Journal of Applied Physics

RESEARCH ARTICLE | AUGUST 03 2023

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J. Appl. Phys. 134, 054101 (2023)
https://doi.org/10.1063/5.0163502

Journal of Applied Physics ARTICLE pubs.aip.org/aip/jap

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Cite as: J. Appl. Phys. **134**, 054101 (2023); doi: 10.1063/5.0163502
Submitted: 17 June 2023 · Accepted: 20 July 2023 ·
Published Online: 3 August 2023

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ABSTRACT

Recently, a series of reports showing ultrahigh electrostrains (>1%) have appeared in several Pb-free piezoceramics. The ultrahigh electrostrain has been attributed exclusively to the defect dipoles created in these systems. We examine these claims based on another report (G. D. Adhikary and R. Ranjan, "Ultrahigh measured unipolar strain >2% in polycrystalline bulk piezoceramics: Effects of disc dimension," arxiv.org/abs/2208.07134), which demonstrated that the measured electric field driven strain increased dramatically simply by reducing the thickness of the ceramic disks. We prepared some representative Pb-free compositions reported to exhibit ultrahigh strain and performed electrostrain measurements. We found that these compositions do not show ultrahigh electrostrain if the thickness of the disks is above 0.30 mm (the disk diameters were in the range of 10–12 mm diameter). The ultrahigh strain values were obtained when the thickness was below 0.30 mm. We compare the electrostrain obtained from specimens designed to exhibit defect dipoles with those obtained from stoichiometric compositions of $Na_{0.5}Bi_{0.5}TiO_3$ and $K_{0.5}Na_{0.5}NbO_3$-based lead-free systems and could obtain much higher strain levels (4%–5%) in the later specimens in the small thickness regime. Our results do not favor the defect dipole theory as the exclusive factor for causing ultrahigh strain in piezoceramics. A new approach is called for to understand the phenomenon of ultrahigh electrostrain caused by the thickness reduction of piezoceramic disks.

I. INTRODUCTION

There is great interest in piezoceramics exhibiting large electrostrain. Earlier, large electrostrains >1% were thought to be possible only in suitably oriented single crystals of morphotropic phase boundary compositions of ferroelectric systems.[1] Polycrystalline piezoceramics were considered to exhibit considerably smaller electrostrain (in the range 0.2%–0.4%).[2] In 2015, Liu and Tan[3] reported an electrostrain of 0.7% in a $Na_{0.5}Bi_{0.5}TiO_3$-based polycrystalline piezocermic disk. Narayan *et al.* reported electrostrain of ∼1% in a polycrystalline piezoceramic of a pseudoternay $BiFeO_3$–$PbTiO_3$–$LaFeO_3$.[4] Recently, Adhikary and Ranjan[5] reported that when the thickness of piezoceramics disks (10–12 mm in diameter) is reduced below 0.5 mm, the measured electrostrain values shoot up sharply. Electrostrain values of ∼2% were observed even in normal piezoceramics like PZT and modified $BaTiO_3$.[5] Soon after the publication of this report, there is a spurt in publications showing large electrostrain >1% in lead-free piezoceramics.[6–12] A common theme in all these reports is that the exceptionally large electrostrain is caused primarily by the defect dipoles deliberately created in the system by suitable design of the compositions in $Na_{0.5}Bi_{0.5}TiO_3$ and (K, Na)NbO_3-based piezoelectrics. Different groups have envisaged different chemical modification strategies to create defect dipoles.[6–12] Feng *et al.*[9] reported that when oxygen vacancies are created by controlled volatilization of the atomic species in $Na_{0.5}Bi_{05}TiO_3$, electrostrain can be increased to ∼0.8% at room temperature. When heated close to the depolarization temperature ∼220 °C, the strain reaches 2.3%.[9] They introduced the term "hetrostrain" to describe the observation of negative strain on the negative field and positive strain on the positive cycle, during field cycling of the piezoceramic. Given that this is merely a defective (oxygen deficient) NBT, the strain of 0.8% is considerably large. Before the publication of this result, the maximum electrostrain of 0.7% was reported at room temperature in a complex NBT-based system, namely, $(Bi_{1/2}(Na_{0.84}K_{0.16})_{1/2})_{0.96}Sr_{0.04})(Ti_{0.975}Nb_{0.025})O_3$.[3] Luo *et al.*[10] introduced oxygen vacancies via modifying NBT with a hypothetical perovskite $BaAlO_{2.5}$ and reported an electrostrain of

1.12% (at 100 kV/cm) at room temperature. Still, higher strain of 1.68% was reported by Jia *et al.*[11] in $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}Ti_{1-x}(Zr_{0.50}Sb_{0.4}\square_{0.1})_xO_3$ and $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}Ti_{1-x}(Sn_{0.50}Sb_{0.4}\square_{0.1})_xO_3$ (x = 0.01 and 0.02) polycrystalline piezoceramics.

