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FAST TRACK COMMUNICATION

Search for the X-phase in poled PZN–PT using very high-resolution single-crystal neutron diffraction

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Abstract

Reports that in $PbZn_{1/3}Nb_{2/3}O_3$–x%$PbTiO_3$ (PZN–PT) relaxor ferroelectric crystals an 'X-phase' exists, which has a cubic interior and a 10–50 μm thick rhombohedrally distorted surface, have been re-examined to resolve the effect of electric poling. The crystal structure of electrically poled and de-poled PZN–4.5%PT single crystals has been studied using a novel rotating single-crystal method on the high-resolution neutron powder diffractometer at the ISIS Facility. The recorded patterns are neutron time-of-flight analogues to the zero layer lines of rotating single-crystal x-ray diffraction patterns. Both [001] and [110] zones were examined and they demonstrate unequivocally that the crystals do not have a cubic core. There appears now to be direct evidence against the occurrence of the 'X-phase' in every circumstance in which, based on synchrotron studies, it was previously proposed to exist.

1. Introduction

Solid solutions in the system $PbZn_{1/3}Nb_{2/3}O_3$–x%$PbTiO_3$ (PZN–PT) have the highest ever recorded piezoelectric coefficients and piezoelectric strains [1, 2]. The strong piezoelectric response is directed along the [001] direction referred to the cubic parent phase, whereas the spontaneous polarization is directed along [111]. The origins of these effects are still being debated, in part due to severe pseudo-symmetry. The materials were originally thought to be rhombohedral at low PT content with a morphotropic phase boundary adjoining a tetragonal phase at around 10% PT. Several theories based around observations of low-symmetry phases (monoclinic and orthorhombic) in synchrotron x-ray studies of poled single crystals and the proposed 'polarization rotation' between them have gained significant support in the literature [3–6].

Although the polarization rotation theory can explain the synchrotron observations of lower symmetry, it does not address the nature and origins of the large ion displacements that are required to give the observed polarizations. The theory has been challenged on that basis and because it does not acknowledge that the natural distortion experienced by a rhombohedral piezo-crystal subjected to an electric field along [001] is monoclinic—this means that no phase transition is required for monoclinic symmetry to be observed in a diffraction pattern [7]. High-resolution neutron powder diffraction studies of as-grown PZN and single-crystal neutron diffraction studies of PZN–4.5%PT showed no unusual features [8, 9].

Additional unusual observations have been made in the synchrotron work. They have been interpreted by postulating the existence of an 'X-phase' [10, 11]. The X-phase was invoked to explain the observation of a single peak in high-energy synchrotron x-ray diffraction, where a doublet due to the rhombohedral domain structure would be expected (and was indeed observed using more heavily absorbed x-rays). It was proposed by Xu *et al* [11] that the crystals consist of a cubic core (hence the single diffraction peak) with a rhombohedrally distorted exterior. The interpretation has been challenged and an alternative explanation put forward on the basis of very high-resolution neutron powder diffraction patterns [12] from coarse powders ($<$140 μm) and many as-grown small single crystals (0.5–2 mm). No sign of a cubic interior to the crystals was found.

However, it may be argued that the X-phase was not observed in the neutron work of Kisi *et al* [12] because that was a study of unpoled crystals, whereas the crystals used by Xu *et al* [9] for the X-phase experiments had previously been electrically poled. Therefore, we have taken PZN–4.5%PT crystals electrically poled along [001] and studied them at very high resolution by adapting the high-resolution powder diffractometer (HRPD) at ISIS.

2. Experimental details

The X-phase has been reported at compositions spanning the $PbZn_{1/3}Nb_{2/3}O_3$–$PbTiO_3$ (PZN–PT) phase diagram from 0 to 8% PT [11]. Here we have chosen to use the composition PZN–4.5%PT, as it is representative of the range of behaviours reported. The samples were commercial flux-grown multi-domain single crystals (TRS Ceramics, USA) of 2 mm $\times$ 2 mm $\times$ 2 mm which had been poled by the supplier along the [001] direction of the parent cubic unit cell. One sample was studied after de-poling by heating to 200 °C and cooling slowly.

