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Auxetic behavior under electrical loads in an induced ferroelectric phase

Abstract
The longitudinal and transverse strains were measured as a function of applied electric fields in a bulk ceramic sample of Pb0.99Nb0.02[(Zr0.57Sn0.43)0.94Ti0.06]0.98O3 at room temperature. Instead of a transverse contraction, a transverse expansion was observed in the electric-field-induced ferroelectric phase after the antiferroelectric-to-ferroelectric phase transition. Therefore, an auxetic behavior was established in monolithic ferroelectric polycrystalline ceramics under electrical loads. The behavior is characterized by a negative strain ratio that is analogous to the Poisson's ratio. The transverse expansion leads to a large hydrostatic piezoelectric coefficient dh, which suggests new applications of antiferroelectricceramics in piezoelectric devices.

Keywords
Ferroelectric phase transitions, Piezoelectric fields, Ceramis, Antiferroelectricity, Ferroelectric materials, Phase transitions, Ferroelectric domain structure, Polarization, Antiferroelectric phase transitions, Strain measurement

Disciplines
Ceramic Materials | Materials Science and Engineering

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Auxetic behavior under electrical loads in an induced ferroelectric phase

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The longitudinal and transverse strains were measured as a function of applied electric fields in a bulk ceramic sample of $Pb_{0.99}Nb_{0.02}[(Zr_{0.57}Sn_{0.43})_{0.94}Ti_{0.06}]_{0.98}O_3$ at room temperature. Instead of a transverse contraction, a transverse expansion was observed in the electric-field-induced ferroelectric phase after the antiferroelectric-to-ferroelectric phase transition. Therefore, an auxetic behavior was established in monolithic ferroelectric polycrystalline ceramics under electrical loads. The behavior is characterized by a negative strain ratio that is analogous to the Poisson's ratio. The transverse expansion leads to a large hydrostatic piezoelectric coefficient d_h, which suggests new applications of antiferroelectric ceramics in piezoelectric devices. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3076109]

Auxetics refer to materials that become thicker in transverse directions when longitudinally stretched.[1] For the case of elongation by a mechanical load, this leads to a negative Poisson's ratio.[2] Auxetic materials are rare and most of them are organic polymers with hingelike structures.[2–5] Here we report an auxetic behavior in monolithic ferroelectric polycrystalline ceramics, a technologically important family of materials, under electrical loads. The behavior is characterized by a negative strain ratio that is analogous to the Poisson's ratio. It occurs in the electric-field-induced ferroelectric phase from an antiferroelectric ceramic. The material expands in both transverse and longitudinal directions under conditions that are far away from the phase transition. Due to the transverse expansion, an effective hydrostatic piezoelectric coefficient d_h with a magnitude two times that of monolithic lead zirconate titanate (PZT) ceramics is observed.

Antiferroelectric ceramics possess electric dipoles with antiparallel orientations so that no macroscopic polarization can arise.[6,7] When subjected to strong external electric fields, they can undergo a phase transition into a ferroelectric phase where a parallel orientation of the dipoles is stable.[6–13] This electric-field-induced phase transition manifests itself in the development of a large polarization and is generally accompanied by a significant volume expansion. Such an expansion is supported by the two sublattice models[14] when an electrostrictive coupling term is introduced.[15] The volume change in the lattice can be positive if the interlattice electrostrictive coupling is positive.[15] In the induced ferroelectric phase, these materials have been assumed to behave like normal ferroelectric ceramics with normal piezoelectric properties where a transverse contraction is expected when subjected to longitudinal electric fields.[11]

$Pb_{0.99}Nb_{0.02}[(Zr_{0.57}Sn_{0.43})_{0.94}Ti_{0.06}]_{0.98}O_3$ (PNZST43/6/2) in the form of bulk ceramic pellets was prepared according to the procedure described previously.[16] The sintered pellet was ground to a cylinder with a diameter of 7 mm, and thin slices were then cut from the cylindrical pellet with a wire saw. After polishing and lapping, whole circular faces of the disk samples were electroded with Ag films by sputtering. A disk sample with diameter of 7.0 mm and thickness of 0.19 mm was picked for strain measurement. The high electric field was provided by a high voltage amplifier in conjunction with a programable function generator. For all the measurements, the applied unipolar electric fields were along the thickness direction, taking a triangular waveform with a loading rate of 10 kV/cm s. Three linear variable displacement transducers were used to measure the electric-field-induced strains, one for the longitudinal strain x_{33} in the thickness direction and two for the transverse strain x_{11} in the radial direction. During the measurement, all the signals (electric field E, polarization P, longitudinal strain x_{33}, and transverse strain x_{11}) were collected and recorded simultaneously with a multichannel oscilloscope.

