

Lead-Free Piezoelectric Freestanding Films with Sheet Geometry-Enhanced High-Field Piezoelectric Coefficients

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(Na_{0.5}K_{0.5})NbO₃-based materials are promising lead-free piezoelectrics because of their relatively high Curie temperatures and piezoelectric coefficients. Using precursor powders made by a coating method, (Na_{0.5}K_{0.5})_{0.945}Li_{0.055}Nb_{0.96}Sb_{0.04}O₃ thick films were successfully fabricated by pressureless sintering. Large high-field $-d_{31}$ value of 1700 pm/V, > 20 times larger than that of the bulk counterpart, was observed at an applied dc electric field of 6–8 kV/cm. *In situ* X-ray diffraction study showed that the large piezoelectric response was partially due to non-180° domain switching under the electric field. Further investigation is needed to elucidate this enhancement effect. The enhanced high-field piezoelectric property observed should encourage the use of lead-free piezoelectrics.

I. Introduction

PIEZOELECTRIC films are widely used in piezoelectric microelectromechanical systems (PMEMS). Most of the PMEMS devices are made of lead-based piezoelectric materials such as lead zirconate titanate. Because of the toxicity of lead, there have been intensive efforts around the globe to limit the use of lead. For instance, the European Union has established environmental guidelines to prohibit lead-containing materials in a majority of electronics starting from 2006.¹ Several Asian countries have taken similar measures because they export electronics to European countries. Because of the reduced size and power consumption, and improved performance, PMEMS have enjoyed steadily increased applications. However, in many applications especially biomedical applications the presence of lead is unacceptable. There is a need to develop lead-free PMEMS for biomedical applications. For PMEMS applications, thick films made by tape casting and sintered without a substrate are most suitable because thin films made on a substrate exhibit a much reduced piezoelectric coefficient due to pinning by the substrate and material interdiffusion with the substrate. Ease of device fabrication is another benefit of substrate-free films.

So far, much of the lead-free piezoelectric research has been devoted to developing the bulk materials and substrate-based thin films; very few studies were carried out for thick films without a substrate² due to the difficulty in preparing good substrate-free lead-free piezoelectric films. Sodium potassium niobate, Na_{0.5}K_{0.5}NbO₃ (NKN)-based piezoelectrics are among

the most studied lead-free piezoelectrics.³ Numerous studies have tried to improve the piezoelectric coefficient of NKN-based piezoelectrics by solid solution and doping.^{4,5} While NKN-based solid solutions offer promising piezoelectric coefficients, the difficulty of making NKN-based films without a substrate is that they require pressure-assisted sintering, which is incompatible with substrate-free processing. Recently, we have shown that by doping antimony in the solid solution of NKN and LiNbO₃ (LN) and with a precursor coating approach, bulk pieces of (Na_{0.5}K_{0.5})_{0.945}Li_{0.055}Nb_{0.96}Sb_{0.04}O₃ (Sb-NKN-LN) could be sintered at 1120°C without pressure with a grain size > 5 μm that exhibited a d_{33} > 240 pC/N, and a dielectric constant of 1000.⁶ With a processing route permitting pressure-less sintering, it is then possible to make lead-free piezoelectric substrate-free films by tape casting for potential PMEMS applications.

The purpose of this study is to fabricate lead-free Sb-NKN-LN films without a substrate using the precursor coating and a pressureless sintering process and evaluate their piezoelectric performance.

II. Experimental Procedure

The Sb-NKN-LN film made without a substrate (freestanding film hereafter) was made from the Sb-NKN-LN precursor powder prepared by coating sodium and potassium precursors on the Nb₂O₅ and Sb₂O₅ particles in an aqueous solution.⁵ After calcination at 850°C for 2 h, the powder was ball-milled for 24 h and sieved using #45 and #100 meshes. The powder was then mixed with a proprietary dispersing resin and ball-milled in an alcohol-ketone mixture for 24 h. With the remaining resin and a phthalate-based plasticizer, the precursor powder was further ball-milled for 24 h, deaired, and cast into tapes of desired thickness. The green tapes were then placed in an alumina crucible sealed with packing powder that had the same composition as the tape and sintered at 1120°C for 2 h. A photograph of a 40 μm thick thus sintered Sb-NKN-LN freestanding film is shown in Fig. 1(a). As observed in the figure, the film was translucent with a yellowish tint. The scanning electron microscopy (SEM) (FEI/Phillips XL30, FEI, Hillsboro, OR) cross-section micrograph of the film is shown in Fig. 1(b).