Although the operation of HRPD for powder diffraction is well established, it is necessary to present additional details of the instrument and its operation so that the veracity of these results may be established. The sample and instrument arrangement is illustrated in figure 1. Crystals were mounted with a low-index zone axis (vector $\boldsymbol{H}$) vertical on a manual goniometer and spinner. The spinner was rotated at $\sim$60 revolutions per minute within the standard diffractometer sample chamber. Neutrons with a wide range of wavelengths enter the instrument and are incident on the sample. Neutrons with these energies can easily penetrate the entire crystal so this can be regarded as a transmission experiment, albeit in backscattering geometry. The highest resolution is obtained in the backscattered detector banks and we will focus on those. Diffracted beams of neutrons occur whenever the normal to a crystal plane (with non-zero structure factor) lies at the bisecting position between the incident beam and a particular detector element. Each detector element records a time-of-flight neutron diffraction pattern that covers the d-spacing range 0.65–2.5 Å.

The diffraction pattern recorded by the entire detector bank, considered as an area detector, should be akin to a rotating crystal photograph, formerly used extensively in crystal structure analysis. We have focused on the equatorial segment of the detector, which should record only the zero layer line of the rotation pattern for zone [hkl], i.e. all reflections within the accessible

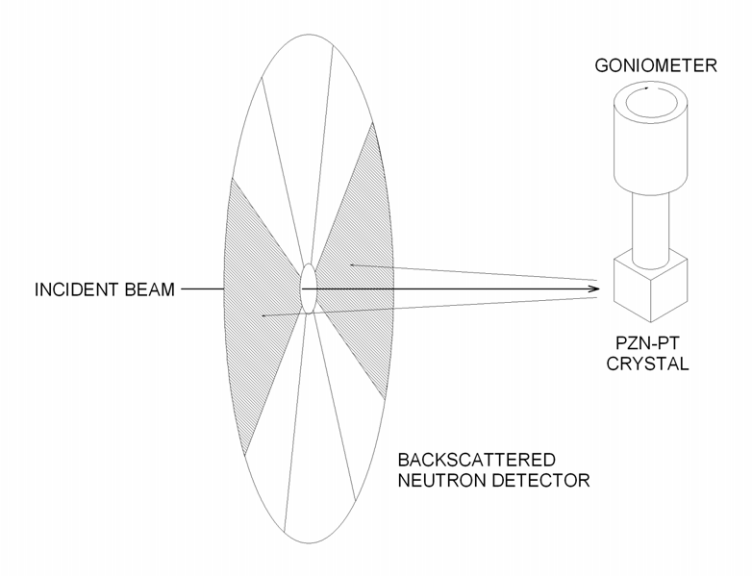

Figure 1. Schematic diagram of the experimental arrangement used on HRPD at ISIS. Neutrons are incident on a crystal mounted with a prominent zone axis vertical and rotated slowly in the neutron beam. Diffracted neutrons are recorded at very high resolution on the equatorial segments (shaded) of the backscattered neutron detector bank.

d-spacing range that lie at 90° to the chosen zone axis. The three rotation zone axes chosen for this work were [001] (parallel to the poling direction), [100] (perpendicular to the poling direction) and [110]. The accessible reflections are illustrated by the stereographic projection shown in figure 2(a). For example, a cubic crystal oriented with [001] as the rotation axis will give all reflections $hk0$ with $h^2 + k^2 \leqslant 37$.

Although the angular information of a classical single-crystal measurement is lost due to the continuous rotation, the time-of-flight data recording provides very precise d-spacing measurements which are difficult to obtain using standard single-crystal methods. Data recorded in this way were analysed using Le Bail fits in the program RIETICA [14]. The peak widths and shapes were constrained to be the same as those recorded from a silicon standard. The only free parameters were the background coefficients and the lattice parameters[4]. Rapid and robust convergence was obtained in this way.

3. Results and discussion

The intensity recorded in the patterns is only moderate. However, figure 3 shows that the data obtained agree with the predictions of figure 2. No significant reflections from higher-order layer lines have intruded into the patterns. In interpreting the data, it must be remembered that these are multi-domain crystals. Whilst the overall poling is along the central $[001]_R$ zone referred to rhombohedral axes[5] (see figure 2), the crystal structure is rhombohedral (or pseudo-rhombohedral) with spontaneous polarization along $[111]_R$. Therefore, the crystal is really composed from populations of domains in which the spontaneous polarization is directed along

[4] The basis of the technique is that the integrated intensities of the reflections are allowed to vary independently of the structure factors.
[5] These differ little from the parent cubic axes.

