp depolarization current peak appears at 140 °C on the thermally stimulated current (TSC) curves because of the disappearance of the low-temperature ferroelectric phase.^[18] For the reduced sample, this peak shifts toward room temperature, indicating destabilization of the ferroelectric phase by the reduction process.^[32] The enhancement of the apparent flexoelectric coefficient and dielectric properties could be related to the change of phase transition behavior after the reduction (see the Supporting Information for details).

As an indication of the strong effective flexoelectric response in the reduced NBBT ceramics, the materials are sensitive to an asymmetric mechanical load. When a flat sample is placed on a plate and pressed by a point force, strong strain gradient can be generated near the point force.^[21] As demonstrated in Figure 2e, a strong effective d_{33} can be measured by the point– plane test (Figure S4a, Supporting Information) from the aforementioned rectangular sample after the curvature is removed by polishing. When the thickness of the sample is polished to ≈ 0.26 mm, the effective d_{33} can be higher than 900 pC N⁻¹. As a comparison, the piezoelectric response of unreduced NBBT8 ceramics (0.5 mm in thickness, not poled) measured by this method is lower than 10 pC N⁻¹.

We present a unique but simple approach to design high performance piezoelectric materials based on flexoelectricity (or effective flexoelectricity) in ferroelectrics. The materials are achieved by applying an asymmetric chemical reduction WATERIA www.advmat.de





Figure 3. a) Typical flexoelectric current versus displacement curves for reduced and unreduced NBBT20 ceramics. Squares, unreduced ceramic sample; upward triangles, reduced sample with the silver electrode; circles, reduced sample with the gold electrode. b) Thermally stimulated current curves for reduced (red line) and unreduced (black line) NBBT8 ceramics.

to lead-free Na_{1/2}Bi_{1/2}TiO₃-based ferroelectrics. After reduction, two gradient-generating mechanisms, curvature structure and chemical inhomogeneity, and a significant enhancement of apparent flexoelectric response are induced. The reduced materials become piezoelectric metamaterials with an enormous piezoelectric response, outperforming the existing piezoelectrics. The primary reason for the conversion of a ceramic piece into a piezoelectric metamaterial is the chemical inhomogeneity, which could be caused by the formation and diffusion of oxygen vacancies during the reduction,^[33] and the reduction approach can likely also be applied to other ferroelectric oxides. The results presented indicate that piezoelectric metamaterials are a feasible approach to achieve high-performance lead-free piezoelectrics to replace lead-oxide-based piezoelectrics. This work opens a new avenue of design for piezoelectric materials with sensing and actuating properties superior to those of existing piezoelectrics.

Experimental Section

NBBT ceramics were fabricated by a conventional solid-state reaction method. The raw materials, Na₂CO₃, BaCO₃, Bi₂O₃, and TiO₂ (all 99.9% except TiO₂, which is 98%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), were mixed in a ball-milling machine and calcined at 850-900 °C for 2 h. The calcined powder was then ball milled to reduce the particle size. Polyvinyl alcohol binder (5 wt%) was added to the milled powder. The powder was pressed into samples of different shapes and sizes. After the binder was burned out at 800 °C for 2 h, the samples were sintered at 1160-1350 °C for 1-2 h. To fabricate flexoelectric piezoelectric metamaterials, an asymmetric one-surface chemical reduction was applied to the NBBT ceramics. One piece of the NBBT ceramic sample was placed on a graphite block, and an alumina plate was then placed on the ceramic sample to maintain intimate contact between the ceramic and graphite. The assembly was then placed in a furnace and heat treated at 650-850 °C for 1-5 h. After the heat treatment, the assembly was removed from the furnace and cooled to room temperature in the air. The structures of the unreduced and reduced samples were determined by X-ray diffraction using a Rigaku Smartlab diffractometer (Rigaku, Tokyo, Japan). The XPS Analysis was performed on an Escalab 250 X-ray Photoelectron Spectrometer (Thermo Fisher Scientific, UK). The thermal expansion of the unreduced and reduced NBBT8 ceramic wafers (≈20 mm in diameter and 1.60 mm in thickness, reduced at 825 °C for 2 h) was characterized using a O400 thermomechanical analyzer (TA Instruments, New Castle, DE, USA). The mechanical properties of the unreduced and reduced ceramics were characterized by the three-point bending method using a Q800 dynamic mechanical analyzer (TA Instruments, New Castle, DE, USA). The dimensions of the samples were 19.00 mm in length, 10.30 mm in width, and 1.45 mm in thickness. The ceramic plate was reduced at 825 °C for 2 h.

For electrical tests, silver or gold electrodes were applied to the surfaces of the ceramic samples. To prepare the silver electrode, silver paste was coated on the sample, and the sample was then fired at 650 °C for 0.5 h. The gold electrode was prepared using a DC sputtering method in a sputter coater (EMS150T, Electron Microscopy Sciences, Hatfield, PA, USA). The effective d_{33} of the flexoelectric piezoelectric metamaterials was measured using a quasi-static d_{33} meter (ZJ-6A, Institute of Acoustics, CAS, Beijing, China). Several test methods were used (see the Supporting Information for details and Figure S4, Supporting Information). The high-temperature piezoelectric response was measured on a high-temperature piezoelectric measurement system, which was composed of a quasistatic d_{33} meter (Z)-3AN, Institute of Acoustics, CAS, Beijing, China), a furnace and a modified test fixture in the furnace. For each test, the sample was held at the measurement temperature for 1 h to make sure that the temperature is homogeneous before the measurement. Point-plane method (Figure S4a, Supporting Information) was used for this test. The electric-field-induced displacement of the reduced ceramic wafer was measured using an inductive microdisplacement probe (DGS-6C/D, Zhongyuan Measuring, Sanmen Xia, Henan Province, China) when the sample was placed on a flat surface (Figure S4d, Supporting Information). The temperature dependence of the weak-field dielectric properties of the materials was measured using an automated measurement system composed of a furnace, an E4980 LCR meter (Agilent Technology, Santa Clara, CA, USA), and a computer. The polarization versus electric field (P-E loop) curves were measured using a modified Sawyer-Tower circuit (Polyktech, State College, USA). The impedance spectra of the poled and unpoled ceramic wafers were measured using an Agilent 4294 impedance analyzer (Agilent Technology, Santa Clara, CA, USA). For the poled samples, a DC electric field of 2-4 kV mm⁻¹ was applied on the samples at room temperature for 5 min before the measurement.



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The thermally stimulated current (TSC) was measured on the poled samples using a system composed of a furnace, a computer and a Keithley 6517B electrometer (Keithley Instruments, Inc., Cleveland, Ohio, USA).

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