To measure the d_{31} piezoelectric coefficient, the 40-μm-thick Sb-NKN-LN freestanding film was first coated with Pt/Pd electrode by sputtering, and then cut to an 11-mm-long, 1.6-mm-wide strips (the inset of Fig. 2) by a wire saw (WS22, Princeton Scientific Corp., Princeton, NJ). A microscope glass slide was glued to one end of the strip with a nonconductive epoxy. The sample was poled at 25 kV/cm and 120°C for 30 min on a hot plate, and then aged for over 24 h before the piezoelectric measurements. A small titanium foil (0.5 mm × 0.5 mm × 0.025 mm) was attached at the free end as a mirror for a Keyence LC-2450 laser displacement meter that had a 0.5 μm resolution (Keyence

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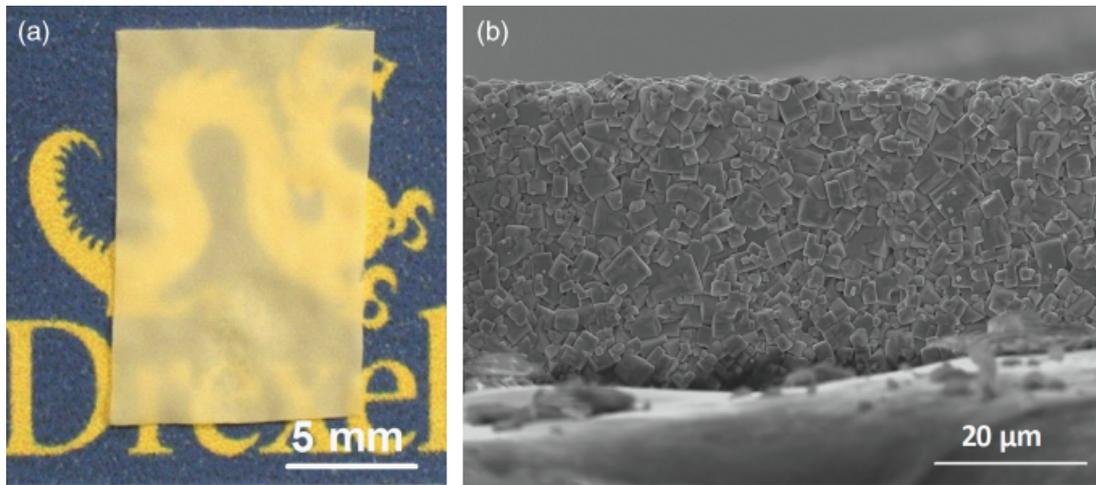


Fig. 1. (a) A photograph and (b) an ESEM cross-section micrograph of a 40- μm -thick Sb-NKN-LN freestanding film.

Corporation, Woodcliff Lake, NJ) to focus on. During the measurement, the sample and the laser head of the displacement meter were fixed on a floated Newport optical table (RS1000, Newport Corporation, Irvine, CA). A direct current (dc) electric field was applied across the thickness of the strip and the lateral displacement was directly measured with the laser displacement meter. For comparison, similar direct lateral displacement measurements were also carried out on strips cut from bulk Sb-NKN-LN pieces that were also made by the precursor-coating and the pressureless sintering process and of the same composition and microstructure and poled with the same field and temperature conditions. The bulk Sb-NKN-LN strips were 10 mm long, 1.9 mm wide, and 550 μm in thickness (not shown).

III. Results and Discussions

The d_{31} piezoelectric coefficient was deduced by dividing the lateral strain by the applied electric field. The resultant lateral strain and $-d_{31}$ vs E of the Sb-NKN-LN freestanding film strip and the bulk strip are plotted in Fig. 2, where E is the dc electric field. Note that no data points below 3 kV/cm for the freestanding film strip and 6 kV/cm for the bulk strip were included as the displacement in these ranges was outside of the resolution of the displacement meter. As can be seen, the freestanding Sb-NKN-LN film exhibited a $-d_{31}$ of about 100 pm/V at $E = 3$ kV/cm, which was comparable to the bulk $-d_{31}$ of 82–116 pm/V