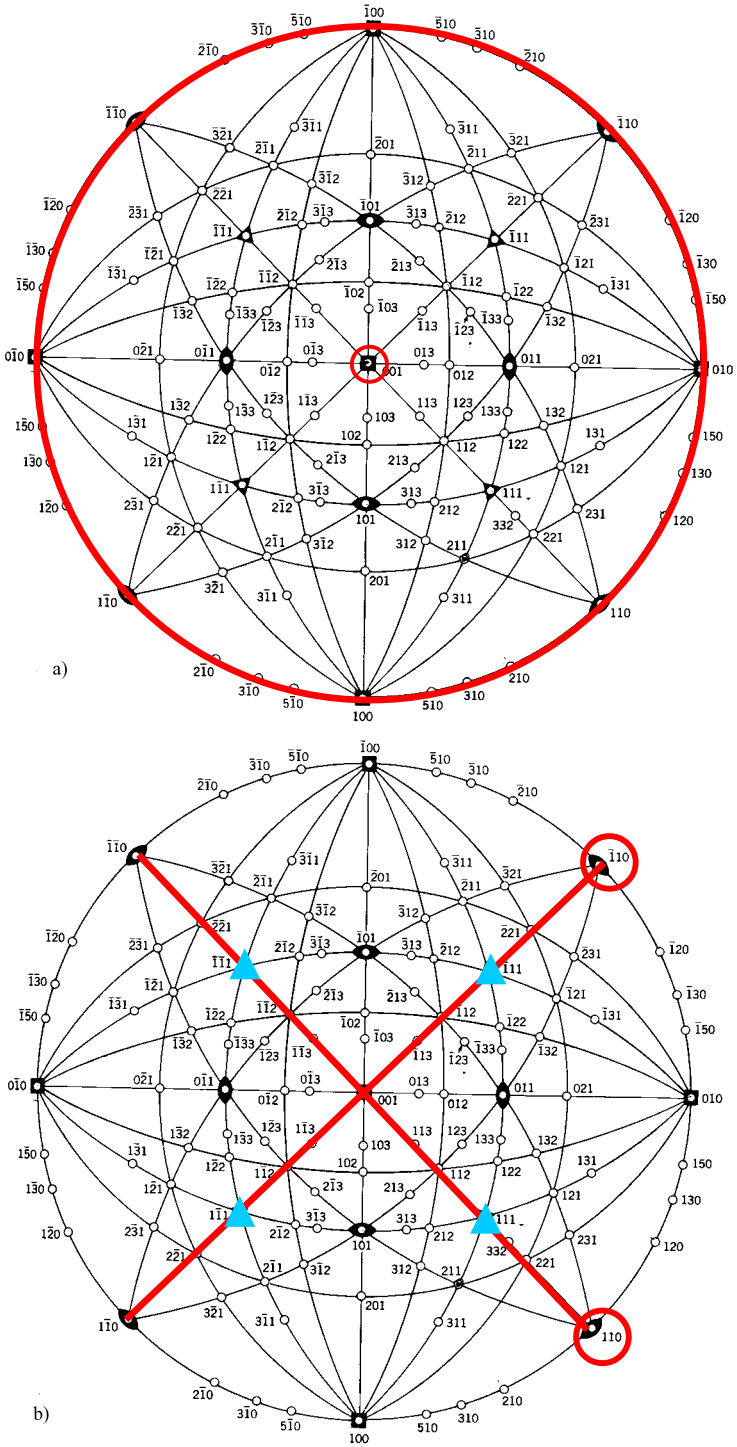

Figure 2. Standard cubic stereographic projections used in predicting the reflections expected from (a) the [001] oriented crystal and (b) the [110] oriented crystal (adapted from [13]).

