Available online at www.sciencedirect.com

SCIENCE DIRECT

Journal of the European Ceramic Society 25 (2005) 2991–2997

www.elsevier.com/locate/jeurceramsoc

Piezoelectric/electrostrictive multimaterial PMN-PT monomorph actuators

A. Hall *, M. Allahverdi, E.K. Akdogan, A. Safari

Department of Ceramic and Materials Engineering, Rutgers University, Piscataway, NJ 08854, USA

Abstract

Fused deposition of multimaterials (FDMM), a CAD-based layered manufacturing technique, was utilized to fabricate monolithic piezoelectric/electrostrictive multimaterial monomorphs. The samples, comprised of piezoelectric $0.65\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$-$0.35\mathrm{PbTiO}_3$ and electrostrictive $0.90\mathrm{Pb}(\mathrm{Mg}_{1/3}\mathrm{Nb}_{2/3})\mathrm{O}_3$-$0.1\mathrm{PbTiO}_3$, have been successfully prototyped and co-sintered. Bimorphs, that are isometric with the co-fired samples, have also been prepared by attaching individual piezoelectric and electrostrictive layers with conductive epoxy, and were used as a comparison for displacement properties. The dielectric permittivity, displacement, and polarization hysteresis were investigated. The permittivity of the multimaterial co-sintered samples followed the two-capacitors in-series model, showing a dielectric constant of 5800 at room temperature. The P–E loop of the multimaterial samples exhibited a saturation polarization, remnant polarization, and hysteresis between that of the single material electrostrictive 0.9PMN-0.1PT and the single material piezoelectric 0.65PMN-0.35PT. Displacement hysteresis was shown to be lower for the monolithic monomorph as compared to the bimorph and reached ∼11 μm at ∼3 kV/cm.

Keywords: Layered manufacturing; Ferroelectric properties; Piezoelectric properties; Actuators

1. Introduction

Piezoelectric unimorph and bimorph bender actuators are employed for applications that require large displacement output, typically ∼35 μm.[1] In conventional designs, these actuators consist of two piezoelectric active layers that are mechanically in parallel and electrically in series; and are bonded together by a non-active layer such as epoxy.[3] Since the non-active bonding layer is typically a material of high elastic compliance (i.e. epoxy), the appertaining interface strength is known to be rather weak.[1] As a consequence, the non-active bonding layer is mostly the cause of failure in bimorph actuators because they act as prolific sites for crack nucleation, and crack growth under piezoelectrically-induced strains. Ultimately, the actuator fails due to delamination at the interface.

Some strides have been made to circumvent the delamination problem while keeping the strain output as high as possible in bimorph actuators, as exemplified by the development of reduced and internally biased oxide wafer (RAINBOW) by Haertling et al.[2] The RAINBOW actuator is comprised of a non-active Pb-rich metallic layer, which is produced by partial carbothermic reduction of a given Pb-based piezoelectric ceramic at elevated temperatures. The reduced layer, which is electrically conductive, and adds an overall stress gradient to the sample, mechanically constrains the piezoelectrically active layer, thereby enhancing the transverse displacement. While the in situ biaxial mechanical clamping is believed to be the main reason for the enhanced displacement in such actuators, it is the very phenomenon for premature failure.

For piezoelectric bimorphs to generate opposite strains in the thickness direction; piezoelectric bimorphs are configured to operate either in series or in parallel electrically.[3] Under an applied electric field, a stress discontinuity is generated at the interface between two piezoelectric active layers. The reliability of the bimorph is largely dependent on the selection of the epoxy, the uniformity of the bonding layer, and the cleanliness of the surfaces of the ceramic or

---

* Corresponding author.
E-mail address: ashahall@rci.rutgers.edu (A. Hall).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.03.196

elastic plate before bonding.[4] Soft piezoelectrics materials are more appealing for actuators applications because of their lower coercive fields (E_c), relatively low modulus of elasticity (Y_{ij}), and high piezoelectric strain coefficients (d_{ij}) albeit their relatively higher dielectric loss (tanδ) in contrast to hard piezoelectrics.[5] While soft polycrystalline piezoelectrics exhibit longitudinal piezoelectric strain coefficients (d_{33}) as high as 700 pC/N, they are intrinsically limited in tanδ (∼3 to 4%) due to easy domain wall motion.[6] Electrostrictive ceramics, on the other hand, exhibit non-hysteretic behavior, since spontaneous polarization is absent in such materials. Furthermore, electrostrictive ceramics can produce large field-induced strains (x_i) as it is a second order effect, i.e. $x_i \propto E_j^2$ ($i = 1$ to 6, $j = 1$ to 3).[6] Electrostrictive ceramics, therefore, are most amenable in high strain actuator applications.