That defect dipole creation is the critical factor for achieving such large electrostrain in piezoceramics, which has also been argued in other Pb-free piezoelectric systems. Li *et al.*[12] reported electrostrain ∼1% at room temperature in a complex derivative of $BiFeO_3$, i.e., $0.695BiFeO_3–0.3BaTiO_3–0.005Bi(Zn_{0.5}Ti_{0.5})O_3$. The authors attributed the extraordinary electrostrain strain to polar nanoregions and the coexistence of phases.

Among the KNN-based piezoceramic derivatives, Huangfu *et al.*,[6] reported electrostrain of 1.05% at room temperature in Sr-modified $(K,Na)NbO_3$ and attributed it to the presence of $V'_{K/Na}–V_O$ defect dipoles. In a subsequent work, the electrostrain was reported to increase to 1.35% in textured ceramic of the same composition.[7]

Given the observation of Adhikary and Ranjan that large strain is measured when the thickness of the disks are thinned down to ∼0.2 mm,[5] it is essential to re-look if the ultrahigh electrostrain reported recently in some of the lead-free compositions owes their origin to the deliberate creation of defect dipoles, or is likely a consequence of reduced disk thickness. The significant interest in high electrostrain materials makes this issue crucial to resolve. Here, we have examined this issue critically. We chose one system based on KNN and another system based on NBT. We synthesized a Sr-modified KNN lead-free piezoceramics for which electrostrain ∼1.05% has been reported.[6] For the NBT-based lead-free piezoelectrics, we followed Luo *et al.*,[10] who reported that oxygen vacancies introduced by modifying NBT with hypothetical perovskite $BaAlO_{2.5}$ caused the electrostrain to increase to 1.12%.

II. EXPERIMENTAL

The specimens were prepared using the conventional solid state sintering method. Electrostrain and polarization measurements were carried out on ∼95% dense sintered disks. For a given composition, measurements were performed on circular disks (diameter 10–12 mm) of different thicknesses in the thickness regime 1–0.2 mm. The strategy of thickness reduction was followed as reported in Ref. 5. Polarization and electrostrain measurements were performed with the modular setup of the radiant ferroelectric measurement system on disks electroded with silver paint.

III. RESULTS AND DISCUSSION

Following Huangfu *et al.*,[6] we synthesized $K_{0.5(1-x)}Na_{0.5(1-x)}Sr_xNbO_3$ with x = 0.02 (KNNS2). The bipolar polarization, electrostrain, as well as the unipolar electrostrain of this composition are shown in Fig. 1.

The maximum bipolar electrostrain measured on the 0.5 mm thick disk is ∼0.35% at a field of +50 kV/cm. The corresponding unipolar electrostrain is nearly half this value (0.18%). As the thickness is reduced, two things happen: (i) the bipolar strain loop becomes increasingly asymmetrical. The strain on the negative cycle decreases, and that on the positive side increases. For thickness below 0.3 mm, the strain is negative in the negative cycle and positive in the positive cycle. Earlier, such shapes were attributed to hetrostrain caused by oxygen vacancies.[9] The strain in the positive cycle reaches ∼3.5% when measured on a 0.22 mm disk. Here, we see that the shape change from "butterfly loop" to "hetrostrain loop" is merely a consequence of thickness reduction of the same material. The unipolar electrostrain (which is the most important parameter for any actuator application) is merely 0.18% when measured on a 0.5 mm thick disk. It could reach 1.4% when the thickness was reduced to 0.22 mm. This value exceeds the one reported by Huangfu *et al.*[6]

Having proven above that the measured ultrahighstrain on KNNS2 is not a compositional (defect dipole) effect but a direct consequence of the reduction in the disk thickness, we also investigated this effect in a conventional MPB composition of KNN-derivatives. KNN exhibits an orthorhombic (Amm2) ferroelectric phase at room temperature. Li modification induces the tetragonal (P4mm) phase.[13] We synthesized a composition $K_{0.5(1-x)}Na_{0.5(1-x)}Li_xNbO_3$ with x = 0.06 (KNNL6) corresponding to a P4mm-Amm2 boundary and measured electrostrain as a function of thickness for this composition, Fig. 2.

