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Correlation of the coercive field and reduced layer thickness in piezoelectric RAINBOW ceramics

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RAINBOWs are a relatively new type of high-displacement, piezoelectric actuator produced by selectively removing oxygen from one side of a lead-containing ceramic using a high-temperature chemical reduction process. This process yields devices which contain a piezoelectric layer and a metallic layer (i.e., the reduced layer). In this study, piezoelectric RAINBOW actuators with reduced layer-to-total-thickness ratios ranging from 0.05 to 0.8 were produced from five soft-piezoelectric formulations. The ferroelectric hysteresis properties of each specimen were then measured while taking the total thickness of the device to be ferroelectric. Because of this assumption and the metallic nature of the reduced layer, the resulting coercive field measurements were found to correlate strongly with the thickness of the piezoelectric portion of each device. A simple, non-destructive method for estimating the reduced layer thickness in RAINBOW ceramics was devised based on this relationship.

1. Introduction

Recently, a new type of piezoelectric actuator, referred to as the Reduced And INternally Biased Oxide Wafer, or RAINBOW, was reported by Haertling [1]. These devices are produced by selectively removing oxygen from one side of a high lead-containing piezoelectric ceramic using a high-temperature chemical reduction process. In this procedure, a piezoelectric ceramic is placed on a graphite block and introduced into a high-temperature (typically 925 to 975 °C), oxidizing environment. While at temperature, oxygen is removed from the side of the piezoelectric that is in contact with the graphite block, thus producing a monolithic device which contains both a piezoelectric layer and a highly metallic layer (i.e., the reduced layer).

Once the prescribed reduction time has expired, the graphite/piezoelectric assembly is removed from the furnace and allowed to return to room temperature. During cooling, the large thermal expansion difference between the two layers comprising the RAINBOW structure results in the formation of a highly-stressed, domed-shaped device. When an electric field is applied, these pre-stressed ceramics are capable of producing axial displacements which are several orders of magnitude greater than those of the piezoelectric ceramics from which they were produced. RAINBOWs have been found to generate the largest displacements when the reduced layer comprises approximately 30 percent of the total thickness of the device [2].

This report describes the correlation of the coercive field, E_C, of RAINBOW devices with the relative thickness of the two layers which comprise these structures. As a result of this investigation, a novel, non-destructive method for estimating the reduced layer thickness in RAINBOW actuators was developed and is described herein.

2. Experimental

The piezoelectric materials used in this study were commercially available ceramics obtained in an unelectroded and unpoled condition. Ceramics with both circular and rectangular geometries were used in this work. The circular specimens possessed diameters ranging from 1.27 to 5.08 cm, whereas the rectangular ceramics were 6.35×3.81 cm. All of the ceramics were between 254 and 508 μm in thickness.

Prior to the production of RAINBOWs from these materials, between five and ten ceramics of each composition were electroded using silver epoxy (DuPont 5504N). The dielectric constant and ferroelectric hysteresis properties of each specimen were then measured to establish average values for each composition to which the RAINBOWs would be compared. All of the ceramics used in this study possessed densities which were at least 95% of the theoretical value for each composition. The trade names, dimensions, dielectric constants (κ), and ferroelectric properties of each composition are shown in Table I.

Next, several RAINBOWs were produced from each composition listed in Table I by chemically reducing the piezoelectric ceramics using graphite blocks. In this study, RAINBOWs with varying reduced-layer-to-total-thickness ratios, hereafter referred to as the thickness ratio, were produced by exposing the ceramics to the reducing conditions for 20 to 150 minutes at

TABLE I Trade names, dimensions, dielectric constants, and ferroelectric hysteresis properties of the piezoelectric ceramics used in this study

