

Cite this: *CrystEngComm*, 2011, **13**, 1280

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Reversal and pinning of Curie point transformations in thin film piezoelectrics†

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Received 10th October 2010, Accepted 1st December 2010

DOI: 10.1039/c0ce00713g

The Curie point for a rhombohedral piezoelectric thin film was established by *in situ* micro-Raman spectroscopy. The hysteresis in phase reversal and specific thermal conditions for disrupting such reversal were determined.

Piezoelectric materials are suitable for a wide range of applications such as transducers, actuators, and sensors. The operating temperature range of the piezoelectric materials for these applications is determined by the Curie point.¹ 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.^{1,2} The determination of the Curie point can be carried out using electrical measurements of changes in the dielectric properties of materials. Kalinin and co-workers have reported on electric field induced first-order transformations in oxide thin films.³ However, techniques that can determine temperature dependent changes in crystal structure shed more scientific insight into transformations, and also enable accurate evaluation of the Curie point of materials and hysteresis in recovery of the asymmetric piezoelectric crystal states.

Probing crystal structure transformations by micro-Raman spectroscopy has been shown to be suitable for the determination of the Curie point for ceramics.⁴ Preliminary work by the authors,⁵ reported on the first determination of phase transformation temperatures for thin films using *in situ* measurements. The determination of the Curie point proved to be challenging due to weak Raman signatures and limited published literature. This indicated the need for further studies to improve understanding of Raman peak assignments for complex perovskite oxides such as the strongly piezoelectric ABO_3 -type lead zirconate titanate (PZT).

PZT is the most popular piezoelectric material given its large piezoelectric response and wide operating temperature range.^{1,6} The

addition of strontium as an *A*-site has been shown to enhance the piezoelectric response,⁷ but is expected to decrease the Curie point of the resulting material composition. The Curie point for these thin films of Sr-doped PZT (PSZT) with composition $(Pb_{0.92}Sr_{0.08})(Zr_{0.65}Ti_{0.35})O_3$ is expected to be around 250–280 °C.^{2,5}

The Curie point induced transformations are considered to be reversible with temperature.^{1,2} This work aimed to study the phase transformations in rhombohedral *c*-axis oriented thin films with increase in temperature, determine the thin film Curie point, and to check the reversibility of the same with controlled or uncontrolled cooling of the thin films.

Piezoelectric, perovskite-structured PSZT thin films were deposited by RF magnetron sputtering onto platinumized silicon substrates (see ESI† for details). These 700 nm thick films were preferentially *c*-axis oriented with rhombohedral structure, as verified by X-ray diffraction (XRD) and transmission electron microscopy (TEM).⁸ A micro-Raman spectrometer combined with a Linkam hot-stage was used extensively for *in situ* measurements (see ESI† for details).

In order to determine the Curie point, PSZT thin film samples were heated with a controlled ramp rate of 10 °C min⁻¹. Heating was carried out to a maximum of 350 °C, based on the estimate of the Curie point being ~280 °C.^{2,5} The sample was held at maximum temperature for 20 minutes. The sample was then cooled with controlled ramp-down (10 °C min⁻¹) until 100 °C, beyond which the cooling occurred more gradually towards room temperature. Micro-Raman measurements were collected at selected set points, during the heating and cooling cycle and twice at maximum temperature, during which the temperature was held constant for 8 minutes for this purpose.