Similar to KNNS2, the strain develops asymmetry in bipolar measurements on thickness reduction. The maximum strain at 50 kV/cm measured on the 0.5 mm thick disk is ∼0.3%, which is almost similar to the value obtained on KNNS2 of the same thickness. In fact, the unipolar electrostrain ∼0.3% of this MPB composition is better than the unipolar electrostrain of the KNNS2 composition. The reduced thickness of the disk increases the dielectric breakdown strength and we could apply higher fields (80 kV/cm). As evident from Fig. 2, the maximum electrostrain in bipolar and unipolar measurements on 0.29 mm disk of KNNL6 is ∼6% and ∼5% (at 80 kV/cm), respectively. Given that, unlike KNNS2, the MPB composition of Li-modified KNN is stoichiometric and was not designed to deliberately introduce point defects (other than that defects the system develops on its own during sintering at high teperatures[14]), the extraordinary electrostrain of KNNL6 suggests that compositional design approaches aimed at the deliberate creation of defect dipoles are not important for obtaining ultrahigh electrostrain in piezoceramics.

We also synthesized oxygen-deficient NBT-based lead-free piezoceramics to examine the hypothesis of oxygen deficiency playing a crucial role in the ultrahigh measured strain in NBT-based systems. We followed Luo *et al.*,[10] who reported that oxygen-deficient (1-x) NBT-(x) $BaAlO_{2.5}$ piezoceramics show electrostrain of 1.12% at room temperature. Here $BaAlO_{2.5}$ is treated as a hypothetical perovskite which, when alloyed with a real stoichiometric perovskite, will yield oxygen-deficient perovskite. We synthesized the same composition x = 0.06 of this system as reported in Ref. 10 and measured the bipolar and unipolar electrostrain for different thicknesses. For this composition, the thick and thin disks could easily survive an electric field up to 80 kV/cm. As shown in Fig. 3, the 0.7 mm thick disk shows bipolar and unipolar electrostrain of 0.5% and 0.35%, respectively, at 80 kV/cm. These values are significantly less than what was reported by Luo *et al.*(∼1.12% at 100 kV/cm).[10]

However, when the thickness of the disk was reduced to 0.2 mm, the measured bipolar strain increased enormously to 3.5%, and the unipolar strain increased to ∼2%. These values are much higher than what was reported by Luo *et al.*[10] These observations confirm that the thickness reduction is the determining factor for the ultrahigh measured strain in $Na_{0.5}Bi_{0.5}TiO_3$-$0.06BaAlO_{2.5}$.