Trade name	Dimensions	κ	E_C (kV/cm)	P_R (μC/cm^2)	P_{SAT} (μC/cm^2)
APC 850[a] (PZT-5A)	2.54 cm dia. × 380 μm 5.08 cm dia. × 380 μm 6.35 cm × 3.81 cm × 250 μm	1200	10.0	23.8	28.3
APC 855[a] (PZT-5H)	5.08 cm dia. × 510 μm	2850	7.3	24.3	32.9
EBL 5[b] (PZT-7A)	2.54 cm dia. × 380 μm 5.08 cm dia. × 380 μm	400	10.3	45.4	47.7
PKI 502[c] (PZT-5A)	1.27 cm dia. × 380 μm 2.54 cm dia. × 380 μm	1100	13.3	30.4	35.6
PKI 552[c] (PZT-5H)	1.27 cm dia. × 380 μm 1.90 cm dia. × 380 μm	2800	7.3	24.4	32.0

[a]American Piezo Ceramics, Inc., Mackeyville, PA.
[b]Stavely Sensors, Inc., East Hartford, CT.
[c]Piezo Kinetics Inc., Bellefonte, PA.

temperatures ranging from 925 to 975 °C. After the reduction time elapsed, the graphite/piezoelectric assembly was removed from the furnace and allowed to return to room temperature. While cooling, a thin reoxidation layer formed along the reduced surface. Once the device had completely cooled, the re-oxidized layer was removed with a micro-sandblaster. The total thickness of each RAINBOW was then measured and silver-epoxy electrodes were applied to the major surfaces of each device.

The ferroelectric polarization versus electric field (P-E) properties of each RAINBOW were then measured using a modified Sawyer-Tower circuit. In this study, the coercive field (E_C) of each device was calculated assuming the total thickness of the actuator was ferroelectric. The E_C, P_R (remanent polarization), and P_{SAT} (saturation polarization) values were determined by averaging the magnitudes of the positive and negative values of each parameter. The measured E_C values of each RAINBOW were then compared to those of the unreduced ceramics. After measurement of the ferroelectric properties, the specimens were sectioned, mounted, and polished for evaluation. The thicknesses of the reduced and piezoelectric layers within each RAINBOW were then determined by optical microscopy.

In addition to the P-E measurements, the resistive properties of the reduced layers were also characterized. In this procedure, lead wires were attached to the unelectroded reduced layers of specimens of each composition using silver epoxy. Once the leads were attached, d.c. four-probe resistance measurements were performed using applied currents ranging from 5 to 100 mA.

3. Results

The circular RAINBOWs produced in this study possessed either domed or saddle-shaped structures as originally reported by Haertling [1]. The rectangular devices produced from the APC 850 composition were curved along the length of the ceramic. Once electroded, the P-E properties of each specimen were measured. The materials exhibited P_R and P_{SAT} values that were similar in magnitude to those of the unreduced ceramics from which the RAINBOWs were produced. In instances where the remaining piezoelectric portion was very thin, a few of the devices electrically shorted before the saturation polarization was reached. Because of the unavailability of P-E data for these specimens, the device under test was deleted from the study at this occurrence.

Optical inspection of the sectioned RAINBOWs revealed the two distinct layers that comprise the structure of these devices. Although the two layers were clearly discernible, some variability in the thickness of the reduced layer was observed along the sectioned length of each device. For this reason, the reduced layer thickness was measured at several points along the interface and an average reduced layer thickness was calculated. Aside from a few exceptions, the variability of the reduced layer thickness was found to be less than 5% along the length of the sectioned materials. A typical example of the reduced and piezoelectric layers in a RAINBOW cross-section is shown in Fig. 1.

As shown in Fig. 2, each of the measured reduced layers exhibited ohmic properties with resistance values ranging from 0.1 to 0.8 Ω. In each case, the reduced layer behaved as a metallic material and exhibited no properties indicative of a ferroelectric. Because of the metallic nature of the reduced layer, an inverse relationship between the thickness ratio and the ratio of the RAINBOW coercive field ($E_{C,RAINBOW}$) to the unreduced ceramic coercive field ($E_{C,Unreduced}$) was found to exist. As shown in Fig. 3a–e, the relationship between these two parameters may be best described by the relation:

$$\text{thickness ratio} = 1 - \frac{E_{C,\text{RAINBOW}}}{E_{C,\text{Unreduced}}} \tag{1}$$