(This figure is in colour only in the electronic version)

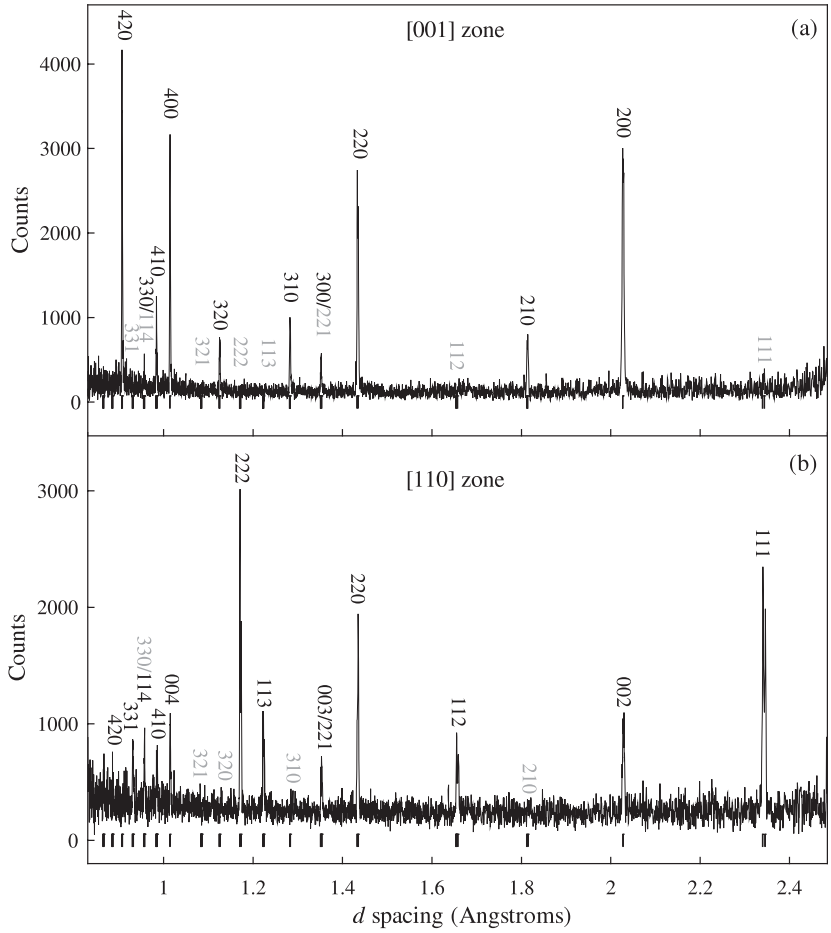

Figure 3. Time-of-flight neutron diffraction patterns recorded from PZN–4.5% PT crystals rotated about (a) [001] and (b) [110] zone axes. Reflection indices are given in normal type for reflections predicted in table 1 and grey type for those expected to be absent.

each of the eight ⟨111⟩ directions of the parent cubic crystal. In crystals poled along $[001]_R$, domain types with l negative are missing, leaving domains with spontaneous polarization along four of the former cubic directions shown in figure 2 ($[\bar{1}11]$, $[1\bar{1}1]$, $[\bar{1}\bar{1}1]$ and [111]). Where we might expect single reflections at unique d-spacings from a true single crystal, here we observe the superposition of diffraction from these four domain types. We may examine the effect of this superposition by imagining successive ∼90° rotations of figure 2 to bring each of the four ⟨111⟩ directions (of the parent cubic crystal) to lie at or close to the 'spontaneous polarization' direction $[111]_R$. Each observed reflection will be the sum of the reflections from the four domain types. In general, reflections from the domains will cluster around the cubic reflection positions but be slightly displaced equatorially and azimuthally. This causes severe problems in interpreting angularly resolved data from constant-wavelength diffraction instruments, e.g. from conventional equatorial θ–2θ scans. If a large detector aperture is used, then the entire cluster of reflections is compressed into one poorly resolved composite reflection. If a small detector aperture is used, then an unrepresentative slice through the cluster is recorded. In this experiment, we have a detector configuration that spreads ±22.5° in the

Table 1. Expected behaviour of some reflection types for a poled multi-domain rhombohedral crystal.