Figure 1(a) shows the development of the electrical polarization (P), the longitudinal strain (x_{33}), and the transverse strain (x_{11}) simultaneously measured from the disk sample. The field-induced phase transition is clearly visible from the large increase in all parameters around 30 kV/cm. The backward ferroelectric-to-antiferroelectric phase transition upon field reduction does not occur until the applied field is decreased below 25 kV/cm. Therefore, the PNZST43/6/2 sample returns to the antiferroelectric state once the fields are removed. However, as can be seen from Fig. 1(a), there is some residual in x_{33} at zero field. It was found that this residual longitudinal strain vanishes within several minutes. In addition, it should be noted that x_{11} shows a monotonic increase with increasing fields up to 60 kV/cm.

The instantaneous strain ratio $-x_{11}/x_{33}$, which is analogous to the Poisson's ratio under mechanical loads, is displayed as a function of the applied electric field in Fig. 1(b). It is interesting to point out that this parameter is effective in delineating the stages in the evolution of the material under the influence of external fields. In the early stage of the loading segment ($0 \rightarrow 20$ kV/cm), the primary response from the ceramic is the switching of the antiferroelectric domains.[11] Corresponding to this event is the wide scatter in the strain ratio. It should be clarified that the strains x_{33} and x_{11} in this antiferroelectric stage are due to electrostriction. A linear fit between x_{33} and P^2 indicates an electrostrictive coefficient of 0.11 m^4/C^2. From 20 to 40 kV/cm, the primary response becomes the electric-field-induced antiferroelectric-to-ferroelectric phase transition with a volume expansion. As a

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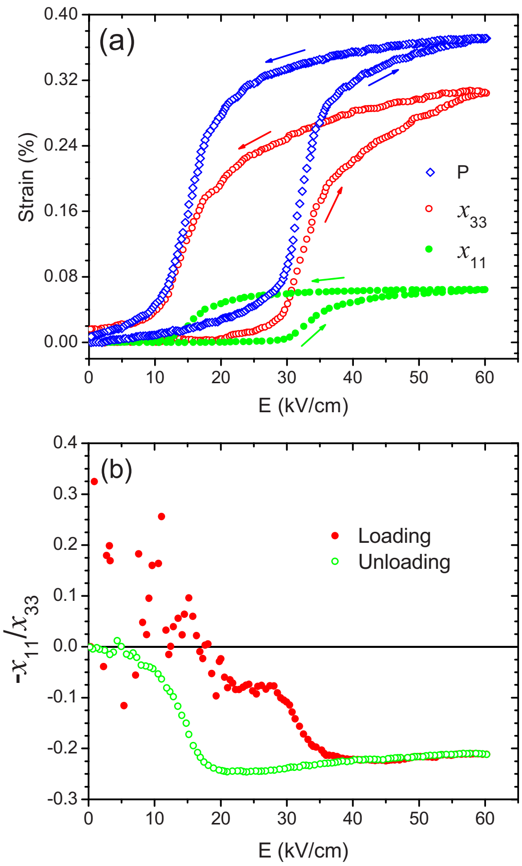

FIG. 1. (Color online) The responses of the antiferroelectric ceramic PNZST43/6/2 to unipolar electric fields of $0 \rightarrow 60 \rightarrow 0$ kV/cm. (a) P, x_{33}, and x_{11} as a function of applied fields. (b) The instantaneous strain ratio $-x_{11}/x_{33}$.

result, continuously decreasing strain ratios with negative values are observed. Above 40 kV/cm, the phase transition is completed and the material has reached a pure ferroelectric phase with aligned polarizations.[11] As the material continues to expand in all directions, the strain ratio remains negative. In this stage, a stable strain ratio around −0.21 is seen. During the unloading segment, the pure ferroelectric phase with aligned polarization persists down to about 25 kV/cm, as evidenced by the slowly changing strain ratio. The backward phase transition (ferroelectric-to-antiferroelectric) occurs between 25 and 10 kV/cm. Below 10 kV/cm, randomization of the antiferroelectric domains occurs at a very limited level.[11] As a result, the strain ratio shows a much reduced scatter compared to the early stage of the loading segment.

