

In Situ Investigation of Thermally Influenced Phase Transformations in $(\text{Pb}_{0.92}\text{Sr}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ Thin Films Using Micro-Raman Spectroscopy and X-Ray Diffraction

Sharath Sriram, Madhu Bhaskaran, Tatiana S. Perova, Vasily A. Melnikov, and Anthony S. Holland

Abstract—Thin films of ferroelectric strontium-doped lead zirconate titanate [PSZT, $(\text{Pb}_{0.92}\text{Sr}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$] deposited by RF magnetron sputtering have been analyzed by *in situ* analysis techniques. The *in situ* techniques employed for this study include micro-Raman spectroscopy and X-ray diffraction (XRD), and variations in thin film structure and orientations for temperatures up to 350°C and 750°C for the respective techniques have been studied. The samples analyzed were PSZT thin films deposited on platinum-coated silicon substrates at either room temperature or at 750°C. *In situ* measurements using micro-Raman spectroscopy and XRD techniques have been used to identify the Curie point for poly-crystalline PSZT thin films and to determine the temperature-activating significant grain growth for room-temperature-deposited PSZT thin films. To study the presence of hysteresis, analysis was carried out during both temperature ramp-up and ramp-down cycles. Raman measurements showed expected bands (albeit weak), and the *in situ* measurements have detected variations in the crystal structure of the thin film samples, with negligible variations between the heating and cooling cycles. A combination of the Raman and XRD results has shown that the temperature-activating significant grain growth for the room-temperature-deposited films is about 275°C and the Curie point lies between 325 and 400°C. This relatively high Curie point makes these films suitable for wide temperature range applications.

I. INTRODUCTION

THE lead zirconate titanate (PZT) family of compounds, especially undoped PZT, is used in a wide variety of commercial applications (e.g., nano-positioning stages). PZT compounds are popular due to the relatively high piezoelectric response exhibited by this class of materials, thereby enabling more sensitive sensors, actuators, or transducers [1], [2]. The addition of strontium as an A-site dopant to the perovskite ABO_3 structure of PZT (resulting in strontium-doped lead zirconate titanate, PSZT) enhances the piezoelectric behavior [3]–[5]. In addition to the high levels of piezoelectric response, PZT compounds

have a relatively high Curie point. The Curie point is the temperature above which the unit cell of piezoelectric compounds transforms from asymmetric tetragonal or rhombohedral arrangement to symmetric cubic arrangement; this renders them non-piezoelectric.

Most reports in literature on Curie point studies of PZT or PSZT involve bulk ceramics and pellets [1], [6]. These reports indicate a Curie point for $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ of 380 to 400°C, with the Curie point decreasing by about 9.5°C for every atomic percentage of strontium added as the A-site dopant. In addition, increasing zirconium concentration also has the influence of decreasing the Curie point. From a combination of these 2 factors, the Curie point for the thin film composition under consideration is estimated to be between 220 and 280°C [6]. Further variations are possible due to the 2-D nature of thin films.

In this article, *in situ* measurements using micro-Raman spectroscopy and X-ray diffraction (XRD) techniques have been used to identify the Curie point for poly-crystalline PSZT thin films and to determine the temperature activating significant grain growth for room temperature deposited PSZT thin films. Analysis has been carried out on PSZT thin films deposited at room temperature and at 750°C; these are expected to be polycrystalline and preferentially oriented, respectively. Raman measurements have revealed interesting variations in the thin film transmission properties, and XRD results have highlighted some limitations in using this measurement technique to identify the Curie point of PSZT thin films. It must be noted that Raman measurements do not present strong signatures for PZT-type films (as is apparent in the references cited for Raman spectra), and XRD was used in cases where results using Raman spectroscopy were inconclusive.

II. EXPERIMENTAL DETAILS

A. Deposition of PSZT Thin Films

PSZT thin films were deposited by RF magnetron sputtering under conditions listed in Table I. Deposition was carried out on (100) silicon samples coated with 200 nm of platinum, with a 20 nm titanium adhesion layer. The silicon samples were dipped in buffered hydrofluoric acid to remove the native oxide, before deposition of metal layers by electron beam evaporation. Samples were deposited

Manuscript received June 11, 2008; accepted September 30, 2008. This research was supported by the Australian Institute of Nuclear Science and Engineering and the CASS Foundation.

