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## Synchrotron x-ray powder diffraction study of $(\text{Pb}_{1-3x/2}\text{La}_x)(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ at elevated temperatures

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**Abstract.** We describe a high-resolution powder diffraction experiment performed on PLZT (8.7/65/35) using the synchrotron radiation source at Daresbury. The experiment confirms the existence of previously reported structural changes at 290 and 360 °C; the results discussed here are more detailed and allow some quantitative analysis. In particular, the synchrotron source allowed the use of a geometry that enabled very small changes in Bragg angle to be detected; these changes were not seen when using a conventional diffractometer.

PLZT ( $100x/100y/100 - 100y$ ) possesses the perovskite structure and has the chemical formula  $(\text{Pb}_{1-3x/2}\text{La}_x)(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ . We studied the composition PLZT (8.7/65/35), which is ferroelectric at room temperature with rhombohedral symmetry, losing the reversibility of part of its electric polarisation around 120 °C. In [1] the onset of a localised non-reversible polarisation was detected at about 360 °C, and it was argued that the transition to a polarised state occurs first in lanthanum-deficient regions. The transition to a ferroelectric state in PZT ( $x = 0$ ) occurs at 360 °C, and the addition of lanthanum lowers the transition temperature.

In [2] the low-frequency (10 kHz) permittivity was measured and a departure from linearity detected in the plot of  $1/\epsilon$  against temperature at 370 °C. This was interpreted as the onset of a localised polarisation at 370 °C and it was found that high-temperature values of  $1/\epsilon$  ( $T > 370$  °C) extrapolated to zero at 300 °C; this latter temperature is the temperature at which there ceases to be a minimum in the Gibbs free energy at zero polarisation.

X-ray diffraction experiments performed by one of us using a conventional diffractometer [3] detected a small increase in linewidth of  $\{h00\}$  reflections at 360 °C, while reflections of the type  $\{hkl\}$  showed a marked increase in broadening below 290 °C. Polarisation couples electrostrictively to the strain in perovskites and these findings were interpreted (following [1]) as evidence of the appearance of a localised, and hence non-uniform, polarisation lying predominantly along  $\langle 111 \rangle$  at 360 °C and the subsequent development of a rhombohedral shear of the unit cell for temperatures below 290 °C.

It was argued in [4] that between 290 and 360 °C the average size of lanthanum-deficient regions is far too small to maintain a fixed direction of polarisation and that the polarisation flips between  $\langle 111 \rangle$  directions at a rate that is sufficiently rapid to prevent the development of a shear; in other words, the material is mechanically clamped against shear within this temperature range.

For temperatures below 290 °C, regions with the average composition cannot support a structure with zero polarisation, and so the mean size of polarised regions is likely to grow rapidly at around this temperature. The probability of reorientation of the polarisation in a small cluster is proportional to  $\exp(-\delta G/k_B T)$ , where  $\delta G$  is the height of barrier separating adjacent minima in free energy. An increase in the size of the polarised regions will result in a proportional increase in  $\delta G$ , and hence a rapid decrease in the rate of reorientation of the polarisation. A rhombohedral shear would now have time to develop within a small region, producing an additional broadening of reflections.

The lineshape of reflections below 360 °C is complex. Firstly, all peaks are exceptionally broad; this is the result of strain broadening caused by chemical disorder (see below). Secondly, the greater portion of the sample does not possess an electric polarisation and produces essentially the same diffraction profile as measured above 360 °C. The remaining part of the sample possesses a spatially varying polarisation, and hence the distortion of the cell will vary in magnitude too. Thus the expected profile will be a weighted sum of broadened lines typical of a chemically inhomogeneous cubic perovskite, and even broader rhombohedrally distorted lines. In addition, since the polarisation develops in lanthanum-deficient regions, the mean lattice spacing in polarised regions may differ a little from the average value.

The diffractometer on station 9.1 was configured with a set of horizontal parallel foils in the diffracted beam as described in [5]. These foils define a constant angular resolution of 0.06° in  $2\theta$  and allow a large beam—10 × 2.1 mm—to illuminate the specimen without loss of angular resolution. A set of vertical foils or Soller slits was also placed in the diffracted beam to limit the effects of axial divergence.