PSZT thin films of this composition (with zirconium–titanium ratio of 65/35) are in the rhombohedral phase at room temperature. Room temperature spectra highlight two main Raman bands at ~575 and ~744 cm⁻¹ (see ESI†, Fig. S1). These two bands have been reported in Raman investigations of PZT powders and thin films.⁹ On heating the PSZT thin films, these bands decrease in intensity, which can be attributed to increased scattering. These two bands are asymmetric, with a few pronounced sub-peaks visible at room temperature. To isolate the constituent peaks, these bands were fitted with a collection of Gaussian/Lorentzian peaks. The band at ~575 cm⁻¹ was fitted with three sub-bands located at 565, 575, and 604 cm⁻¹. The broad band centred at ~744 cm⁻¹ was also fitted with three sub-bands positioned at 725, 744, and 766 cm⁻¹. In addition a small shoulder is observed at ~815 cm⁻¹. The position of some of these

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† Electronic supplementary information (ESI) available: Experimental conditions for PSZT thin film deposition and for micro-Raman spectroscopy measurements; additional micro-Raman spectroscopy measurement results. See DOI: 10.1039/c0ce00713g

peaks is quite close to that obtained after the deconvolution of the two wide bands observed in the region from 450–620 cm^{-1} and 620–900 cm^{-1} for poled polycrystalline composites based on PZT.¹⁰ It should be noted that our deconvolution produced three peaks for the $\sim 744 \text{ cm}^{-1}$ band, with only two previously reported. This can be attributed to the more pronounced sub-bands in our spectra as a result of the preferentially textured polycrystalline crystallography of PSZT thin films grown under optimised conditions; whereas, the sub-bands in published literature^{10,11} were not as pronounced. The stronger spectral contribution from the preferentially oriented PSZT, verified by XRD and TEM results,⁸ can also be confirmed from the results obtained by Foster *et al.*,¹² where the Raman spectra of the oblique phonons of single-domain single crystal PbTiO_3 were demonstrated. These results show that a large number of different phonon modes can be observed at room temperature (300 K) in the region from 420–800 cm^{-1} in platelet geometry for various directions of the phonon wave vector k for the PbTiO_3 crystal.

Having established the constituent peaks in the spectra, we now analyse the temperature dependence of different phonon modes obtained after fitting of the two wide bands described above. A comparison of the intensity ratios of the two peaks provides accurate evidence of phase transformations. As can be observed in Fig. 1, the intensity ratio of the 744 and 575 cm^{-1} peaks increases at higher temperatures, following an apparent change at 275 °C. The sharp intensity ratio variations signify phase transformation, starting at the theoretically expected value of $\sim 280 \text{ }^\circ\text{C}$.

This phase transition observed can be related to the crystal structure of the thin film. The 575 cm^{-1} peak corresponds to the rhombohedral phase with a phonon assignment of $\text{A}_1(3\text{TO})$.^{9,12} The 744 cm^{-1} peak is a combination of the rhombohedral $\text{A}_1(3\text{TO})$ and cubic $\text{E}(3\text{LO})$ phonon assignments.^{9,12} As a consequence of this, while both peaks should appear at room temperature (for rhombohedral structure), on heating the $\text{E}(3\text{LO})$ should dominate.¹² This should result in an increased intensity ratio of the 744 and 575 cm^{-1} peaks, as seen in Fig. 1.

With controlled cooling at 10 $^\circ\text{C min}^{-1}$, the cubic phase reverses back to the rhombohedral phase in the same temperature window of 275–300 $^\circ\text{C}$, indicating minimal hysteresis in the Curie point phase

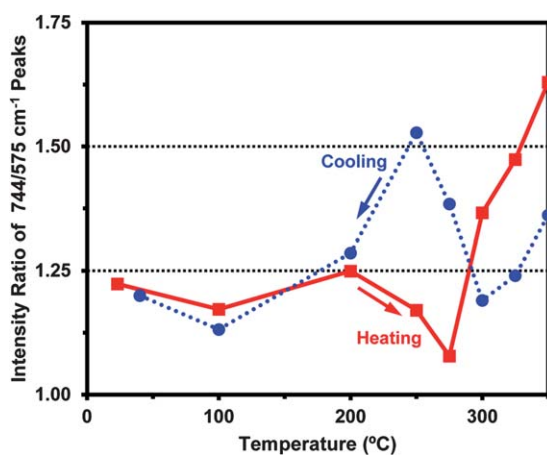


Fig. 1 Variation in the ratio of the intensities of the 744 and 575 cm^{-1} peaks with temperature during controlled heating and controlled cooling of the PSZT sample.

transformation. This reversal occurs with the peak intensity ratio returning to ~ 1.2 .