The focus of the present study is to develop a multimaterial monomorph and to investigate the electromechanical properties of co-sintered piezoelectric and electrostrictive bending actuators. For these types of actuators, a transverse strain differential can be generated similar to that of a bimorph when operated under a unipolar electric field as shown in Fig. 1. In the present study, we have chosen the perovskites Pb(Mg$_{1/3}$Nb$_{2/3}$)O-PbTiO$_3$, 0.65PMN-0.35PT and 0.9PMN-0.1PT, which are piezoelectric and electrostrictive, respectively. We have utilized a layered manufacturing technique called fused deposition of multimaterials (FDMM), developed at Rutgers University, to fabricate multimaterial monolithic monomorphs. Both of these materials are of particular interest due to their compatible thermal expansion and sintering behavior, and hence, constitute an ideal pair of materials to accomplish co-sintering. The purpose here is to impart more reliability by eliminating interface related problems[5] in such actuators delineated previously, and also to benefit from both electrostrictive low hysteresis while retaining if not improving the generated electromechanical displacement.

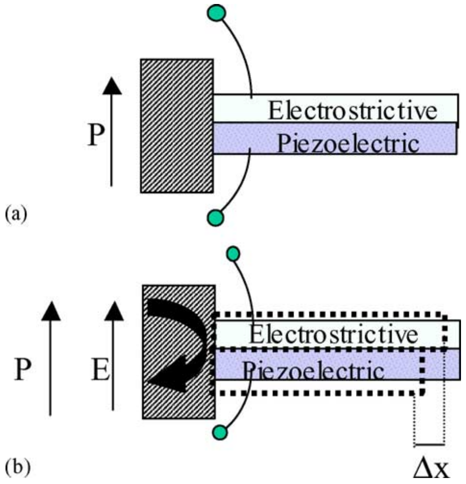

Fig. 1. Typical bender configuration used in the present study, (a) application of an electric field causes a transverse differential strain Δx; (b) transverse differential strain cause tip deflection due to the cantilever configuration.

2. Experimental procedure

2.1. Actuator fabrication

Two compositions of PMN-PT, piezoelectric 0.65PMN-0.35PT and electrostrictive 0.9PMN-0.1PT were used in fabricating multimaterial monomorph actuators. The 0.65PMN-0.35PT and 0.9PMN-0.1PT ceramic powder (TRS Ceramics, PA, USA), ∼2 to 3 μm in average particle size, were used to synthesize filament feedstock for the fused deposition of multimaterials (FDMM) process.[7–9] As shown in Fig. 2, the FDMM technique enables the creation of layered manufacturing of 3D ceramic objects generated directly from a computer-aided design (CAD) file. The CAD file is converted into a QuickSlice^{TM} file (Stratasys Inc., Eden Prairie, MN), which sends a tool path file to the FDMM machine for fabrication. The feedstock filament composed of both

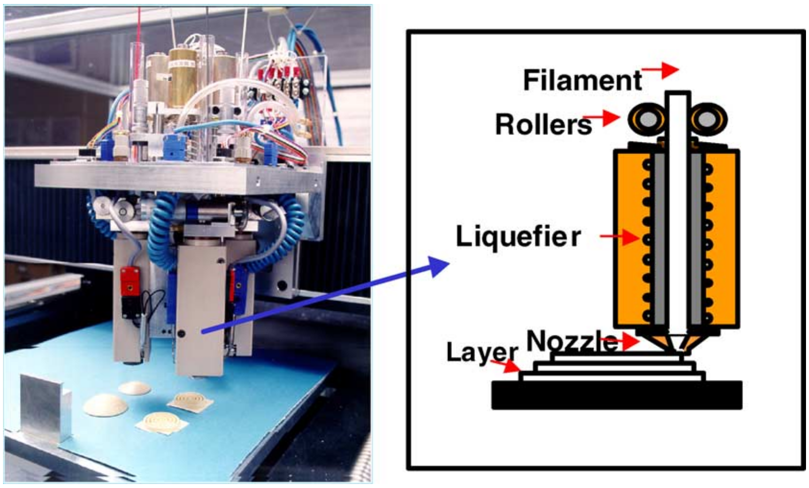

Fig. 2. The Rutgers fused deposition of multimaterials system used in this study, showing the head assembly with four delivery systems which enables the co-deposition of up to four different materials.

ceramic powders and polymer is fed into a heated liquefier (134 °C) by way of counter rotating rollers. The softened material is subsequently extruded through the nozzle (500 μm in diameter) and deposited in a layer-by-layer fashion onto the platform (stage). The tool path file controls the X–Y plane motion of the liquefier, and the Z-direction of the stage.