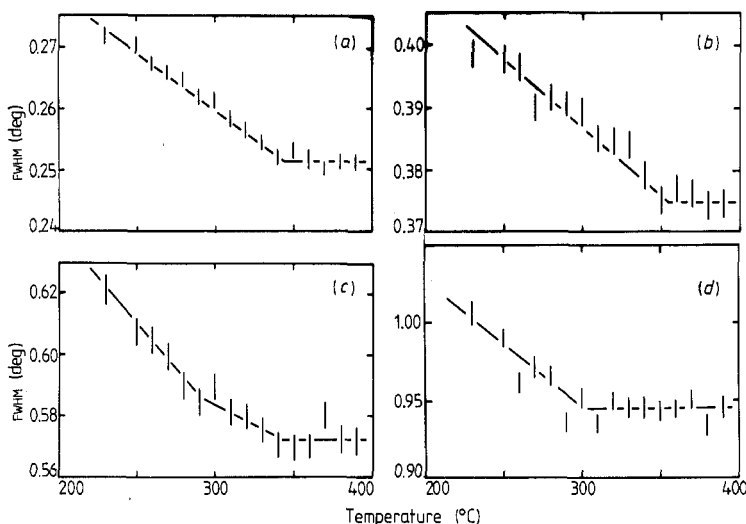
One notable advantage of the foil system is that it makes measurements of angles of diffraction insensitive to small changes in the specimen height [6, 7], a feature which is particularly useful when working at elevated temperatures.

Temperature was controlled automatically to better than 1 °C, and the wavelength used was  $1.5486 \pm 0.00005$  Å.

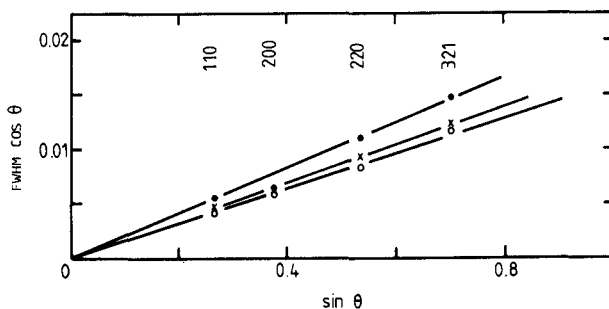
We measured the angular position as well as the width of four reflections at room temperature and at several temperatures between 230 and 390 °C. Figures 1(a)–1(d) give the temperature dependences of the angular widths of (110), (200), (220) and (321) reflections, respectively, obtained by fitting a single pseudo-Voigt function to the experimental profiles. Since the measured linewidths from standard samples of silicon, ZnO and BaF<sub>2</sub> have been found to range from 0.04° to 0.07° in  $2\theta$  [8], all the broadening measured here can be attributed to the sample.

None of the reflections showed more than a single maximum at all temperatures, even though one would expect a uniform rhombohedral distortion to split (110) and (220) into symmetric doublets, and (321) into an asymmetric quadruplet, and to shift but not to broaden (200). A Williamson–Hall plot (figure 2) indicates that the cause of the broadening is strain, and most of this will be the result of chemical disorder; the mean particle size is 4 μm, leading to insignificant size broadening. Note that (200) lies below a straight line connecting the origin and the other three points; (200) is the only reflection on the plot that would not be broadened by a uniform rhombohedral distortion. The increase in slope with decreasing temperature clearly indicates an increase in the rhombohedral distortion with falling temperature.

Since a uniform rhombohedral distortion would not cause a broadening of the (200) reflection, the increase in width of this reflection is taken to be due to the appearance of a localised polarisation in lanthanum-deficient regions as first proposed in [1].



**Figure 1.** Temperature dependence of the FWHM of (a) (110), (b) (200) (c) (220) and (d) (321) reflections obtained by fitting a single symmetrical pseudo-Voigt function to the experimental profiles. The length of the vertical bars is equal to twice the estimated standard deviation.



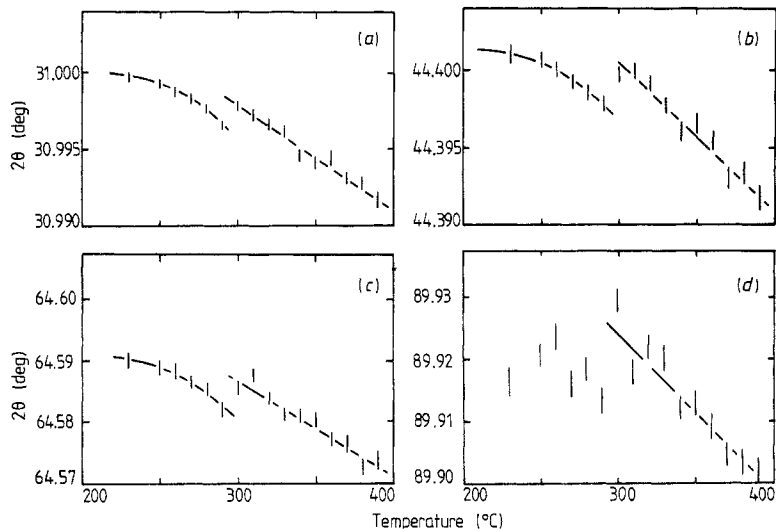
**Figure 2.** Williamson-Hall plot of FWHM  $\cos \theta$  against  $\sin \theta$  for three selected temperatures (●, 20 °C; ×, 230 °C; ○, 390 °C), indicating considerable strain broadening as discussed in the text.