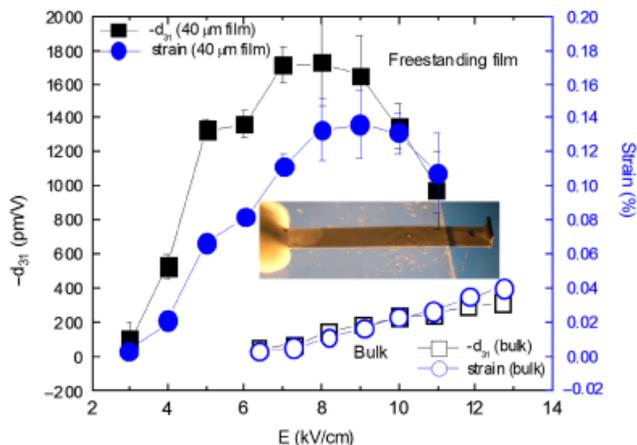


Fig. 2. $-d_{31}$ and lateral strain versus E of a 40- μm -thick Sb-NKN-LN freestanding film strip (full squares and full circles, respectively), and a bulk Sb-NKN-LN strip of the same composition (open squares and open circles, respectively). The insert is a photograph of a Sb-NKN-LN freestanding film strip.

reported in the literature⁷ and also comparable to $-d_{31} = 80$ – 100 pm/V of the bulk strip at $E = 6$ – 7 kV/cm. In many studies, thick films were shown to exhibit inferior microstructures and a lower piezoelectric coefficient to the bulk.^{8,9} That the present freestanding Sb-NKN-LN film exhibited a low-field d_{31} close to that of its bulk piece and also close to the bulk values reported in the literature, indicates that the present freestanding Sb-NKN-LN films were well sintered without pressure. Furthermore, the $-d_{31}$ of the freestanding film increased rapidly with an increasing E and reached a maximum of about 1700 pm/V at around $E = 7$ kV/cm, more than 17-fold enhancement over the low-field value. In comparison, the bulk strip did not exhibit such a large enhancement. Although the $-d_{31}$ of the bulk strip also increased with an increasing E , it only increased to about 100 pm/V at $E = 7$ kV/cm. Comparing the $-d_{31} = 1700$ pm/V of the freestanding film at $E = 7$ kV/cm to $-d_{31} = 100$ pm/V of the bulk at the same electric field, one can see, again, that the freestanding film exhibited a >17 -fold enhancement in d_{31} over the bulk strip. The d_{31} enhancement observed in the present freestanding Sb-NKN-LN films over their bulk counterpart clearly indicated that they behave very differently from the bulk. It is of interest to note that previous experiments on freestanding $(\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3)_{0.65}$ – $(\text{PbTiO}_3)_{0.35}$ (PMN-PT) films 8–75 μm in thickness also exhibited electric-field-enhanced piezoelectric performance^{10,11}: The $-d_{31}$ of freestanding PMN-PT films increased from around 300 pm/V at zero field to about 2000 pm/V at $E = 5$ kV/cm. *In situ* X-ray diffraction (XRD) analysis and piezoelectric force microscopy indicated that the enhanced piezoelectric response of these freestanding PMN-PT films at higher E was the result of the sheet-geometry-enhanced polarization orientation switching in these freestanding films at an elevated electric field, i.e., due to the depolarization effect of the sheet geometry of the freestanding films, more lateral polarization was retained after poling. As a result, more polarization switching occurs in a freestanding film than in the bulk at a high enough field, resulting in a large enhancement of the lateral strain, and hence the $-d_{31}$ coefficient. Although the present $-d_{31}$ was derived from the strain method involving high fields, which is different from the typical resonance method involving a low alternating current (ac) field, it was still a $-d_{31}$ albeit at a higher field. To distinguish the $-d_{31}$ coefficient measurement by the current direct strain method from those obtained by the typical resonance method, we will refer to the piezoelectric coefficient obtained by the present method as “high-field piezoelectric coefficient.”^{12,13} In the following, we will simply call the “high-field $-d_{31}$ ” obtained in the present study “ $-d_{31}$ ” for convenience.