Two feedstocks filament of 0.65PMN-0.35PT and 0.9PMN-0.1PT powders were prepared. The first step in filament fabrication is the coating of PMN-PT powders with 3 wt% of stearic acid surfactant. The surfactant coats the powders aiding dispersion of ceramic powders in the polymer (binder). For the FDMM process, it is important that the binder provides strength, flexibility, and stiffness to the feed filament. Consequently having these properties, the filament acts as a piston for the liquefier and extrudes the material through a 500 μm round nozzle. The polymer that was used in this process is called ECG-9 binder formulated at Rutgers University.[8] It is composed of four components consisting of a base binder, tackifier, wax, and plasticizer.

For this study, we chose to co-sinter two materials, 0.65PMN-0.35PT and 0.9PMN-0.1PT, of the same compositional family with similar thermal expansion coefficient ($\sim 10 \times 10^{-6}$/°C) to alleviate co-sintering problems. By employing specific solids loading content of 57.5 vol.% for 0.65PMN-0.35PT and 54.5 vol.% for 0.9PMN-0.1PT, the differences between the sintering shrinkage were minimized.

In the fabrication of 50/50 vol% multimaterial monomorph actuators, six layers of 0.65PMN-0.35PT were deposited first, followed by another six layers of 0.9PMN-0.1PT. The green samples had undergone a binder removal cycle up 550 °C, slow enough to safely remove the organics without damaging the integrity of the part. After binder removal, the samples were co-sintered (co-fired) at 1150 °C for 2 h. The average final dimensions were 26 mm in length by 11 mm in width, and 2.3 mm in thickness.

2.2. Actuator characterization

Sintered samples were cut and polished for the observation of microstructure using a scanning electron microscope, SEM (Amray 1400, Medford, MA), equipped with an Energy Dispersive Spectrometer (EDS). Samples were also examined under an Olympus Optical Microscope (Olympus America, Inc., Melville, NY) 20× magnification.

The samples were electroded with silver epoxy, and then poled in the thickness direction in a silicon oil bath with applied 20 kV/cm field strength for 20 min at room temperature. The electromechanical properties were characterized and displacement comparisons were made with glued multimaterial samples, which were obtained by simply attaching the piezoelectric and electrostrictive layers together using conductive epoxy (Chemtronics Inc., Hartford, CT). In the glued bimorph specimens, the piezoelectric 0.65PMN-0.35PT layer was first poled, and then glued onto the electrostrictive layer with a conductive epoxy resin.

The displacement of the actuators was determined as a function of applied E-field strength with a differential variable reluctance transducer (Microstrain Inc., Burlington, VT, USA). The capacitance and dissipation factor of the samples were measured at 1 kHz in the temperature range 0–210 °C in an environmental chamber (Delta Design, Model 9023, Poway, CA, USA) using an impedance gain/phase analyzer (HP 4194, Hewlett Packard, Palo Alto, CA, USA). The polarization versus E-field measurements was carried out by using Radiant Precision LC system (Radiant Technologies, Albuquerque, NM, USA). Piezoelectric coefficients were directly obtained using a Berlincourt d_{33} piezometer (Channel Products Inc., CA, USA).

3. Results and discussion

Fig. 3a shows a scanning electron microscope (SEM) image of a multimaterial monomorph sample, containing 0.65PMN-0.35PT (left) and 0.9PMN-0.1PT (right). The X-ray line profile, as shown in Fig. 3b, was generated from an energy dispersive spectrometer (EDS) attached to the SEM. The line scan provides a qualitative analysis of material concentrations of Pb, Mg, Nb, and Ti from the left to the right side of the sample. Analysis of the data indicates a higher concentration of Ti on the left side of the scan in the 0.65PMN-0.35PT regions, and a decrease in Ti concentration as the scan continues into the 0.9PMN-0.1PT region. This analysis is consistent with the difference in PT content between the two materials. At around 1.2 mm into the sample, there is a gradual drop in the Ti profile, indicating the location of the thickness of the interface. Optical microscope data, as shown in Fig. 3c, supports this data, as an interface is evident between the two materials at lower magnification (20×).