Fig. 4a and b show specific examples of this behavior for RAINBOWs produced from APC 855 and EBL 5 ceramics, respectively. In the first example, the unreduced ceramic possesses and $E_C = 7.3$ kV/cm, and the reduced ceramics have thickness ratios of 0.15 and 0.30. These specimens exhibited E_C values of 6.2 and 5.1 kV/cm, respectively. In the latter case, the ceramic possesses an $E_C = 10.3$ kV/cm and the reduced specimens with thickness ratios of 0.55 and 0.65 possessed E_C values of 4.6 and 3.6, respectively. In each

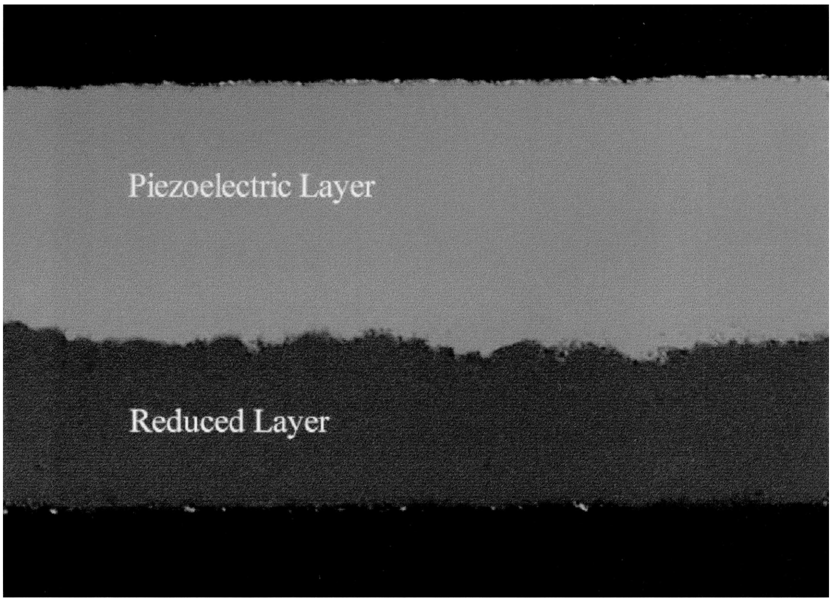

Figure 1 Typical example of the reduced and piezoelectric layers in an APC 850 RAINBOW. The total thickness of this device is 380 μm.

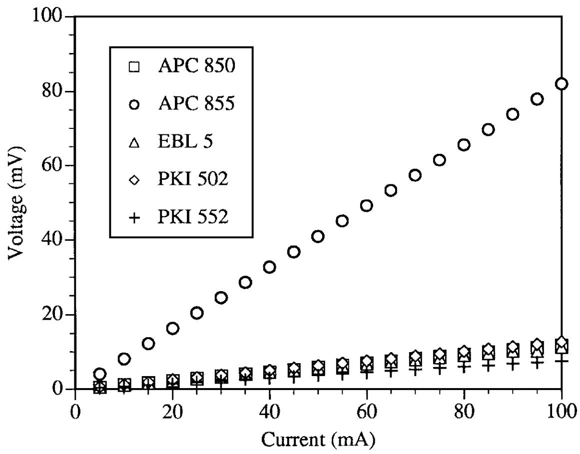

Figure 2 Typical voltage versus current behavior of the reduced layers in RAINBOW devices produced from each composition.