Domain switching in ferroelectrics can be classified into two types: 180° domain switching and non- 180° switching. Only the non- 180° domain switching induces strain in the material. Measuring the change in the XRD pattern around 002/200 peak as a

function of applied electric fields provides information about the non-180° domain switching. In an attempt to find out how the d_{31} of the present freestanding Sb–NKN–LN film was enhanced by the electric field, *in situ* XRD experiments were carried out in a dc electric field. For a tetragonal phase, the integrated intensities of the (200) and (002) peaks are related to the populations of *a*-domains (corresponding to the in-plane polarization) and *c*-domains (corresponding to the polarization normal to the film plane), respectively.¹⁴ Meanwhile, for the orthorhombic phase, the integrated intensities of the (020) and (002) peaks are related to the populations of orthorhombic *a*-domains and *c*-domains, respectively. As an example, the *in situ* XRD patterns of a poled 40- μm -thick Sb–NKN–LN film at 0 and 10 kV/cm are shown in Fig. 3(a) as thick dashed and solid lines, respectively. Because of the coexistence of the orthorhombic phase and tetragonal phase in this material,⁵ the XRD pattern of the Sb–NKN–LN film in the range $45^\circ < 2\theta < 46.5^\circ$ can be deconvoluted into four individual peaks: tetragonal (200)_T, tetragonal (002)_T, orthorhombic (020)_O, and orthorhombic (002)_O, with the two tetragonal peaks on the outside bracketing the two orthorhombic peaks in the middle.⁵ The deconvoluted peaks at 0 and 10 kV/cm are shown as the thin dashed and solid lines, respectively. As can be seen, mostly (002)_O and some (002)_T grew at the expense of (200)_T. A schematic depicting the orientation switching in the freestanding film is shown in the insert of Fig. 3(a). The weight fraction of each of the four peaks at 0 and 10 kV/cm as obtained by integrating the area under each peak is listed in Table I. Quantitatively, with a 10 kV/cm dc electric field, the weight fraction of the (002)_T peak increased from 0.27 to 0.29 and that of (200)_T decreased from 0.49 to 0.43, while the weight fraction of the (002)_O peak increased from 0.12 to 0.19 and that of the (020)_O peak changed from 0.12 to 0.11. This result indicates that the in-plane polarization such as (200)_T switched to out-of-plane directions such as (002)_O and (002)_T. For comparison, Fig. 3(b) shows the XRD patterns of a bulk sample at 0 and 10 kV/cm as thick dashed and solid lines, respectively. The deconvoluted peaks at 0 and 10 kV/cm are shown as thin dashed and solid lines, respectively. In contrast to the freestanding film, at 10 kV/cm, there was negligible switching from the (200)_T, only some (020)_O was converted to (002)_O. This indicates that robust polarization domain switching via field-induced phase transformation only occurred in the present Sb–NKN–LN films but not in the bulk and that the switching at $E = 10$ kV/cm was mostly from the in-plane polarization of the tetragonal *a*-domain to a partially vertical, face diagonal polarization of the orthorhombic phase (orthorhombic *c*-domain) instead of a complete conversion to a vertical polarization of the tetragonal *c*-domain as was the case in the PMN–PT films. Furthermore, it is known that dielectric constant is higher when the field is normal to the polarization and lower when the field is parallel to the polarization.¹⁵ In Fig. 4, we plot the dielectric constant versus the applied electric field. As can be seen that the dielectric constant decreased with an increasing electric field, supporting the XRD results of Fig. 3 that non-180° domain switching occurred in the freestanding Sb–NKN–LN film.

Even though domain switching is responsible for the high-field d_{31} enhancement, the domain switching in the present Sb–NKN–LN freestanding film goes mostly from tetragonal *a*-domains to orthorhombic *c*-domains, which is different from the PMN–PT freestanding films where the polarization domain switching goes from the tetragonal *a*-domains to the tetragonal *c*-domains. The situation in the Sb–NKN–LN freestanding films are more complex and involves phase transformation. Further study is needed to fully understand the role of the phase transformation to the large strain enhancement.

III. Summary

In summary, 40- μm -thick lead-free Sb–NKN–LN freestanding films were successfully fabricated. Direct lateral displacement measurements indicated that at zero electric field the Sb–NKN–LN