Fig. 4 shows the relative permittivity (K_{33}) and loss tangent (tanδ) as a function of temperature at 1 kHz for piezoelectric 0.65PMN-0.35PT and electrostrictive 0.9PMN-0.1PT. The relative permittivity versus temperature plot for 0.65PMN-0.35PT displayed a ferroelectric–paraelectric phase transition at 175 °C with $K_{\max}$ ∼41,000. The room temperature (RT) K_{33} is ∼3500 (a tetragonal crystal structure), while the loss tangent is ∼2.5% (Fig. 4a). On the other hand, at room temperature the 0.9PMN-0.1PT was found to be paraelectric (cubic crystal structure), with a ferroelectric–paraelectric (FE–PE) phase transition around ∼20 °C, and a maximum relative permittivity ($K_{\max}$) of 21,000 at the transition temperature. The dielectric loss is 1% from 200 °C down to 50 °C, and increases to 11% at the onset of the ferroelectric–paraelectric phase transition. The K_{33} at RT is ∼19,000.

Fig. 5 shows temperature dependence of the relative permittivity (K_{33}) for multimaterial monomorph composed of 50 vol.% piezoelectric to 50 vol.% of electrostrictive PMN-PT measured at 1 kHz. Included in Fig. 5 is the calculated dielectric response as a function of temperature. These curves depict a 2-2 composite (a configuration where the main plane