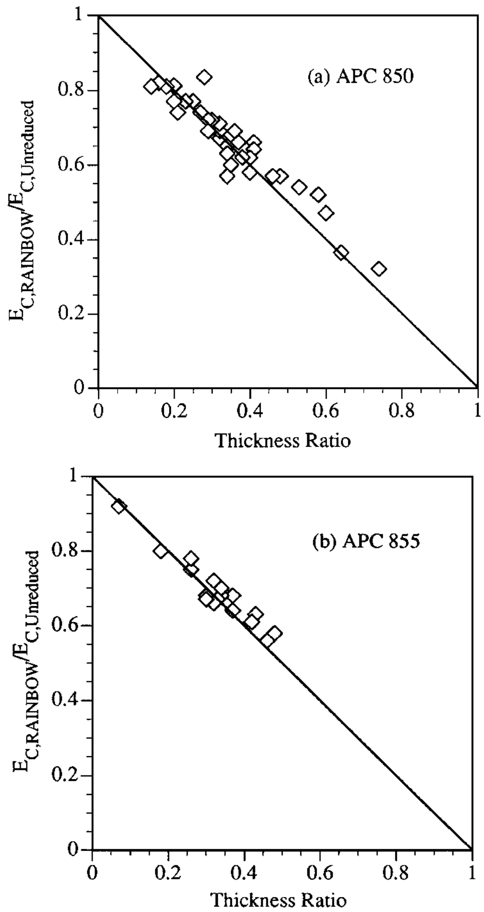

Figure 3 $E_{\text{C,RAINBOW}}/E_{\text{C, Unreduced}}$ versus thickness ratio for RAINBOWs produced from (a) APC 850, (b) APC 855, (c) EBL 5, (d) PKI 502, and (e) PKI 552 ceramics. (*Continued*).

instance, the reduced layer thickness and the relative coercive field values followed the relationship shown in Equation 1. No correlations between the reduced layer thickness and the P_R and P_{SAT} values were found.

4. Discussion

The resistive properties of the reduced layers indicate that the reduced portion of the RAINBOW structure is behaving as a continuous metallic phase. This finding is consistent with two recently published studies on RAINBOW ceramics. In the first of these studies [3], an X-ray diffraction analysis of the reduced layers in RAINBOW ceramics was conducted. In that work, reduced layers in PLZT ceramics were found to be primarily metallic lead with some secondary oxide phases also identified. In the latter report [4], the reduced layer was described as a cermet and was considered to be a continuous metal matrix containing isolated pockets of mixed-oxide phases.

Because of the metallic nature of the reduced layer, this portion of the RAINBOW thickness does not contribute to the calculated E_C values of these devices. Therefore, the effective decrease in the coercive field measured across the total thickness of each RAINBOW was found to correlate strongly with the thickness of the remaining piezoelectric material.

Throughout this study, some variability was found to exist within each data set. These uncertainties were likely caused by the use of average values for both the thickness of the reduced layer and the coercive

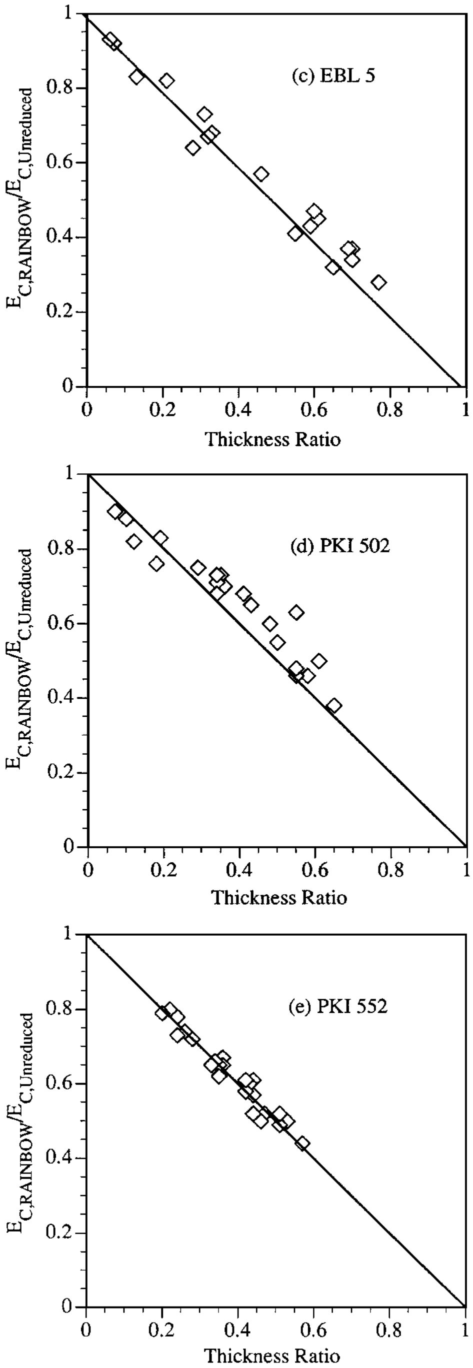

Figure 3 (*Continued*).