In addition to the intensity ratios, the position changes with temperature for the two main peaks were also studied, as this highlights changes in bond lengths corresponding to crystal structure. These results for the ~ 575 and $\sim 744 \text{ cm}^{-1}$ peaks are presented in Fig. 2. After accounting for shifts related to thermal expansion, clear features of phase transformation can be observed. For the $\sim 575 \text{ cm}^{-1}$ peak in Fig. 2(a), the peak position gradually decreases from 582 cm^{-1} (at 23 $^\circ\text{C}$) on heating. A sharp change in the slope of the position variation occurs beyond 250 $^\circ\text{C}$, corresponding to the intensity ratio changes in Fig. 1. However, the peak position behaviour is not as sharp as the peak intensity shown in Fig. 1 due to the fact that normally the peak intensity is more sensitive to the local change in the structure. The $\sim 744 \text{ cm}^{-1}$ peak showed similar behaviour during heating as seen in Fig. 2(b). On cooling, reversal in peak positions of both peaks was observed (Fig. 2), with a hysteresis behaviour present.

The Curie point phase reversal is a critical contributor to high temperature deposition of piezoelectric thin films. Post-deposition cooling rate is known to greatly influence the final crystal structure of the piezoelectric materials, with slower cooling producing best results

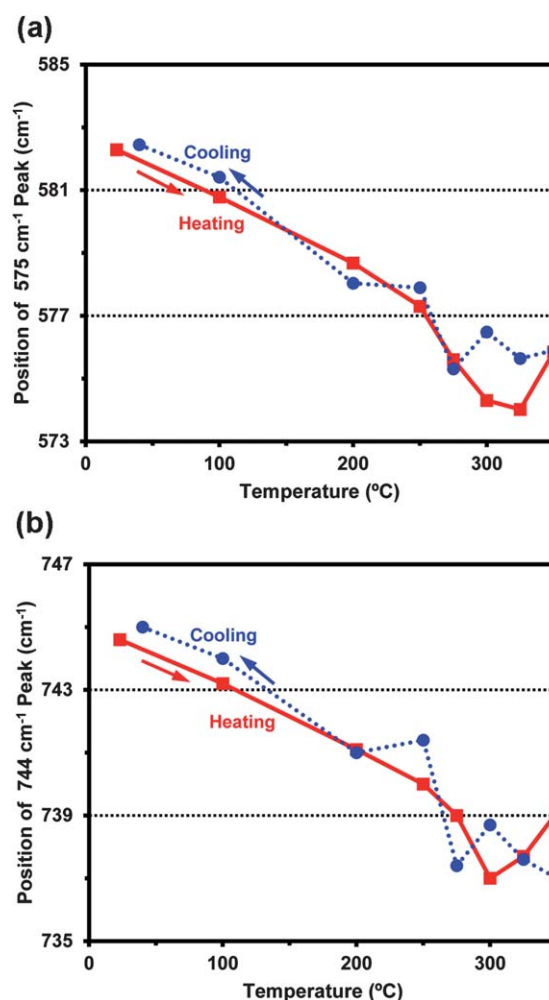


Fig. 2 Variation in the position of the (a) 575 and (b) 744 cm^{-1} peaks during controlled heating and controlled cooling of the PSZT sample.