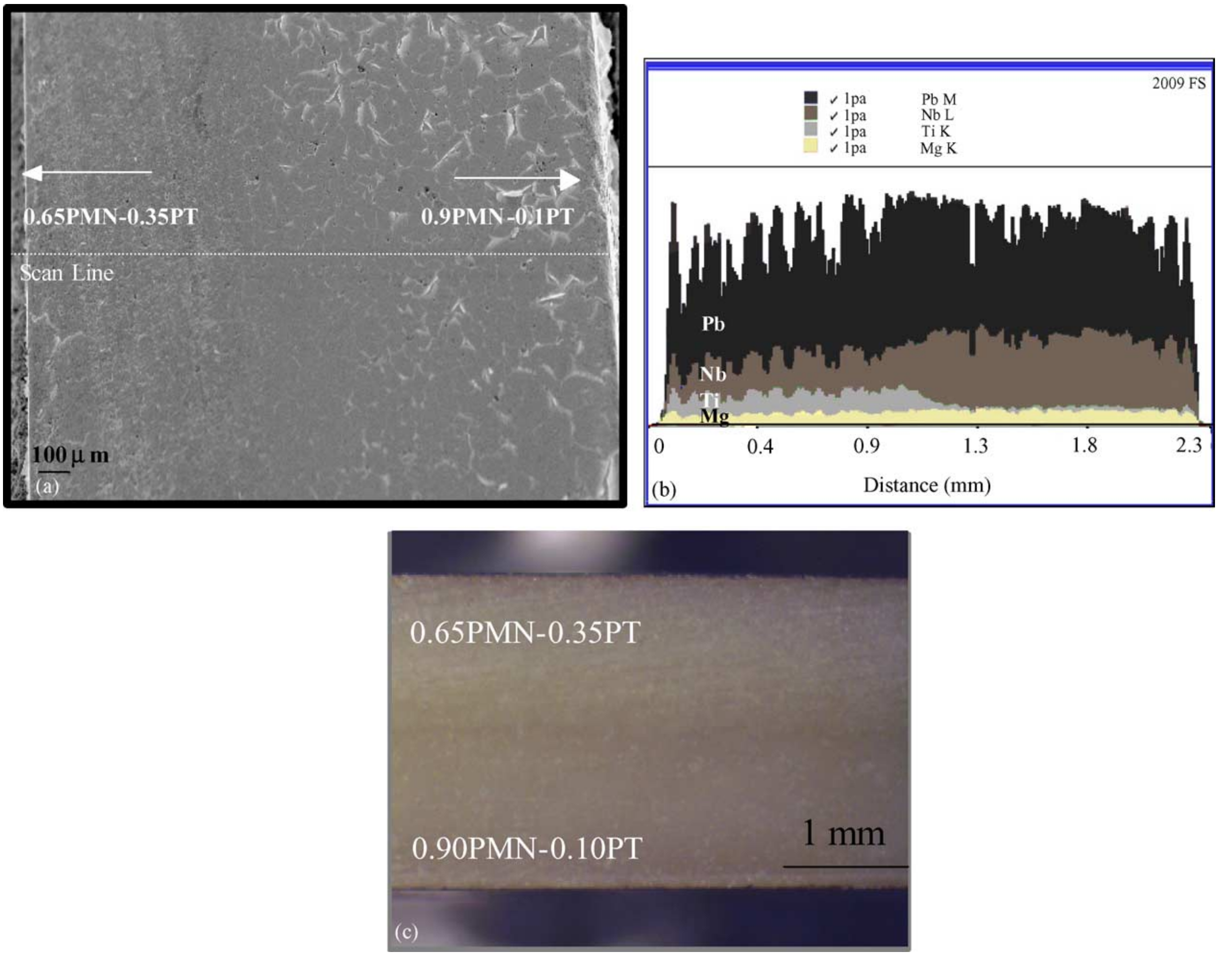

Fig. 3. (a) SEM image of multimaterial monomorph: 0.65PMN-0.35PT on the left and 0.9PMN-0.35PT on the right; (b) EDS- X-ray line profile from right to left of the SEM image of Pb, Nb, Ti and Mg across the multimaterial monomorph sample; (c.) 20× optical microscope digital image: 0.65PMN-PT on the top and 0.9PMN-0.1PT on the bottom.

of two phases are parallel to the electrodes) for comparison. The dielectric response of the composite is modeled in accordance to the two capacitors in series model, such as the one considered in this study is given by Eq. (1) [10,11]:

$$K_{33_{\text{effective}}} = \frac{K'_{33}K''_{33}}{K'_{33}V_2 + K''_{33}V_1} \tag{1}$$

where V_1 and V_2 are the volume fractions, K'_{33} and K''_{33} are the relative permittivity of the piezoelectric and electrostrictive phases, respectively, and $K_{33_{\text{effective}}}$ is the relative permittivity of the composite.[10,11] For instance, for the multimaterial monomorphs considered in this work the volume fraction is 0.5 for each phase, with the piezoelectric (0.65PMN-0.35PT) having ε_1 of 3550 and the electrostrictive (0.9PMN-0.1PT) ε_2 ~17,000 measured at room temperature. As shown in Fig. 5 the calculated effective relative permittivity of the multimaterial monomorph at room temperature is 5400, which is about 7% deviation from the experimental measured permittivity value of 5800. The K_{33} of the experimentally measured multimaterial monomorph reached a maximum value of 7100 at ~65 °C, while the calculated valued had reached to 6600 at the same temperature. A slight shoulder is revealed at 175 °C, which is attributed to the ferroelectric–paraelectric phase transition of the piezoelectric 0.65PMN-0.35PT composition of the monomorph. It seems likely that 50/50 composite of piezoelectric and electrostrictive materials yield an effective relative permittivity that is a combination of both properties. In this case, they are effectively like two capacitors in series.[11] The calculated data of the multimaterial monomorph generated from the two-capacitor in-series model is within a reasonable agreement to the experimental data.

Fig. 6 depicts the 0.65PMN-0.35PT with typical ferroelectric behavior of remnant polarization, $P_r = 30\,\mu\text{C/cm}^2$, polarization saturation, P_{sat}, of $33\,\mu\text{C/cm}^2$ at 13 kV/cm, and a coercive field E_c of 5 kV/cm. Whereas, the 0.9PMN-0.1PT has zero remnant polarization and $P_s = 20\,\mu\text{C/cm}^2$ at 13 kV/cm with no hysteresis, which is typical behavior of electrostrictive materials. At temperatures above their phase transition temperatures, electrostrictive materials that exhibit strains (0.1 to 0.2%) proportional to the square of the electric fields, have phase transition temperatures lower