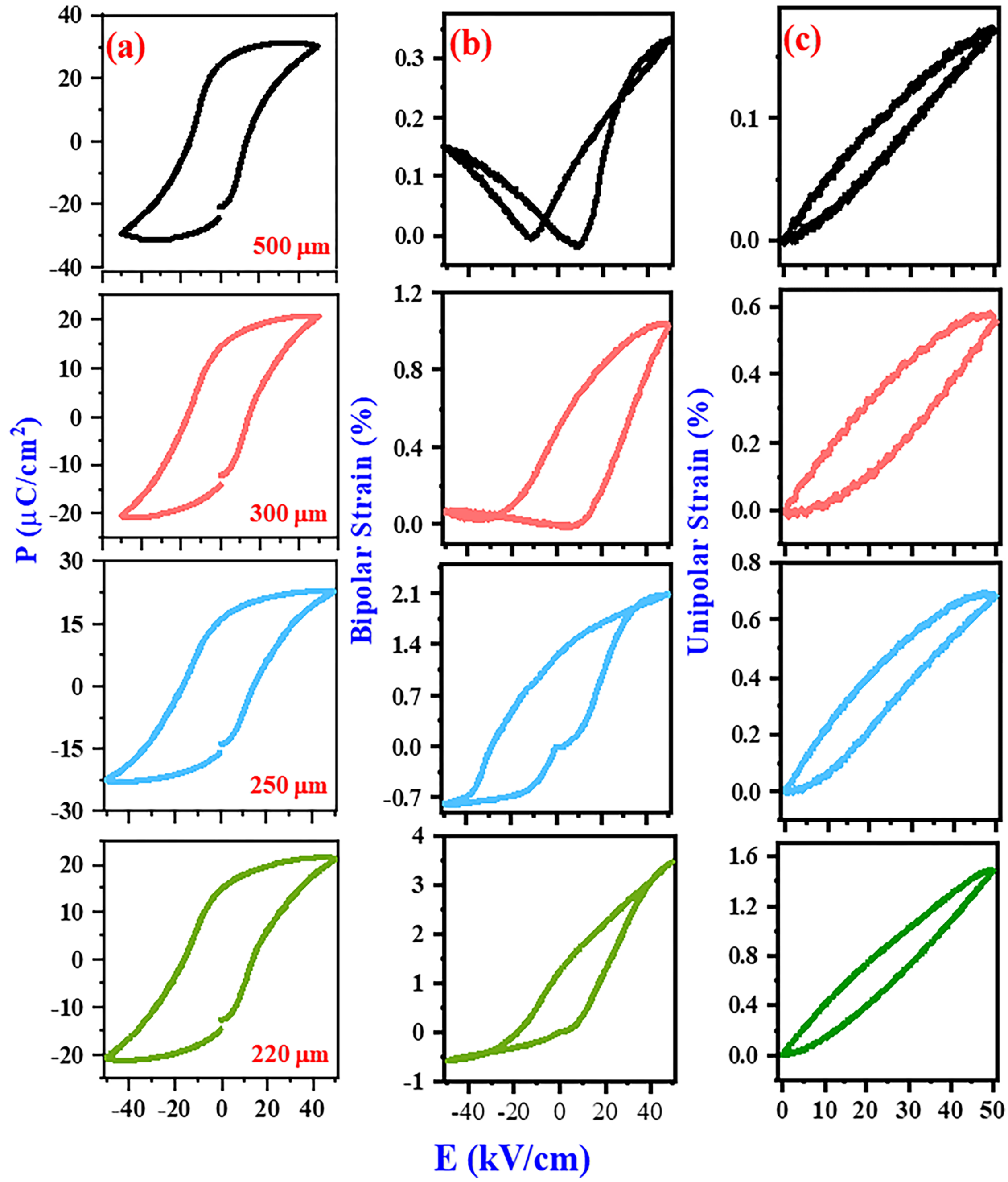

FIG. 1. Ferroelectric and electrostrain measurements of KNNS2. (a) Electric polarization as a function of the electric field, (b) strain–electric (S–E) field (bi-polar) curves, and (c) strain–electric (S–E) field (mono-polar) curves for 500, 300, 250, and 220 μm thick pellets, recorded at room temperature.

For direct comparison, we also performed electrostrain measurements on stoichiometric NBT derivatives. Here, we present results on two systems, namely, $0.62Na_{0.5}Bi_{0.5}TiO_3$–$0.28SrTiO_3$ [NBT-0.28ST] (Fig. 4) and $0.62Na_{0.5}Bi_{0.5}TiO_3$–$0.20K_{0.5}Bi_{0.5}TiO_3$–$0.08NaNbO_3$ (Fig. 5). Both the compositions correspond to the ergodic–non ergodic relaxor state boundary at room temperature. The 0.7 mm thick NBT-0.28ST disk shows bipolar and unipolar electrostrain of 0.25% at 50 kV/cm. However, when the thickness is