S. Sriram, M. Bhaskaran, and A. S. Holland are with Microelectronics and Materials Technology Centre, School of Electrical and Computer Engineering, RMIT University, Melbourne, Victoria, Australia (e-mail: sharath.sriram@gmail.com).

T. S. Perova and V. A. Melnikov are with Microelectronics Technology Group, Department of Electronic and Electrical Engineering, University of Dublin, Trinity College, Dublin, Ireland.

Digital Object Identifier 10.1109/TUFFC.2009.1032

TABLE I. PSZT THIN FILM DEPOSITION CONDITIONS.

Target	$(\text{Pb}_{0.92}\text{Sr}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$
Target diameter	100 mm
RF power	100 W
Target to substrate distance	70 mm
Process gas	10% oxygen in argon
Base pressure	9.0×10^{-6} Torr
Sputtering pressure	1.0×10^{-2} Torr

either at room temperature or at 750°C and at a process pressure of 10 mTorr, which was found to be most suitable [7]. In the case of samples deposited at temperatures of 750°C, the samples were heated to temperature at a ramp rate of 10°C/min and cooled, subsequent to deposition, at 5°C/min; as previous work [8] has shown, these conditions improve the degree of perovskite orientation in the thin films.

B. Micro-Raman Spectroscopy Analysis

Raman spectra were registered in backscattering geometry using a Renishaw (Renishaw plc, Gloucestershire, UK) 1000 micro-Raman system equipped with a Peltier-cooled CCD camera and a Leica microscope (Leica Microsystems, Wetzlar, Germany). An 1800 lines/mm grating was used for all measurements, giving a spectral resolution of approximately 1 cm^{-1} . Excitation sources used were an Ar^+ laser (operating at wavelengths of 457 and 514 nm) and a He-Ne laser operating at 633 nm. The laser spot was focused on the sample surface using 50× objective with short-focus working distance at room temperature. For measurements at higher temperatures (20°C to 350°C), a Linkam temperature stage (Linkam Scientific Instruments, Surrey, UK) and a 50× long-focus objective were used. With these objectives the lateral resolution on the sample was approximately 2 μm and 3 μm for excitation of 514 nm and 633 nm, respectively. The accumulation time at excitations of 514 nm and 633 nm were 200 s and 50 s, respectively. Considering the volume of data gathered, only spectra (and bands) showing significant variations have been included in the figures in this article.

C. X-Ray Diffraction Analysis

A PANalytical X'Pert Pro diffractometer (PANalytical, Almelo, The Netherlands) was used to carry out the *in situ* XRD measurements. The diffractometer operated with a copper $\text{K}\alpha$ source and was equipped with a heating and cooling stage (made of platinum) that enabled recording of diffractograms at different temperatures. The desired temperatures and dwell times were programmed before the start of the analysis, and the analysis was carried out in high purity argon on samples pre-cleaned by rinsing in solvents (acetone and isopropyl alcohol) and deionized water. Considering the volume of data gathered, only diffractograms (and 2θ ranges) showing significant variations have been included in the figures in this article.

To determine the orientation of the as-deposited PSZT thin films, glancing angle XRD (GA-XRD) was used. Glancing angle XRD analysis of these samples was done using a Scintag X-ray diffractometer (Scintag, Inc., Cupertino, CA) operating with a cobalt X-ray source (at a wavelength of 0.179020 nm) at an X-ray incidence angle of 5°.

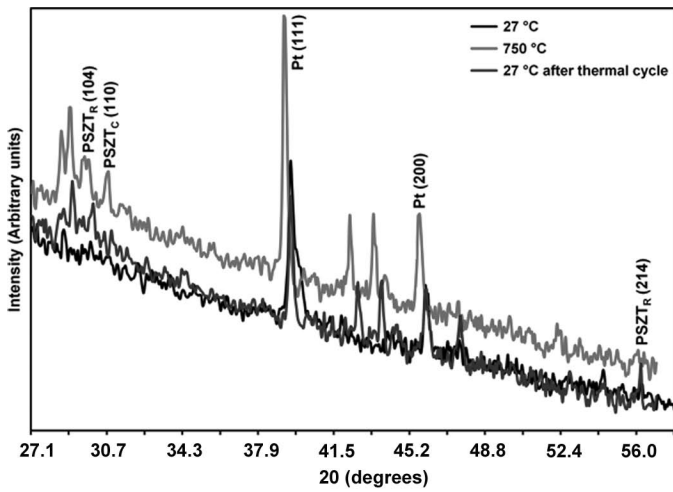
III. RESULTS AND DISCUSSION

This section discusses the *in situ* analysis carried out on PSZT thin films deposited at room temperature (Section III-A) and on PSZT thin films deposited at 750°C (Section III-B). The changes in the thin film crystallinity have been studied using micro-Raman spectroscopy and Bragg Brentano XRD.