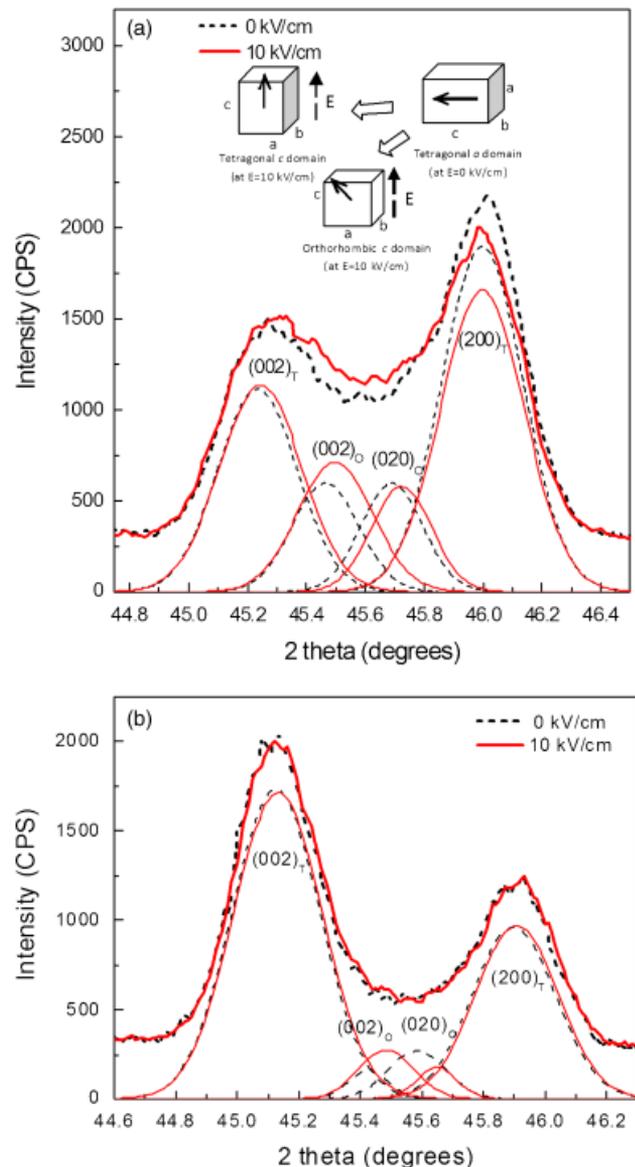


Fig. 3. (a) *In situ* XRD of a poled 40 μm Sb–NKN–LN freestanding film at 0 kV/cm and 10 kV/cm (b) *In situ* XRD of a poled 550- μm -thick Sb–NKN–LN bulk sample at 0 and 10 kV/cm. The insert in (a) is a schematic of the polarization switching from the in-plane tetragonal *a*-domain at $E = 0$ kV/cm to mostly orthorhombic *c*-domains and some tetragonal *c* domain at $E = 10$ kV/cm.

freestanding films exhibited a similar $-d_{31}$ of about 100 pm/V to that of its bulk counterpart as well as the bulk d_{31} reported in the literature. Interestingly, the $-d_{31}$ of the Sb–NKN–LN freestanding film increased rapidly to about 1700 pm/V at 7 kV/cm, while the same measurement on the bulk sample of the same composition exhibited no such dramatic enhancement. *In Situ* XRD studies indicated that the field-induced polarization domain switching was mainly from the in-plane tetragonal

Table I. Weight Fractions of the (002)_T, (002)_O, (020)_O, and (200)_T Peaks the XRD Patterns in Fig. 3(a) obtained by Peak Deconvolution Analysis

E (kV/cm)	Weight fraction			
	(002) _T	(002) _O	(020) _O	(200) _T
0	0.27	0.12	0.12	0.49
10	0.29	0.17	0.11	0.43

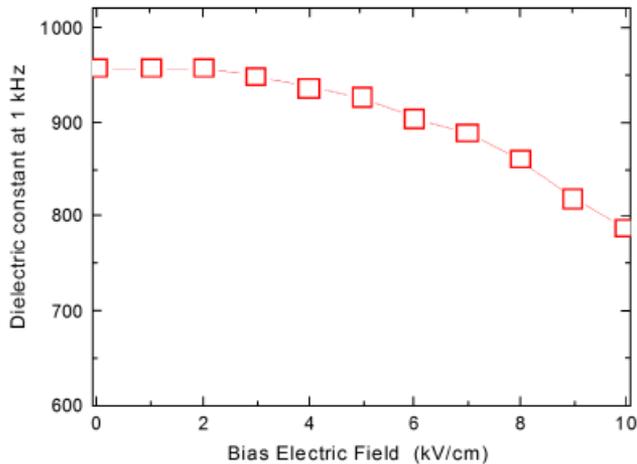


Fig. 4. Dielectric constant behavior of the 40 μm Sb-NKN-LN free-standing film as a function of applied dc field.

a -domain to a face diagonal polarization of the orthorhombic c -domains. Consequently, the domain switching in Sb-NKN-LN freestanding films involves phase transformation and is different from the field-induced piezoelectric enhancement observed in PMN-PT freestanding film where the domain switching goes from tetragonal a -domains to tetragonal c -domains without phase transformation. The large piezoelectric response enhancement in the Sb-NKN-LN freestanding films should allow lead-free piezoelectrics and PMEMS to be used more widely.