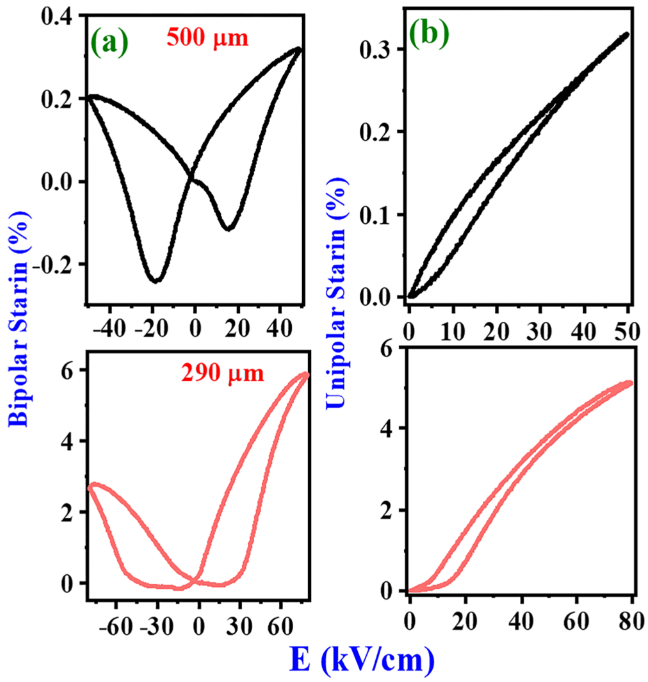

FIG. 2. (a) Bipolar and (b) unipolar electrostrain measured on 0.5 and 0.29 mm thick pellets of the KNNL6 system.

reduced to 0.2 mm, the bipolar strain in the positive cycle reaches 5%. The unipolar strain reaches 4.5%

For the other system $0.68Na_{0.5}Bi_{0.5}TiO_3$–$0.20K_{0.5}Bi_{0.5}TiO_3$–$0.08NaNbO_3$, the 0.7 mm thick disk exhibits a strain of 0.4% at 80 kV/cm. It shoots to 4% and 3.5% in bipolar and unipolar measurements, respectively. Interesting to note that these values are significantly larger than the one obtained for the defect dipole containing system 0.94 NBT–$0.06BaAlO_3$ (Ref. 10 and Fig. 3).

Figures 6(a) and 6(b) compare the frequency dependence of the S–E curves measured on 0.7 and 0.2 mm disks of NBT-0.28ST. Both shows the strain to decrease with increasing frequency. However, the frequency dispersion is comparatively larger in the thin (0.2 mm) disks. The maximum strain (at 60 kV/cm) in the 0.20 mm disk decreased from 4.7% at 50 mHz to 3.3% at 12 Hz. We also performed the cycling reliability test of the 0.20 mm thick disk NBT-0.28ST composition. For this test, the amplitude of the field was reduced to 40 kV/cm at which one still observes unipolar strain of ~1.9%. As evident from Fig. 6(c), there is insignificant degradation after 0.5×10^5 cycles, suggesting a good fatigue-resistant behavior.

Recently, He *et al*[15] reported a nominal strain of 0.7% at 150 kV/cm in a non-perovskite piezoceramic Bi_2WO_6. The shape of the bipolar S–E strain reported by the authors is similar to the "hetrostrain" reported by Feng *et al.*[9] for NBT showing large electrostrain. He *et al.*[15] argued that the peculiar shaped bipolar S–E curve originates from the reversible bending deformation induced by asymmetric 90° ferroelastic switching in the upper and lower surfaces. The ceramics used in the study was 0.3 mm thick,[15] a value close to what we report here. In this context, it is important