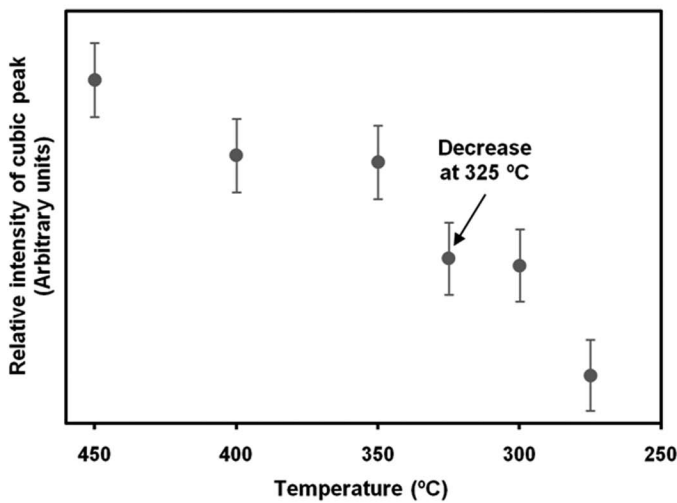
A. PSZT Thin Films Deposited at Room Temperature on Platinum

PSZT thin films were deposited by sputtering on platinum-coated silicon samples without substrate heating; these films had no prominent XRD peaks, possibly due to inhibited grain growth resulting in a nano-crystalline disordered structure. XRD spectra were obtained at various points during the ramp-up and ramp-down when these samples were heated to 750°C and cooled to room temperature. Fig. 1(a) shows the peaks obtained before, during, and after the sample was heated to 750°C. The diffractogram before the heating process only shows peaks for platinum (from the heating stage and from bottom electrode), which are located at 39.40° and 45.88° [9]. The heating process resulted in many new peaks in the diffractogram, while also increasing the background in the diffractograms.

The diffractogram at 750°C looks similar to the one obtained after cooling down, except that peaks have been shifted left (at 750°C, due to thermal expansion of the lattice). The peaks at 29.54° and 30.67° correspond to shifted PSZT rhombohedral and cubic peaks, respectively [10]; the rhombohedral peak is a double peak due to the presence of 2 symmetries. A peak at 28.87° (which could not be indexed) appeared at a temperature of 600°C, the rhombohedral 29.54° peak at 275°C (corresponding to grain growth), and the cubic 30.67° peak at 400°C. On cooling down, the peak at 30.67° disappears at a temperature of 325°C, while a new peak at 56.20° appears corresponding to perovskite PSZT. Additional peaks at 42.67°, 43.04°, and 47.56° correspond to platinum-titanium silicide, which forms due to the heating process as the bottom metal layers react. This results in increased roughening of the platinum layer, which in turn results in a rough PSZT film surface, with an average surface roughness of ~ 20 nm. This undesirable reaction can be prevented by changing the adhesion layer, but it does not influence the phase transformations occurring in the PSZT thin films.



(a)



(b)

Fig. 1. *In situ* XRD results for a PSZT thin film deposited at room temperature and heated to 750°C. (a) Sample set of 3 diffractograms. Unlabeled peaks are a result of a reaction between the bottom electrode layers and silicon. (b) The variations in the relative intensity of the PSZT cubic peak at 2θ of $\sim 31^\circ$ during cooling, indicating a marked decrease at 325°C.

The peak at 30.67° at 750°C corresponds to the cubic peak for PSZT (31.04°) [10], as the peak position shifted due to thermal expansion. This peak appears during the heating process at 400°C and disappears while cooling down at 325°C; see Fig. 1(b). This indicates a phase transformation from rhombohedral to cubic and vice versa, and therefore, the Curie point for this sample is in the range of 325 to 400°C. The variations in switching temperatures during the ramp-up and ramp-down cycles could be attributed to Curie point hysteresis; this is often observed in many piezoelectric ceramics [1].