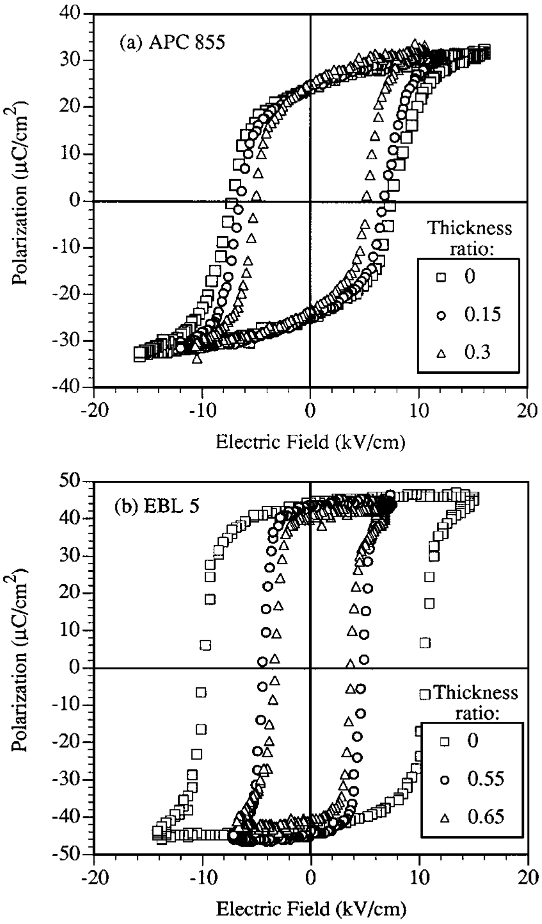

Figure 4 Ferroelectric polarization versus electric field (P-E) plots for (a) APC 855 RAINBOWs with thickness ratios of zero (i.e., unreduced), 0.15, and 0.30, and (b) EBL 5 RAINBOWs with thickness ratios of zero, 0.55 and 0.65. In each case, the data are centered about both axes.

field of each composition. Even with these variabilities, the degree of deviation from the linear relationship described by Equation 1 was found to be typically less than ±5 percent. Therefore, because P-E properties are representative of the entire electroded volume, and the reduced layer is metallic in nature, the $E_{C,RAINBOW}/E_{C,Unreduced}$ ratio can be used to estimate the thickness of the remaining piezoelectric layer.

Although a strong correlation was found to exist between the coercive field of RAINBOWs and the thickness of the piezoelectric layer within the structure, the technique based on this relationship would be very difficult to apply to devices produced from slimloop ferroelectrics (e.g., PLZT 9/65/35) or anti-ferroelectric compositions. In these materials, the P-E behaviors exhibit relatively small E_C values as compared to the soft piezoelectric compositions evaluated herein.

5. Conclusion

RAINBOW ceramics having thickness ratios ranging from 0.05 to 0.8 were produced from five commercially available, lead-containing piezoelectric formulations. Additionally, I-V measurements were performed on the reduced layers of selected devices produced from each composition. The reduced layers within the RAINBOW devices were found to exhibit resistance properties typical of a metal. Therefore, when P-E measurements were performed while taking the total thickness of each device to be ferroelectric, the resulting coercive field strength values were reduced by an amount inversely proportional to the thickness of the reduced layer. Hence, a simple, non-destructive technique for estimating the reduced layer thickness in piezoelectric RAINBOW actuators has been shown to exist.

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