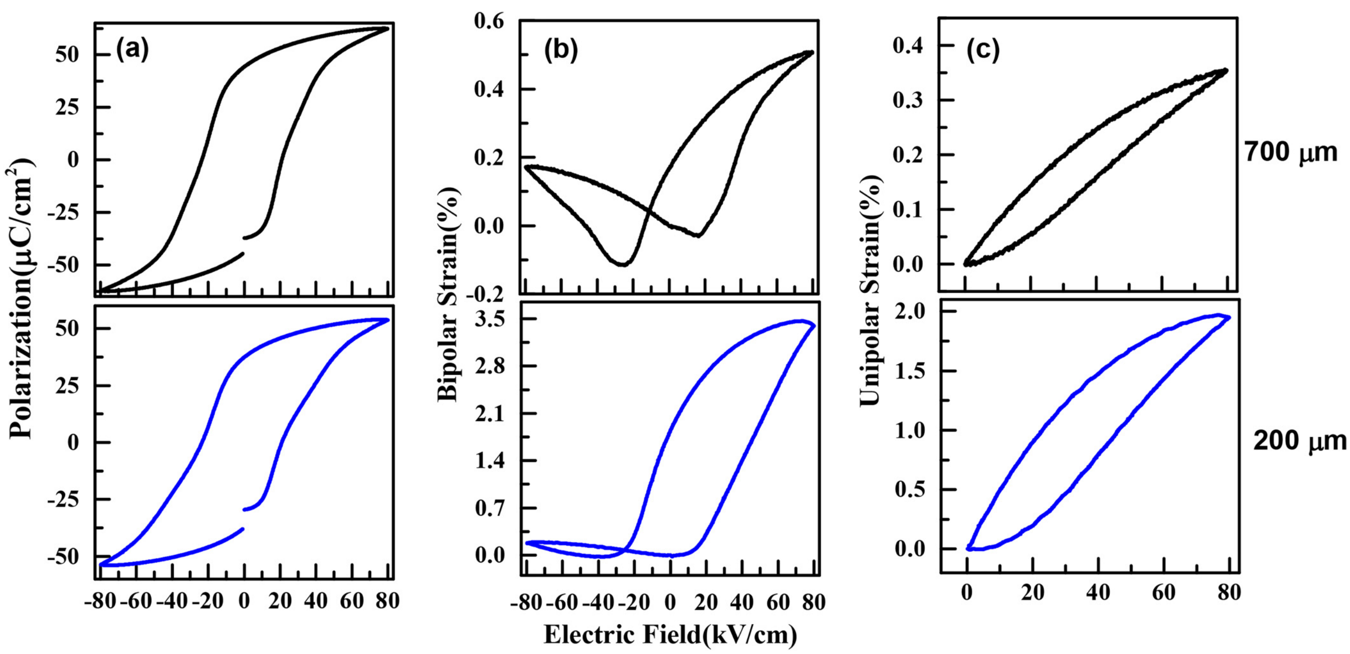

FIG. 3. (a) P–E loops, (b) bipolar strain, and (c) unipolar strain loops measured on 700 and 200 *μ*m thick pellets of $Na_{0.5}Bi_{0.5}TiO_3$-$0.06BaAlO_{2.5}$.