Micro-Raman spectra registered *in situ* for this sample under heating from room temperature to 350°C are shown in Fig. 2 (excitation wavelength 633 nm). The spectra

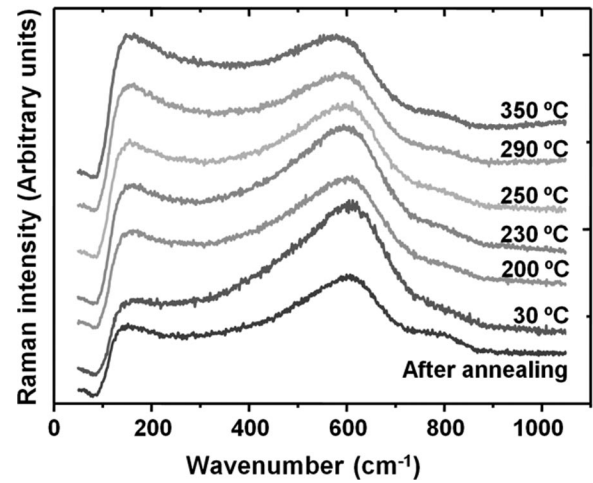


Fig. 2. Raman spectra registered *in situ* on heating a PSZT thin film deposited at room temperature to 350°C at 633 nm excitation wavelength.

obtained during the cooling cycle were quite similar and, therefore, are not presented in this figure with the exception of the spectrum obtained at room temperature after cooling (see the bottom spectrum in Fig. 2). The pronounced wide peak observed at approximately 600 cm^{-1} looks quite similar to the Raman spectra obtained by Souza Filho *et al.* [11] for PZT samples with Zr concentration more than 52%, which was assigned to the rhombohedral phase (although no strong signatures are apparent). It is evident that the broad features in the Raman spectra are getting less pronounced with increase in temperature, which can be related to the partial transition to the cubic phase. No specific temperature indicating complete transition could be identified.

B. PSZT Thin Films Deposited at 750°C on Platinum

In situ unpolarized Raman measurements were performed during heating and cooling of the samples in the temperature range from 20° to 350°. Raman spectra registered at 514 nm excitation for one such sample are shown in Fig. 3. The spectra during both heating and cooling cycles were identical; hence, only the spectra obtained during the heating process are shown in Fig. 3. Several narrow peaks located at 138, 152, 260, 310, and 353 cm^{-1} as well as wide peaks centered at approximately 260, 600, and 800 cm^{-1} are present in the spectrum registered at room temperature. Most of these bands are slightly shifted to the low frequency side by approximately 5 to 7 cm^{-1} with increase in temperature to 350°C.

For the assignment of these bands, several different factors need to be taken into account for the samples under investigation, because the position of Raman peaks in these PSZT samples depends on the Zr/Ti ratio, the Sr content, the size and orientation of the grains, and the intrinsic stress in the films. As shown in literature, the addition of Zr, as well as Sr, reduces the Raman frequency for the majority of vibrational modes observed for crys-