The observed negative values of the $-x_{11}/x_{33}$ ratio during the antiferroelectric$\leftrightarrow$ferroelectric phase switching are rationalized due to the associated large volume change.[7–13] In fields above 40 kV/cm, as indicated in Fig. 1(b), the ceramic is in a pure ferroelectric phase. However, this electric-field-induced ferroelectric phase does not behave like a normal ferroelectric material as it was assumed previously.[11] Normal ferroelectric ceramics such as PZT always contract in transverse directions when stretched by uniaxial electric fields[6] with very rare exceptions observed in certain doped lead titanates.[17] To investigate the anomalous behavior of PZSNT43/6/2 more closely, we focus on this ferroelectric phase in fields above 60 kV/cm in the following: far away from the phase transition between 20 and 40 kV/cm in order to rule out any contributions by phase transition.

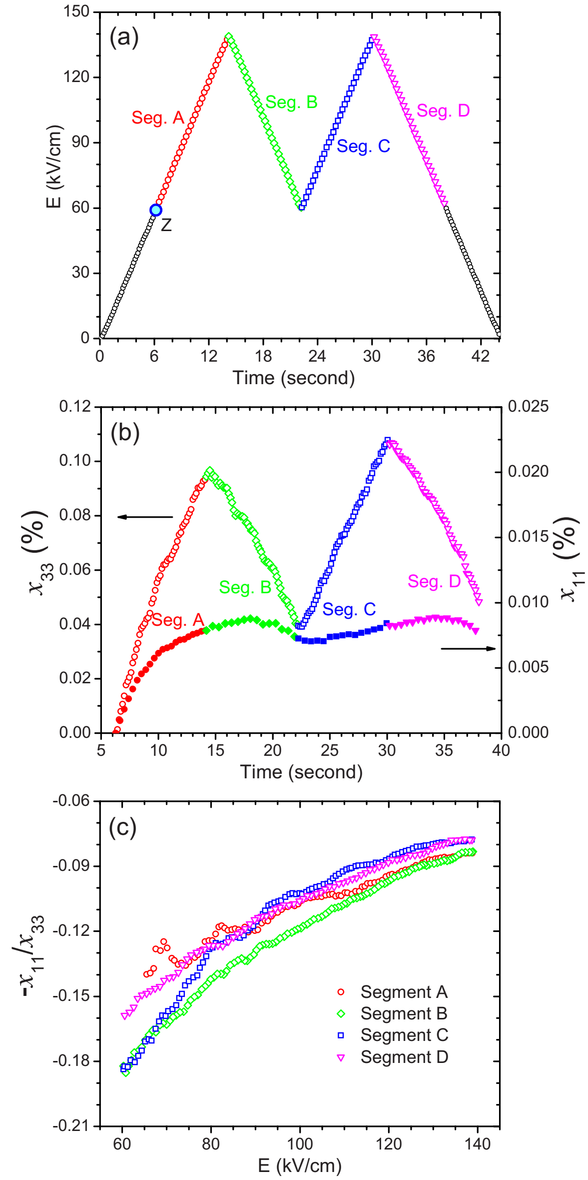

FIG. 2. (Color online) The responses of the same ceramic sample under unipolar electric fields of up to 140 kV/cm. (a) The profile of the applied electric field. Point Z denotes the condition where the electric-field-induced strains x_{33} and x_{11} are set to zero. (b) The strains x_{33} and x_{11} developed under electric fields in segments A, B, C, and D. (c) The instantaneous strain ratio $-x_{11}/x_{33}$ calculated with original dimensions set at point Z in (a).

We applied two cycles of unipolar fields between 60 and 140 kV/cm to investigate the field-induced strains in the induced ferroelectric phase, with the intention to reveal possible different responses to the two successive applications. The profile of the applied field is shown in Fig. 2(a), where portions above 60 kV/cm are denoted as segments A, B, C, and D. When the strains are normalized with respect to sample dimensions at 60 kV/cm [under conditions represented by point Z in Fig. 2(a), the field-induced deformation above 60 kV/cm in the four segments is not associated to the antiferroelectric$\leftrightarrow$ferroelectric switching any more. In this way, the deformation in segments A and B represents the first full ferroelectric cycle immediately after the transformation from the antiferroelectric phase, while the deformation in segments C and D represents the second ferroelectric cycle, i.e., after the ferroelectric domain structure has been exposed to high fields.