We attribute the increase in width of (110) and (220) reflections to two causes: firstly, between 290 and 360 °C, the non-uniform polarisation produces an increase in strain broadening and secondly, below 290 °C, the onset of a shear turns both lines into unresolved doublets, making a much greater change in width for these two reflections than for (200). The width of (200) at room temperature is  $0.395 \pm 0.003^\circ$  in  $2\theta$ , slightly less than at 230 °C, while the widths of (110) and (220) at room temperature are  $0.337 \pm 0.003^\circ$  and  $0.750 \pm 0.006^\circ$ , respectively, both approximately 1.25 times their values at 230 °C.

There is a distinct change in slope in figure 1(c) for (220) at 290 °C, which is not apparent for (110) (figure 1(a)). Presumably this arises because of the different dispersion in Bragg angle for the two reflections. We have

$$-\Delta\theta = \tan \theta \Delta d/d \quad \tan[\theta(220)]/\tan[\theta(110)] = 2.30.$$

The ratio of the increases in width from 360 to 290 °C for the two reflections  $\Delta[\text{FWHM}(220)]/\Delta[\text{FWHM}(110)]$  is about  $1.8 \pm 1.0$ .



**Figure 3.** Temperature dependence of twice the Bragg angle of (a) (110), (b) (200), (c) (220) and (d) (321). The slopes drawn in (b)–(d) were calculated from the slope obtained in (a).

The additional broadening of (220) below 290 °C can be translated into a spatially averaged rhombohedral angle giving a value for  $|90 - \alpha|$  of 0.06° at 230 °C. This value is smaller than that quoted in [3], where no allowance for broadening produced by non-uniformity in polarisation was made.

(321) shows little change in width at 360 °C but a marked increase at 290 °C. Using the value obtained from the increase in width of (110), then the corresponding increase at (321) between 360 and 290 °C should be about 0.022° ( $2\theta$ ) which is about 1.6 times the estimated standard deviation obtained by fitting a symmetric pseudo-Voigt function to the line.

A uniform rhombohedral distortion produces an asymmetric quadruplet for (321) and, adding in the singlet from the unpolarised portions, one expects five components to contribute to the overall profile. The lineshape becomes skewed, showing maximum effect at about 230 °C—the lowest temperature studied in this run, apart from room temperature. The small-angle side of the peak corresponds rather well to a Gaussian profile, with the large-angle side being better represented by a Lorentzian. Consequently, the numerical values obtained from our simplified analysis for this particular line cannot be given much weight, although the general behaviour of the temperature dependence of the linewidth is in keeping with the proposed model.

The Hart–Parrish design of the diffractometer allows accurate measurement of  $\theta$  even when small vertical movement of the specimen occurs because of thermal expansion of the apparatus and sample. Figure 3 gives the temperature dependences of the maximum peak positions of the four lines, obtained by fitting a single symmetric pseudo-Voigt function to the profiles. We used steps in  $2\theta$  of 0.02°, resulting in a minimum of 12 points (for the (110) reflection) within the angular range of the half-width.

The slopes of the straight lines drawn through the points above 290 °C in figures 3(b)–3(d) were calculated from the slope of the straight line above 290 °C in figure 3(a). The thermal expansion coefficient in this temperature interval is  $(4.3 \pm 0.2) \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ .

The coupling between strain and polarisation for a perovskite is

$$x_1 = Q_{11}P_1^2 + Q_{12}(P_2^2 + P_3^2) \quad x_4 = Q_{44}P_2P_3.$$

where typically  $Q_{11} + 2Q_{12} \approx 0$  [9]. Consequently, one would not expect there to be much change in the Bragg angle of the composite peak caused by the onset of a dynamically reorienting polarisation at 360 °C in a small fraction of the sample.

The change in angles at 290 °C for (110), (200) and (220) scale as  $\tan \theta$ . (No meaningful value can be obtained for (321).) This suggests a uniform expansion of the real-space lattice with a fractional change in  $d$ -spacing of  $(8.1 \pm 1.8) \times 10^{-5}$ ,  $(7.5 \pm 2.7) \times 10^{-5}$  and  $(9.5 \pm 4.5) \times 10^{-5}$  obtained from (110), (200) and (220), respectively.

The volume  $U$  of a parallelepiped is given by the product of the edges multiplied by the determinant of their direction cosines, i.e.

$$U = abcD$$

where

$$D = (1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}.$$

Applying the formula to our case, where  $a = b = c$  and  $\alpha = \beta = \gamma$ , any small departure from 90° of the inter-axial angle can only decrease the volume of the cell. Experimentally, however, there is an increase in volume, and hence there must be an increase in the cell edge length at this temperature. Thus there is a relaxation of the lattice at 290 °C, the temperature at which  $1/\epsilon$  extrapolates to zero. At the same temperature an anomalous increase in the Debye–Waller factor of atoms on A sites was detected [3].

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