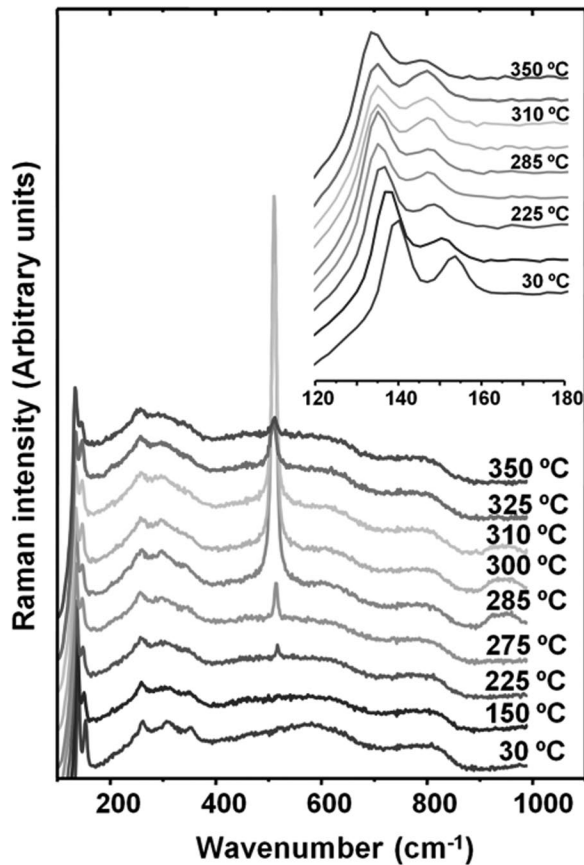


Fig. 3. *In situ* Raman spectra of a PSZT thin film deposited at 750°C registered on heating at 514 nm excitation wavelength. *Inset*: Raman spectra showing details of the low frequency range.

talline lead titanate [11]–[13] and lead strontium titanate [14], [15].

The presence of narrow lines as seen in the spectra in Fig. 3 indicates a crystalline or polycrystalline structure in the film. The peaks seen at 138 cm^{-1} and 152 cm^{-1} (inset of Fig. 3) can be assigned to $E(\text{LO}_2)$ and $A_1(\text{TO}_1)$ symmetries, respectively. Detailed assignment of peak symmetries is not discussed in this article (see [11]–[15]).

On heating these samples, the 2 main maxima shift to the low frequency side of the spectra. The peak at 520 cm^{-1} , which corresponds to silicon, appears on heating to 285°C and disappears during the ramp-down at the same temperature. This indicates that the films become transparent to visible light at higher temperatures. The temperature range ($285\text{--}310^\circ\text{C}$) at which this variation occurs could correspond to transformation from the perovskite-structured phase to a cubic phase. Disagreements between these Raman results and the XRD results in Section III-A for the Curie point can be attributed to the fact that Raman probes short-range structural order, while XRD averages the structural order in the entire film thickness. In addition, grain growth activation in the room-temperature-deposited PSZT sample could have introduced this variation: the Curie point (325°C) estimated from the cooling down process of the room temperature deposited

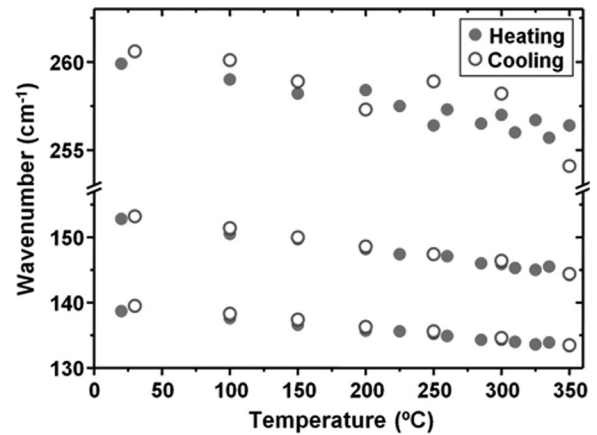


Fig. 4. The dependence of the Raman peak positions at 138 , 152 , and 259 cm^{-1} with temperature for a PSZT thin film deposited at 750°C on heating to 350°C and cooling to 20°C (633 nm excitation wavelength).

PSZT shows better agreement with the 285°C estimated from Raman measurements.

Raman spectra obtained at 633 nm excitation (not shown here) are similar to Fig. 3, except for the presence of an additional peak seen at 259 cm^{-1} , which shows similar behavior (as the other maxima) and shifts with changes in temperature (which is shown in Fig. 4). In addition, the intensities of the low-frequency bands are larger, due to larger scattering volume from the 633 nm wavelength laser.

IV. CONCLUSIONS

This article has used *in situ* micro-Raman spectroscopy and X-ray diffraction to identify phase transitions in PSZT thin films. For films deposited at room temperature, and which are possibly nano-crystalline in nature, the temperature for activation of grain growth resulting in preferential orientations has been found to be 275°C using XRD. The Curie point appears to be between 325 and 400°C . Raman measurements for these samples indicate a rhombohedral structure with partial transition to a cubic phase. For films deposited at 750°C , Raman measurements showed that the films become transparent to visible light at temperatures above 285°C ; this corresponds to a phase transformation and could correspond to the transition to a cubic phase.

ACKNOWLEDGMENTS

The authors thank K. T. Short and G. J. Thorogood for helpful discussions and assistance with the XRD measurements.

REFERENCES

- [1] B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics*. New York: Academic Press, 1971.