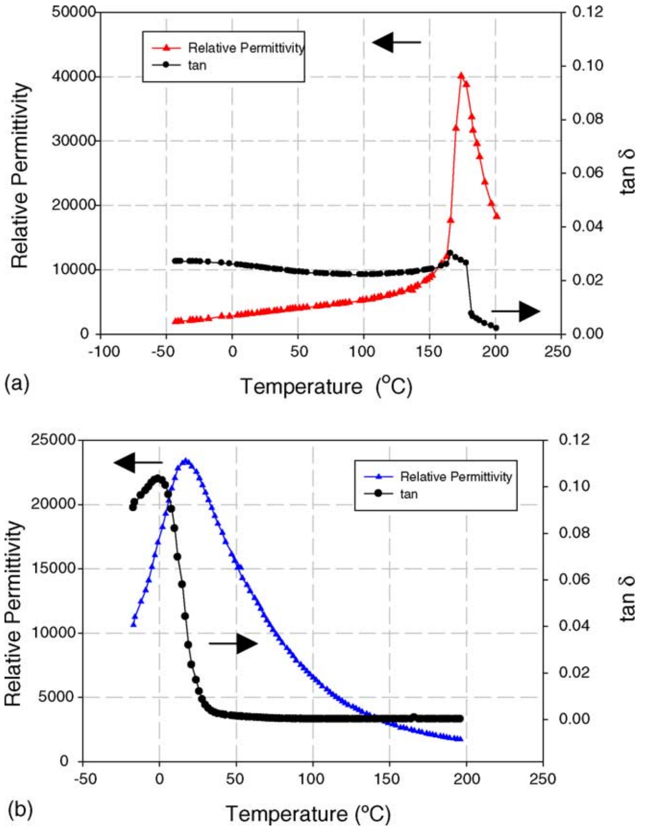

Fig. 4. Relative permittivity and loss tangent vs. temperature traces for (a) 0.65 PMN-0.35PT at 1 kHz; (b) 0.9PMN-0.1PT at 1 kHz.

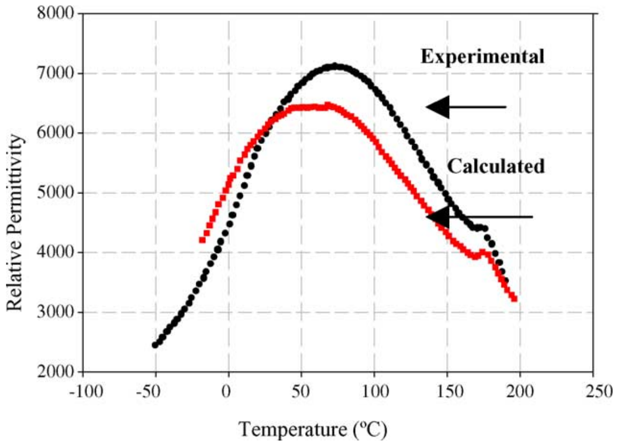

Fig. 5. Relative permittivity vs. temperature for multimaterial PMN-PT, the curves show the experimental and calculated data. The latter was computed from the relative permittivity of individual materials.

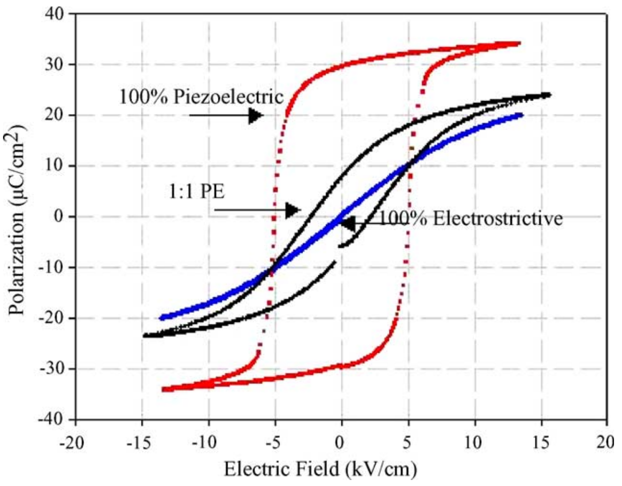

Fig. 6. P–E hysteresis loops for 65/35PMN-PT-single material, 90/10 PMN-PT single material, and 1:1 PE monomorph.

than room temperature, coercive fields less than 1 kV/cm, and no hysteresis.[12] The conventional polarization versus electric field behavior is due to polarization re-orientation, which is caused by the change of ferroelectric domain status upon an applied electric field. Since electrostrictive 0.9PMN-0.1PT does not posses spontaneous polarization and the curie temperature is below room temperature, there are no ferroelectric domains for switching purposes.[12] The multimaterial monomorph has a $P_{\text{sat}} = 24\,\mu\text{C/cm}^2$, a remnant polarization $P_{\text{r}} = 9\,\mu\text{C/cm}^2$, and a coercive field, E_{c}, of 3.0 kV/cm. The P_{sat} for the co-fired monomorph is close to that of the pure piezoelectric phase, while the P_{r} is drastically reduced. The advantage of the multimaterial monomorph is that the monomorph has lower hysteresis due to the electrostrictive contribution.