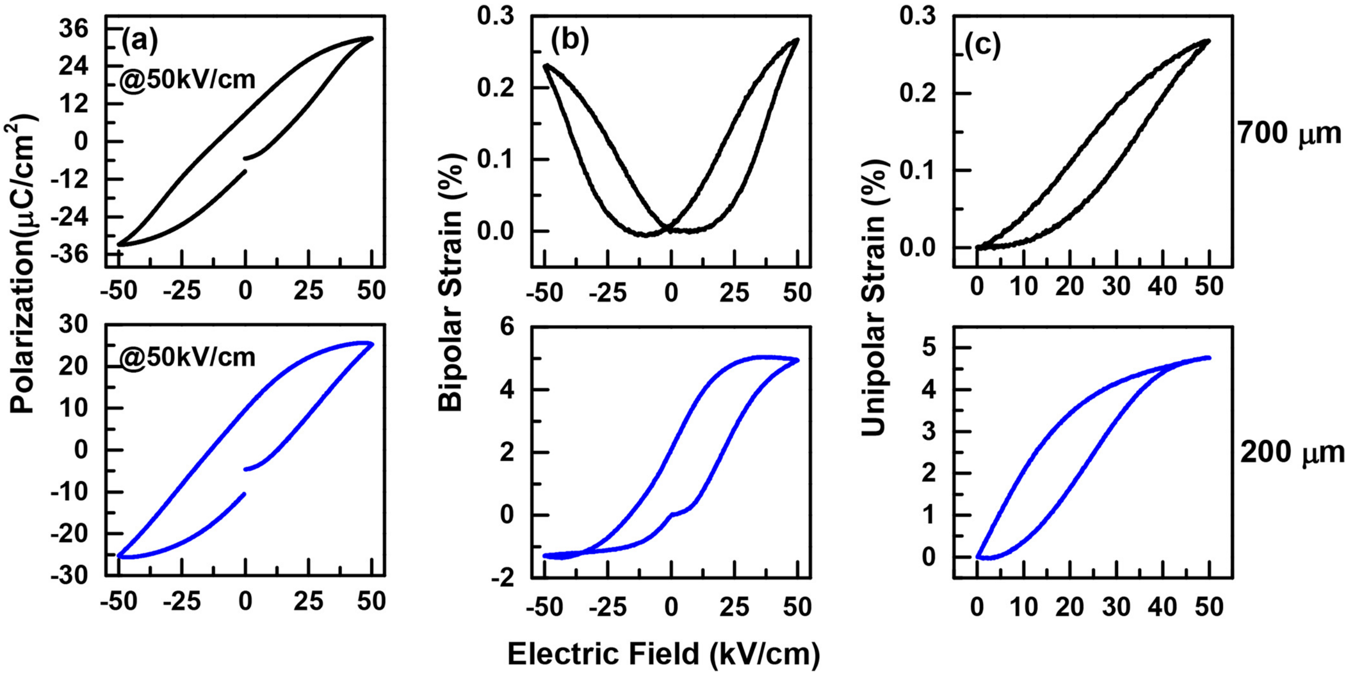

FIG. 4. (a) P–E loops, (b) bipolar strain, and (c) unipolar strain loops measured on 700 and 200 μm thick pellets of $0.62Na_{0.5}Bi_{0.5}TiO_3$-$0.28SrTiO_3$ (NBT-0.28ST)system.

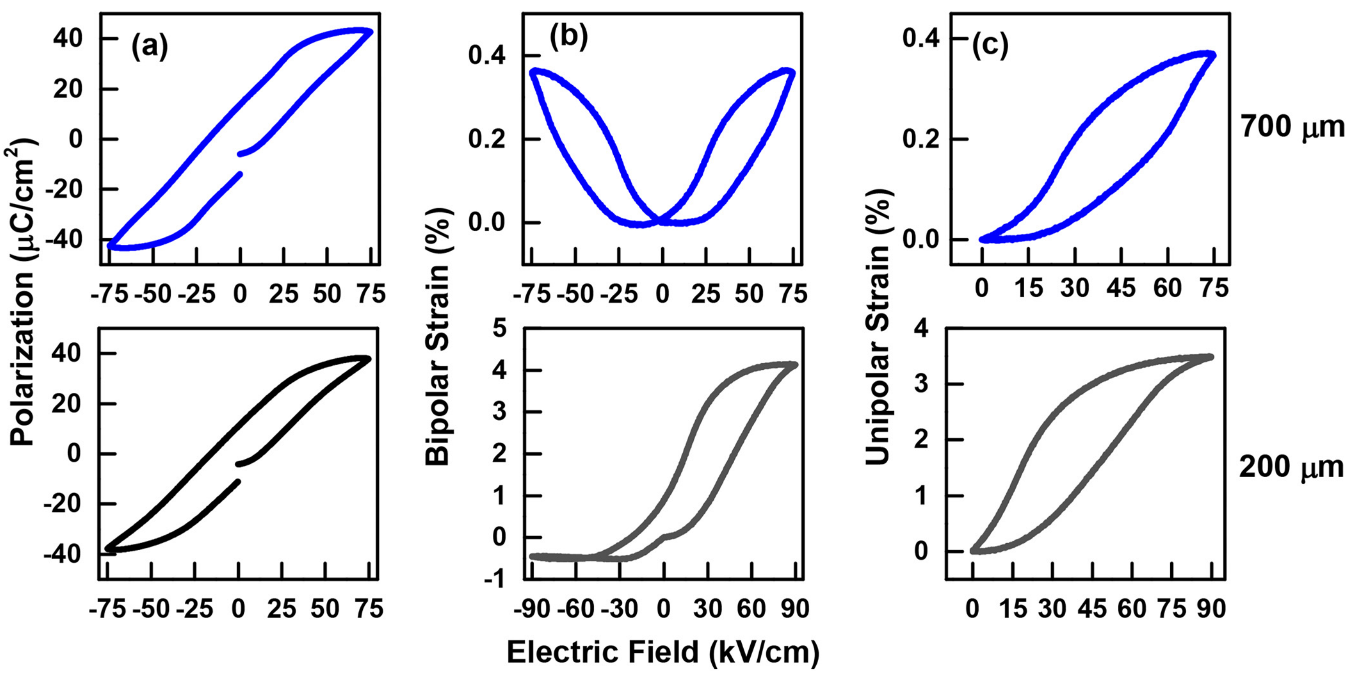

FIG. 5. (a) P–E loops, (b) bipolar strain, and (c) unipolar strain loops measured on 700 and 200 μm thick pellets of $0.68Na_{0.5}Bi_{0.5}TiO_3$-$0.20K_{0.5}Bi_{0.5}TiO_3$-$0.08NaNbO_3$ system.