Zone	hkl	$2(hk+kl+hl)$	$(h^2+k^2+l^2)$	Expectation
[001]	$\pm h00$	0	h^2	Single reflection
	$\pm h\pm h0$	$2h^2, -2h^2$	$2h^2$	Reflections with same sign indices split from those with indices of opposite sign in ∼1:1 ratio
	$\pm h\pm k0$	$2hk, -2hk$	h^2+k^2	As above
[±110]	$00\pm h$	0	h^2	Single reflection
	$\pm h\pm h0$	$2h^2, -2h^2$	$2h^2$	Reflections with same sign indices split from those with indices of opposite sign in ∼1:1 ratio
	$\pm h\pm h\ h$	$6h^2, -2h^2$	$3h^2$	Reflections with same sign indices widely split from those with indices of mixed sign in ∼1:3 ratio
	$\pm h\pm h\ l$	$2h^2+4hl, 2h^2-4hl, -2h^2$	$2h^2+l^2$	Reflections split three ways as indicated, in ∼1:1:2 ratio

azimuthal direction (refer to figure 1) and d-spacing determination through the time-of-flight analysis that is *independent* of the angular superposition of reflections.

The d-spacing of planes in a rhombohedral crystal is given by:

$$\frac{1}{d^2} = \frac{\left(h^2+k^2+l^2\right)\sin^2\alpha + 2\left(hk+kl+hl\right)\left(\cos^2\alpha - \cos\alpha\right)}{a^2\left(1-3\cos^2\alpha+2\cos^3\alpha\right)}. \tag{1}$$

For α close to 90° as in PZN–PT, the positions of hkl reflections are determined largely by the term $(h^2+k^2+l^2)$, while the values taken by the term $2(hk+kl+hl)$ in equation (1) for the various overlapping or superimposed reflections determines whether reflection splitting will be observed or not. The size of the latter term relative to the former determines the separation $\Delta d/d$ of the split reflections. This allows us to predict, in table 1, the expected behaviour of each reflection type for later comparison with observation.

For the crystal oriented with the [001] zone as the rotation axis, the observed reflections are those around the outer rim of the stereographic projection figure 2(a) (at ∼90° to the central rotation axis). In this case, the multi-domain nature of the crystal has no effect on the types of reflections observed and we note that $h00$ are unsplit and the more general $hh0$ and $hk0$ are split into two. For data recorded with a [110] type rotation axis, the situation is more complex. Consider a single domain rotated about the $[\bar{1}10]$ axis (figure 2(b)). The reflections expected are those along the diagonal joining the $\bar{1}\bar{1}0$ pole to the 110 pole and, since $\bar{1}\bar{1}0$ and 110 have the same d-spacing, only one 110 reflection would be observed. In our domain crystal, however, the [110] zone will also be present, from which we expect to see the $1\bar{1}0/\bar{1}10$ reflection with a different d-spacing. In general, the $h00$ reflections are expected to be unsplit, hhh reflections split into two and hhl into three. Since, in an X-phase crystal, the 10–50 μm thick rhombohedral skin would only account for between 3% and 15% of the neutron diffraction pattern, the X-phase reported by Xu *et al* [9] would result in largely single (cubic) reflections with only minor components splitting in the manner outlined in table 1.

Figure 4 shows details of the Le Bail fits obtained for the [001] and [110] oriented crystals for a selection of reflections of the types listed in table 1. The observed behaviour is very close to that predicted in the table. For the [001] oriented crystal, the greatest departure visible in the figure is 210, for which the ratio of the split reflections is slightly different from 1:1. Similarly, reflections for the [110] oriented crystal also show the expected splitting. Note that the split in