For comparison purposes, a bimorph sample has been made. A transverse strain differential, which causes the tip deflection in the cantilever configuration, is generated similar to that of a bimorph when operated under a unipolar electric field. In the case of the multimaterial monomorph actuators the differential transverse strain is given by:

$$\Delta x_{31} = d_{31}E_3 + M_{12}E_3^2 \qquad (2)$$

where Δx_{31} is the differential strain dictating the tip deflection for a given actuator length, d_{31} is the transverse piezocharge coefficient of the piezoelectric, and M_{12} is the transverse electrostrictive coefficient of the electrostrictor in electric field notation. Furthermore, when the direction of the applied electric field is in the same direction as that of the poling direction of the piezoelectric material, then maximum displacement is observed. Otherwise, if the electric field is applied opposite the poling direction, less displacement is seen over several cycles were depoling develops within the sample. In this case, it is desirable to apply the electric field in the same direction as the poling direction of the piezoelectric constituent (eliminating the aspect of depoling). Since the electrostrictive strain is independent of the direction of the electric field, the piezoelectric and electrostrictive layers are going to strain in the same direction. As can be verified from Fig. 7, the displacement of both types of actuators is asymmetric in accordance to Eq. (2), which is an odd function.

As shown in Fig. 7, the deflection of the glued bimorph sample was found to be three times higher than that of the multimaterial monomorph sample. The displacement of

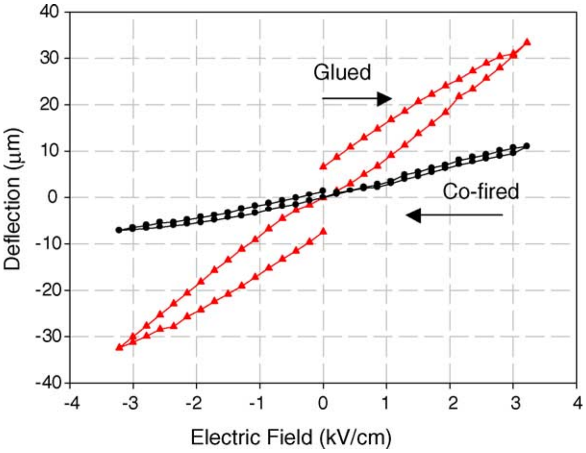

Fig. 7. Deflection vs. electric field (kV/cm) for the multimaterial co-fired monomorph actuator compared to the bimorph actuator.

the multimaterial monomorph actuator was 11 μm under 3 kV/cm electric field. The origin of the enhanced displacement of the bimorphs (connected in series) in comparison to the co-sintered monomorph can be traced back to the poling of such actuators. In the bimorph, the piezoelectric 0.65PMN-0.35PT plate is poled to saturation prior to attaching it to the electrostrictive 0.9PMN-0.1PT plate. The d_{33} of the piezoelectric 0.65PMN-0.35PT plates was measured as 600 pC/N. As a result, the bimorph effective piezoelectric charge coefficient, d_{33}, was measured to be ∼300pC/N using the Berlincourt piezometer. The co-sintered monomorph had an effective piezoelectric charge coefficient slightly lower (∼200 pC/N) than the bimorph. A plausible explanation for the lower effective d_{33} coefficient for the multimaterial monomorph may be attributed to compressive stresses. Since it is a co-sintered multimaterial monomorph, residual stresses that develop during the cooling process may cause compressive stresses to facilitate ferroelastic non-180° domain wall switching in the piezoelectric material, which would drive depolarization processes. Similar principles was discussed by Lynch,[13] where he measured the polarization and strain versus electric field hysteresis loops for PLZT ceramics at various compression preloads levels up to −60 MPa. In his experiments, he observed that when the field is reduced at constant stress, the material began to depole, resulting in lower piezoelectric coefficients.[13] Also, Zhou et al. have studied the uniaxial compressive stress dependence of the piezoelectric performance of soft PZT ceramics. He concluded that when the compressive stress is higher than −200 MPa the piezoelectric coefficients become very small, which indicates that there is hardly any piezoelectric effect under such high stress preload conditions.[14] However, he also observed an enhanced piezoelectric performance induced by small compressive stress (less than −10 MPa) preload. We have not measured the internal stresses in the multilayer actuator as it is beyond the scope of this study. However, the effects of internal stresses are prevalent from the comparison of co-fired and multimaterial bimorph actuators. More research is in progress to investigate this topic.