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References

- ¹The European Parliament and the Council of the European Union, "Directive 2002/95/EC of the European Parliament and of the Council of January 27, 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment," *Official J Eur Union*, **L37**, 19–23 (2003).
- ²H. Zhang and S. Jiang, "Effect of Repeated Composite Sol Infiltrations on the Dielectric and Piezoelectric Properties of a $\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{TiO}_3$ Lead Free Thick Film," *J. Eur. Ceram. Soc.*, **29**, 717–23 (2009).
- ³R. E. Jaeger and L. Egerton, "Hot Pressing of Potassium-Sodium Niobates," *J. Am. Ceram. Soc.*, **45**, 209–13 (1962).
- ⁴H. T. Y. Saito, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, "Lead-Free Piezoceramics," *Nature*, **432**, 84–7 (2004).
- ⁵E. Hollenstein, M. Davis, D. Damjanovic, and N. Setter, "Piezoelectric Properties of Li- and Ta-Modified $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ Ceramics," *Appl. Phys. Lett.*, **87**, 182905, 1pp (2005).
- ⁶H. Li, W. Y. Shih, and W.-H. Shih, "Effect of Antimony Concentration on the Crystalline Structure, Dielectric, and Piezoelectric Properties of $(\text{Na}_{0.5}\text{K}_{0.5})_{0.945}\text{Li}_{0.055}\text{Nb}_{1-x}\text{Sb}_x\text{O}_3$ Solid Solutions," *J. Am. Ceram. Soc.*, **90**, 3070–2 (2007).
- ⁷S. Zhang, R. Xia, T. R. Shrout, G. Zang, and J. Wang, "Piezoelectric Properties in Perovskite $0.948(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ - 0.052LiSbO_3 Lead-Free Ceramics," *J. Appl. Phys.*, **100**, 104108–6 (2006).
- ⁸M. Es-Souni, M. Kuhnke, A. Piorra, and C. H. Solterbeck, "Pyroelectric and Piezoelectric Properties of Thick PZT Films Produced by a New Sol-Gel Route," *J. Eur. Ceram. Soc.*, **25**, 2499–503 (2005).
- ⁹S. Osone, K. Brinkman, Y. Shimojo, and T. Iijima, "Ferroelectric and Piezoelectric Properties of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ Thick Films Prepared by Chemical Solution Deposition Process," *Thin Solid Films*, **516**, 4325–9 (2008).
- ¹⁰W. Y. Shih, H. Luo, H. Li, C. Martorano, and W.-H. Shih, "Sheet Geometry Enhanced Giant Piezoelectric Coefficients," *Appl. Phys. Lett.*, **89**, 242913–3 (2006).
- ¹¹W.-S. Su, Y.-F. Chen, W. Y. Shih, H. Luo, and W.-H. Shih, "Domain Switching in Lead Magnesium Niobate-Lead Titanate Polycrystalline Sheets at Single Grain Level," *Appl. Phys. Lett.*, **91**, 112903–3 (2007).
- ¹²A. J. Masys, W. Ren, G. Yang, and B. K. Mukherjee, "Piezoelectric Strain in Lead Zirconate Titanate Ceramics as a Function of Electric Field, Frequency, and dc Bias," *J. Appl. Phys.*, **94** [2] 1155–62 (2003).
- ¹³V. Perrin, M. Troccaz, and P. Gonnard, "Non Linear Behavior of the Permittivity and of the Piezoelectric Strain Constant Under High Electric Field Drive," *J. Electroceram.*, **4** [1] 189–94 (1999).
- ¹⁴X. Li, W. Y. Shih, J. S. Vartuli, D. L. Milius, I. A. Aksay, and W.-H. Shih, "Effect of a Transverse Tensile Stress on the Electric-Field-Induced Domain Reorientation in Soft PZT: *In Situ* XRD Study," *J. Am. Ceram. Soc.*, **85**, 844–50 (2002).
- ¹⁵F. Xu, S. Trolrier-McKinstry, W. Ren, B. Xu, Z. L. Xie, and K. J. Hemker, "Domain Wall Motion and its Contribution to the Dielectric and Piezoelectric Properties of Lead Zirconate Titanate Films," *J. Appl. Phys.*, **89**, 1336–48 (2001). □