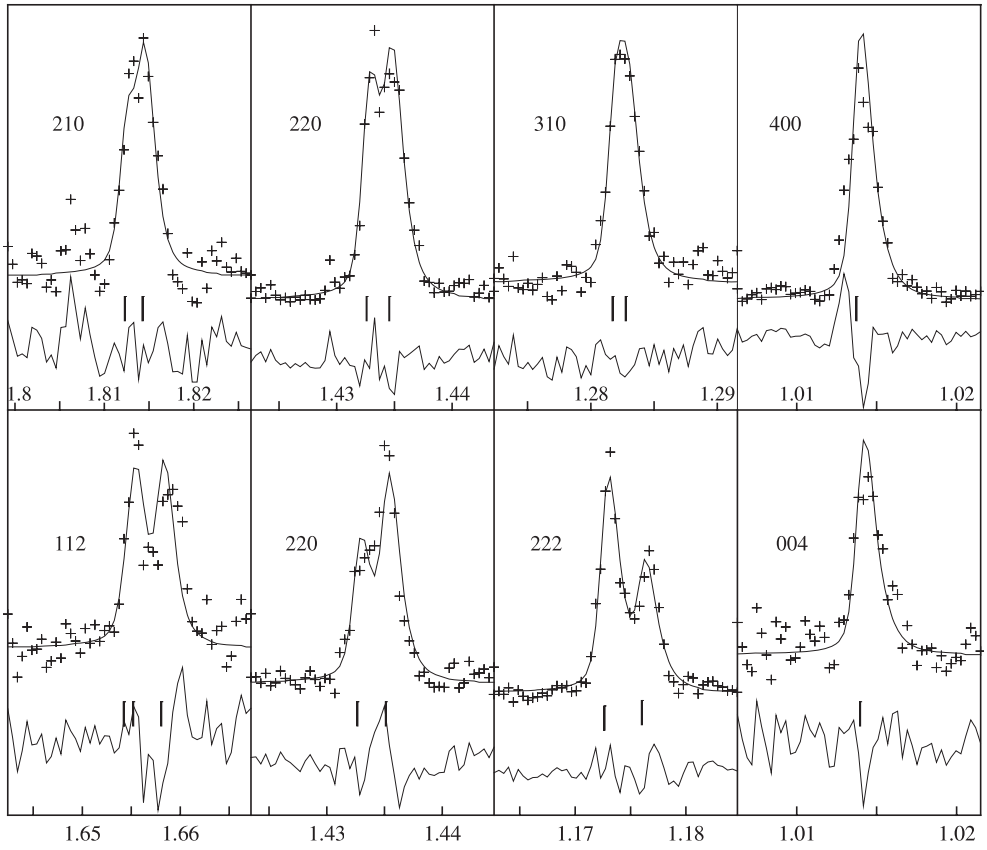

Figure 4. Detail of several diffraction peaks from the patterns shown at (a) (top row) and (b) (bottom row) in figure 3. The solid lines are from a Le Bail fit using standard peak shapes and widths. Reflection markers from the refined lattice parameters and difference profiles from the Le Bail fit are also given.

220 proves the multi-domain nature of the crystal. The relative intensities of some of the split reflections are not as predicted, especially for hhh where the $\{\overline{h}hh\}$ reflection is much less than three times the intensity of the hhh reflection. Three possible causes have been considered: unequal domain populations, different structure factors and extinction. A diffraction pattern previously recorded from a polycrystalline PZN sample composed of many 0.5–2 mm as-grown single crystals shows the same effect but to a lesser degree. We therefore consider the effect to be largely due to extinction but with some contribution from structure factor differences. No signs of the X-phase were observed in any of the crystals studied. Any doubt that results obtained using coarse powders and as-grown single crystals are unrepresentative of poled single crystals may now be set aside. In our previous paper, we posed an interpretation of the results of Xu *et al* [9] whereby the synchrotron beam was centred upon a single large rhombohedral domain giving a single Bragg reflection and the impression of a cubic structure. This new experiment reinforces that interpretation and confirms that the X-phase interpretation is incorrect.

As with our powder diffraction results [8], the $h00$ reflections are broadened. Given that the other reflections are well modelled by the rhombohedral structure with instrumental reflection

widths, the broadening is most likely due to inter-domain strains, although we are unable to rule out a slight monoclinic or orthorhombic distortion on the basis of these data. New data at higher intensity will be recorded once the upgraded ISIS source is operational.

4. Conclusions

The X-phase has not been observed in the three neutron diffraction studies that we have conducted—one using powder diffraction, one using a collection of large as-grown crystals in a pseudo-powder [12] and this one using poled single crystals. We therefore conclude that PZN and PZN–4.5%PT crystals are rhombohedral throughout in both the as-grown and electrically poled conditions.

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