Also as shown in Fig. 7 is less hysteresis in multimaterial monomorph samples as compared to the glued-bimorph. The displacement hysteresis and/or the positioning accuracy that accompany bimorph actuators are at a disadvantage. Therefore, multimaterial monomorph actuators incorporating an electrostrictor seem to be a good candidate for better positioning accuracy and lower mechanical losses. Furthermore, low mechanical losses and low dielectric losses are needed to achieve a longer life span of the actuators.[15,16] Hence, the loss could in principle be reduced by the careful selection of the type and volume fraction of the electrostrictor in multimaterial actuators.

4. Conclusion

Multimaterial piezoelectric and electrostrictive PMN-PT monomorph actuators were successfully co-sintered, and shown to possess interesting electromechanical properties with potential use as bending actuators. The use of piezoelectrics and electrostrictors in combination in such bending actuators reduced the mechanical losses inherent to their piezoelectric counterparts, while maintaining appreciable tip displacement at reasonable field levels. The maximum tip displacement for co-sintered monomorph actuators has been found to be 11 μm at ∼3 kV/cm. Even though for the co-fired multimaterial monomorph the displacement does not achieve the same amount as the glued bender, the hysteresis is lower which is desirable for applications requiring non-hysteretic behavior.

Acknowledgments

The authors gratefully acknowledge the funding provided by the Office of Naval Research (USA), The Howatt Foundation, and the State of New Jersey Commission on Higher Education.

References

1. Qui, J., Tani, J., Ueno, T., Morita, T., Takahashi, H. and Du, H., Fabrication and high durability of functionally graded piezoelectric bending actuators. *Smart Mater. Struct.*, 2003, **12**, 115–121.
2. Furman, E., Li, G. and Heartling, G. H., An investigation of the resonance properties of RAINBOW actuators. *Ferroelectrics*, 1994, **10**, 357–369.
3. Wang, Q., Zhang, Q., Xu, B., Liu, R. and Cross, L. E., Nonlinear piezoelectric behavior of ceramic bending mode actuators under strong electric fields. *J. Appl. Phys.*, 1999, **86**(6), 3352–3360.
4. Wang, Q., Du, X., Baomin, X. and Cross, L. E., Theoretical analysis of the sensor effect of cantilever piezoelectric benders. *J. Appl. Phys.*, 1999, **85**(3), 1702–1706.
5. Zhu, X. and Meng, Z., Operational principle, fabrication, and displacement characteristics of a functionally gradient piezoelectric ceramic actuator. *Sens. Actuators A*, 1995, **48**, 169–176.

6. Park, S. and Shrout, T., Ultrahigh strain and piezoelectric behavior in Relaxor based ferroelectric single crystals. *J. Appl. Phys.*, 1997, **82**(4), 1804–18117.
7. Mohammadi, F., *An Investigation on the Development of High Performance Piezoelectric Actuators by Fused Deposition of Ceramics* (*FDC*), Ph.D. thesis, Rutgers University, New Brunswick, NJ, 2001.
8. McNulty, T. F., Mohammadi, F., Bandyopadhyay, A., Shanefield, D. F. and Danforth, S. C., Development of a binder formulation for fused deposition of ceramics. *Rapid Prototyp. J.*, 1998, **4**(4), 144–150.
9. Safari, A., Processing of Advanced electroceramic components by fused deposition technique. *Ferroelectrics*, 2001, **263**, 45–54.
10. Sihvola, A., *Electromagnetic Mixing Formulas and applications*. IEE Electromagnetic Waves Series 47, London, UK, 1999.
11. Moulson, A. J. and Herbet, J., *Electroceramics*. Chapman and Hall, London, 1990.
12. Uchino, K., *Piezoelectric Actuators and Ultrasonic Motors*. Kluwer Academic Publishers, Norwell, MA, 1996.
13. Lynch, C. S., The effect of uniaxial stress on the electro-mechanical response of 8/65/35 PLZT. *Acta Mater.*, 1996, **44**(10), 4137–4148.
14. Zhou, D., Kamlah, M. and Munz, D., Uniaxial compressive stress dependence of the high-field dielectric and piezoelectric performance of soft PZT piezoceramics. *J. Mater. Res.*, 2004, **19**(3), 834–842.
15. He, Z., Ma, J., Zhang, R. and Li, T., Fabrication and characterization of bilayered Pb(Zr, Ti)03-based ceramics. *Mater. Lett.*, 2002, **56**, 1084–1088.
16. Or, Y. T., Wong, C. K., Ploss, B. and Shin, F. G., Polarization behavior of ferroelectric multilayered composite structures. *J. Appl. Phys.*, 2003, **93**(7), 4112–4119.