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The strains x_{33} and x_{11} with respect to the new origin are plotted in Fig. 2(b) for the four segments. The longitudinal strain x_{33} responds almost instantaneously to the applied electric field. In contrast, the transverse strain x_{11} appears to decouple from the longitudinal strain with a time delay with respect to the applied electric field. This decoupling has also been noted before in ceramics with similar compositions.[11,12] Another striking feature in Fig. 2(b) is the significant difference in both x_{33} and x_{11} between segments A and C, indicating different domain structures between the two successive cycles of unipolar fields in the induced ferroelectric phase.

With the new origin for strains x_{33} and x_{11}, the ratio $-x_{11}/x_{33}$ for the four segments is plotted in Fig. 2(c). It remains negative in the range between -0.19 and -0.07 for all four segments, indicating an auxetic behavior under electrical loads in the induced ferroelectric phase. Although fluctuations are seen, the ratio generally increases with increasing applied fields. Starting from 60 kV/cm, the almost linear increase in x_{33} is indicative of a constant d_{33} and can be attributed to the intrinsic piezoelectric response, which includes lattice distortion and domain wall motion. If the induced ferroelectric phase behaved like a normal ferroelectric ceramic, it would contract along transverse directions during the loading segments A and C and recover the contraction in the unloading segments B and D. Apparently, the transverse strain x_{11} (especially its significant increase in segment A) dictates the sign of the strain ratio $-x_{11}/x_{33}$.

The mechanism for the unexpected auxetic behavior under electric fields is not clear at this moment, although we may refer to concepts from situations under mechanical stresses. Kittinger *et al.*[18] pointed out that for crystals with point groups of 32, $3m$, and $\bar{3}m$, such as α-quartz, a negative Poisson's ratio can be expected along certain directions if the crystal has large elastic anisotropy. Later the auxetic behavior under mechanical loads was also confirmed in nonferroelectric α-cristobalite in both experiment and theory.[3,4] The key for the presence of negative Poisson's ratios in α-cristobalite is the large elastic anisotropy and the rigidity of the SiO_4 tetrahedra. The corner-linked tetrahedron network resembles the hingelike structure at the molecular level that has been shown to result in auxetic behavior in organic polymers.

It is interesting to notice the structural similarities in the field-induced ferroelectric phase under electrical loads to α-quartz and α-cristobalite crystals under mechanical loads: the induced ferroelectric phase consists of corner-linked and tilted oxygen octahedra.[19,20] The space group of the induced ferroelectric phase is $R3c$.[10,11] In rhombohedral PZT ceramics, the tilt angle lies in the range of 1°–5°.[20] When an electric field is applied along the polar axis [111], an expansion along this direction will follow as a consequence of the piezoelectric effect. At the same time, the tilted oxygen octahedra may get straightened if certain conditions are met. This will produce a transverse expansion, that is, the auxetic behavior.

The certain conditions required for straightening the tilted oxygen octahedra with electric fields may be unique to the antiferroelectric ceramic studied here. These conditions should at least include the unique domain patterns formed after the antiferroelectric-to-ferroelectric phase transition. The antiferroelectric ceramic before phase transition displays a hierarchical subgrain structure: large antiferroelectric 90° domains with a checkerboardlike morphology and thin 180° domain slabs (thickness around 1 nm) within the 90° domains.[13] Although the strong electric field flips and rotates the polarization during the antiferroelectric-to-ferroelectric phase transition, the resulting ferroelectric domain structure in the induced ferroelectric phase may still carry, to some extent, the hierarchical characteristics from its parent antiferroelectric phase. Such a unique ferroelectric domain structure then provides the key distinction to the normal ferroelectric phase, which does not exhibit an auxetic behavior. It should be noted that the mechanisms (detilting of oxygen octahedra and unique domain patterns) we proposed here are different from that of a recent phenomenological treatment of tetragonal single crystals where a positive transverse piezoelectric coefficient d_{31} is attributed to the polarization extension.[21]

In summary, an auxetic behavior under electrical loads is established in the electric-field-induced ferroelectric phase from an antiferroelectric ceramic. Such an unexpected behavior leads to ultrahigh hydrostatic piezoelectric properties. The detilting of tilted oxygen octahedra and the hierarchical domains structure in the induced ferroelectric phase are suggested to be the microscopic mechanism for the transverse expansion under electric fields.

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