- [2] Y. Xu, *Ferroelectric Materials and Their Applications*. Amsterdam: North-Holland, 1991.
- [3] S. Sriram, M. Bhaskaran, A. S. Holland, K. T. Short, and B. A. Latella, "Measurement of high piezoelectric response of strontium-doped lead zirconate titanate thin films using a nanoindenter," *J. Appl. Phys.*, vol. 101, no. 10, art. no. 104910, 2007.
- [4] H. Zheng, I. M. Reaney, W. E. Lee, N. Jones, and H. Thomas, "Surface decomposition of strontium-doped soft $\text{PbZrO}_3\text{-PbTiO}_3$," *J. Am. Ceram. Soc.*, vol. 85, no. 1, pp. 207–212, 2002.
- [5] C. Bedoya, Ch. Muller, J.-L. Baudour, V. Madigou, M. Anne, and M. Roubin, "Sr-doped $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ ceramic: Structural study and field-induced reorientation of ferroelectric domains," *Mater. Sci. Eng. B*, vol. 75, no. 1, pp. 43–52, 2000.
- [6] H. Zheng, I. M. Reaney, W. E. Lee, N. Jones, and H. Thomas, "Effects of octahedral tilting on the piezoelectric properties of strontium/barium/niobium-doped soft lead zirconate titanate ceramics," *J. Am. Ceram. Soc.*, vol. 85, no. 9, pp. 2337–2344, 2002.
- [7] S. Sriram, M. Bhaskaran, J. du Plessis, K. T. Short, V. P. Sivan, and A. S. Holland, "Influence of oxygen partial pressure on the composition and orientation of strontium-doped lead zirconate titanate thin films," *Micron*, vol. 40, no. 1, pp. 104–108, doi 10.1016/j.micron.2007.12.009, 2009.
- [8] S. Sriram, M. Bhaskaran, and A. S. Holland, "The effect of post-deposition cooling rate on the orientation of piezoelectric $(\text{Pb}_{0.92}\text{Sr}_{0.08})(\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3$ thin films deposited by RF magnetron sputtering," *Semicond. Sci. Technol.*, vol. 21, no. 9, pp. 1236–1243, 2006.
- [9] Powder Diffraction Pattern Files, Card 04–0802, International Centre for Diffraction Data (ICDD, formerly the Joint Committee for Powder Diffraction Studies), Newtown Square, PA.
- [10] Powder Diffraction Pattern Files, Card 04–006–6495, International Centre for Diffraction Data (ICDD, formerly the Joint Committee for Powder Diffraction Studies), Newtown Square, PA.
- [11] A. G. Souza Filho, K. S. V. Lima, A. P. Ayala, I. Guedes, P. T. C. Freire, F. E. A. Melo, J. Mendes Filho, E. B. Araújo, and J. A. Eiras, "Raman scattering study of the $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ system: Rhombohedral-monoclinic-tetragonal phase transitions," *Phys. Rev. B*, vol. 66, no. 13, art. no. 132107, 2002.
- [12] G. Burns and B. A. Scott, "Raman spectra of polycrystalline solids: Application to the $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$ system," *Phys. Rev. Lett.*, vol. 25, no. 17, pp. 1191–1194, 1970.
- [13] W. J. Brya, "Polarized Raman scattering in transparent polycrystalline solids," *Phys. Rev. Lett.*, vol. 26, no. 18, pp. 1114–1118, 1971.
- [14] F. M. Pontes, S. H. Leal, P. S. Pizani, M. R. M. C. Santos, E. R. Leite, E. Longo, F. Lanciotti, T. M. Boschi, and J. A. Varela, "Structural phase evolution of strontium-doped lead titanate thin films prepared by the soft chemical technique," *J. Mater. Res.*, vol. 18, no. 3, pp. 659–666, 2003.
- [15] C. E. F. Costa, F. M. Pontes, A. G. Souza, E. R. Leite, P. S. Pizani, and E. Longo, "Influence of strontium concentration on the structural, morphological, and electrical properties of lead zirconate titanate thin films," *Appl. Phys., A Mater. Sci. Process.*, vol. 79, no. 3, pp. 593–597, 2004.
- S. Sriram, M. Bhaskaran, T. S. Perova, V. A. Melnikov, and A. S. Holland** photographs and biographies not available at time of publication.