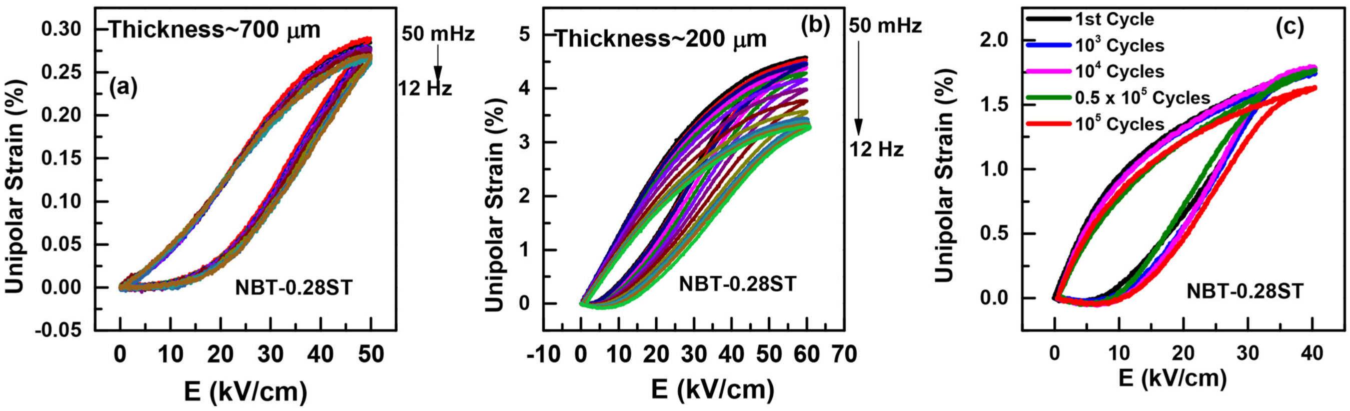

FIG. 6. Unipolar electrostrain at different frequencies (50 mHz–12 Hz) measured on (a) 700 and (b) 200 μm thick pellets of $0.62Na_{0.5}Bi_{0.5}TiO_3$-$0.28SrTiO_3$. (c) Fatigue test on the 200 μm thick pellet of NBT-0.28ST up to 10^5 cycles under 40 kV/cm at 1 Hz.

to note that the giant electrostrain of 1.05% reported in $K_{0.5(1-x)}Na_{0.5(1-x)}Sr_x]NbO_3$ was performed on ceramic disks, the thickness of which was in the range 0.2–0.5 mm thick.[6] The large electrostrain of 1.6% in Sr/Nb-doped $Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3$[7] was performed on disks ∼0.3 mm thickness. Evidently, the thicknesses of the disks used in these studies are in the range where the effect of thickness variation produces large variations in the measured strain.

IV. CONCLUSIONS

Our results confirm that the ultrahigh strain (>1%) reported in some of the lead-free piezoceramics is not primarily due to the defect dipoles, as generally proposed. The measured ultrahigh electrostrain is a phenomenon rather associated with the reduction in the thickness of the piezoceramic disks. We show that much larger electrostrain can be obtained in systems that are not designed to have defect dipoles (as in the MPB composition of the Li-modified KNN system or NBT systems at the ergodic–nonergodic relaxor boundary). Given the huge effect of reduced thickness on the measured strain, the emphasis should focus on understanding what thickness reduction does to make the piezoceramic disks exhibit such anomalous increase in the measured strain on application of the electric field.

ACKNOWLEDGMENTS

R.R. acknowledges Science and Engineering Research Board for financial assistance (Grant No. CRG/2021/000134). D.N.S. acknowledges University Grant Commission, Government of India for financial support as Dr. D. S. Kothari Postdoctoral Fellowship Award [No. F4-2/2006 (BSRYPH/20-21/0100)].

AUTHOR DECLARATIONS

Conflicts of Interest

The authors have no conflicts to disclose.

Author Contributions

Gobinda Das Adhikary: Data curation (equal); Formal analysis (equal); Methodology (equal); Validation (equal); Writing – original draft (equal). **Digivijay Narayan Singh:** Investigation (equal). **Getaw Abebe Tina:** Investigation (equal). **Gudeta Jafo Muleta:** Investigation (equal). **Rajeev Ranjan:** Conceptualization (equal); Funding acquisition (lead); Investigation (equal); Methodology (equal); Project administration (lead); Supervision (lead); Writing – original draft (equal); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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