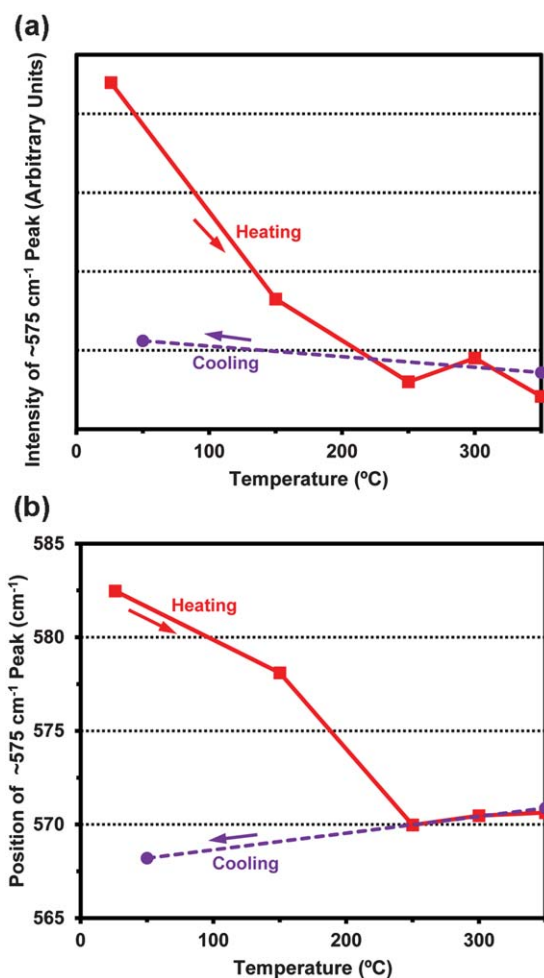


Fig. 3 Intensity and position variations of the 575 cm⁻¹ peak during controlled heating and uncontrolled cooling are shown in (a) and (b), respectively.

(at ~ 5 °C min⁻¹).^{6,13} Some hypothesise, in a principally intuitive manner, that this is due to temperature-driven crystallisation given the larger duration available for crystallisation.⁶ This theory can be tested by rapid cooling of a known rhombohedral film. We carried out this investigation, using a fully characterised film, as discussed in the earlier sections of this work. The temperature of the PSZT thin films was allowed to ramp up slowly to enable phase transformations, following which the effect of uncontrolled cooling on these films was studied.

The PSZT thin films produced spectra similar to the heating cycle (see ESI†), carried out under identical conditions with a ramp rate of 10 °C min⁻¹. The expected Curie point transformation was observed beyond 275 °C. From the maximum temperature of 350 °C, the sample was cooled naturally. The behaviour of the 575 and 744 cm⁻¹ PSZT micro-Raman peaks was studied in detail, with changes in intensity and position of the 575 cm⁻¹ peak shown in Fig. 3. The behaviour of composite peak areas is similar to that of the earlier experiment during the controlled ramp-up of temperature. However, on rapid cooling of the sample, the peak intensities and positions remain locked in the cubic phase, indicating a permanent phase

change has occurred (Fig. 3). Evidence of this pinning to the cubic phase is provided by the observation of invariance in peak heights for the cooling measurements at 350 °C and 50 °C, and by identical full range micro-Raman spectra (see ESI†, Fig. S2). The absence of any relaxation to the room temperature rhombohedral phase was verified by a repeated measurement of these samples after a period of four days and observing the same high temperature cubic phases at room temperature, indicating that this phase change is permanent. This result shows that actual cooling rate induced phase lock-in dominates any crystallisation process for these thin films.

In summary, we have carried out *in situ* heating with micro-Raman spectroscopy to study Curie point induced phase transformation in piezoelectric PSZT thin films. We have identified that Curie point transformation for these room temperature rhombohedral films occurs at 275 °C and is a reversible process with minimum hysteresis. The significance of the rate of cooling post-deposition on reversal of Curie point transformations was studied. The results show that this can strongly disrupt Curie point transformations, by pinning the material to the high temperature cubic phase, if the cooling process is rapid and uncontrolled.

Acknowledgements

The authors acknowledge funding support from the Australian Research Council Discovery Project DP1092717 (MB); the ARC Australian Research Network for Advanced Materials (MB); and the IRCSET, Ireland Postgraduate Award (DA).

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