Crystal structure of the relaxor ferroelectric PZN: demise of the 'X-phase'

LETTER TO THE EDITOR

Crystal structure of the relaxor ferroelectric PZN: demise of the 'X-phase'

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Abstract
The crystal structure of lead zinc niobate (PZN) was studied by very high-resolution neutron powder diffraction using both small (<143 μm) and large (1–2 mm) crystals. No evidence was found for the rhombohedral exterior/cubic interior 'X-phase' structure reported by Xu *et al* (2004 *Appl. Phys. Lett.* **84** 3975–7). The structure is confirmed to be a rhombohedral perovskite in space group $R3m$. It is concluded that the X-phase observations were due to a rhombohedral domain size and population gradient within the crystals sampled by a small x-ray beam.

1. Introduction

$Pb(Zn_{1/3}Nb_{2/3})O_3$ (lead zinc niobate or PZN) has been widely studied because of the exceptional piezoelectric properties that occur in this material and its alloys with $PbTiO_3$. These include piezoelectric strains up to 1.7%, the largest of any practical piezoelectric material [1]. Although phase transitions to tetragonal [1], monoclinic [2, 3] and orthorhombic [4, 5] symmetry in PZN–4.5% PT and PZN–8% PT during or after electrical poling have been reported and debated [6], there is not much in the literature concerning the structure of PZN itself. The room-temperature crystal structure of PZN was reported by Kuwata *et al* [7] to be a rhombohedrally distorted perovskite. Single crystal laboratory x-ray diffraction has led to similar conclusions [8]. Single crystal neutron diffraction data have shown that the lattice parameters and systematic absences of poly-domain PZN–4.5% PT which, according to the phase diagram, is iso-structural with PZN, are consistent with the rhombohedral $BaTiO_3$ structure in space group $R3m$ [9].

Very recently, faith in the basic lattice symmetry of *un-poled* PZN crystals has been shaken. Based upon synchrotron studies of the 111 reflection at two energies and penetration depths, Xu *et al* have suggested that PZN crystals are not rhombohedral at all. Data such as in figure 1, redrawn from Xu *et al*, show for low-energy low-penetration x-rays, two peaks with the expected rhombohedral splitting due to the coexistence of many {111}-type and {$\bar{1}11$}-type
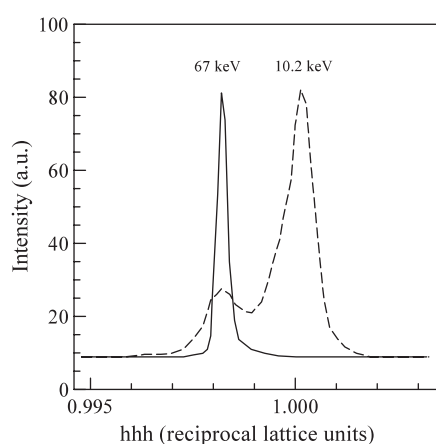
Figure 1. Schematic diagram, redrawn from figure 2 of [11], showing the longitudinal synchrotron x-ray scans around 111 used as the basis for proposing the X-phase. The 10.2 keV x-rays have a penetration depth of ~13 μm whereas the 67 keV x-rays have a penetration depth of ~400 μm.

rhombohedral domains [11]. When high-energy, high-penetration x-rays were used, only a single peak was observed. The model proposed was that the crystals were internally *cubic* with a rhombohedrally distorted exterior of between 10 and 50 μm deep (the so-called X-phase) [10]. Follow-up work by Xu *et al* [11] confirmed the PZN observations and also reported that the interior of PZN–4.5% PT and PZN–8% PT crystals is different from the outside 10–50 μm layer, but in a different manner to PZN crystals.

This letter reports the results of a very high-resolution neutron powder diffraction study of the crystal structure of PZN at 4.2 and 300 K in which we find the material to have the conventional rhombohedral structure in space group $R3m$. In light of this, we have reinterpreted observations of the 'X-phase' in PZN as a rhombohedral domain size and population gradient effect.

2. Experimental details

Single crystals of composition $Pb(Zn_{1/3}Nb_{2/3})O_3$ were produced by the flux-growth method [12]. Crystals in the size range 0.5–15 mm were extracted from the flux in a hot HNO_3 solution. Two collections of crystals were studied. In the first, the crystals were lightly crushed in an agate mortar and pestle to pass through a coarse sieve (143 μm) in order to ensure good powder averaging in the ~2 cm^3 sample without causing particle size broadening or undue lattice strains. The second sample contained a few hundred crystals in the range 1–2 mm. Neutron powder diffraction patterns were recorded in transmission on the HRPD diffractometer (resolution $\Delta d/d \sim 4 \times 10^{-4}$) at the ISIS facility, Rutherford Appleton Laboratory, UK. Samples were held in a thin-walled vanadium can within a liquid helium cryostat with the large crystal sample rocked a few degrees periodically to improve the powder averaging. Diffraction patterns were recorded from 30 000 to 130 000 μs at room temperature and 4.2 K.

3. Results and discussion

Visual inspection of the high-resolution neutron diffraction patterns strongly suggests that the conventional rhombohedral symmetry is correct. Figure 2 demonstrates this using the 111, 200 and 222 reflections from both samples at 4.2 K and the small crystal sample at 295 K. The integrated intensities from the large crystal sample are slightly affected by extinction and graininess; however, it is clear that the 111 and 222 reflections are split approximately in the
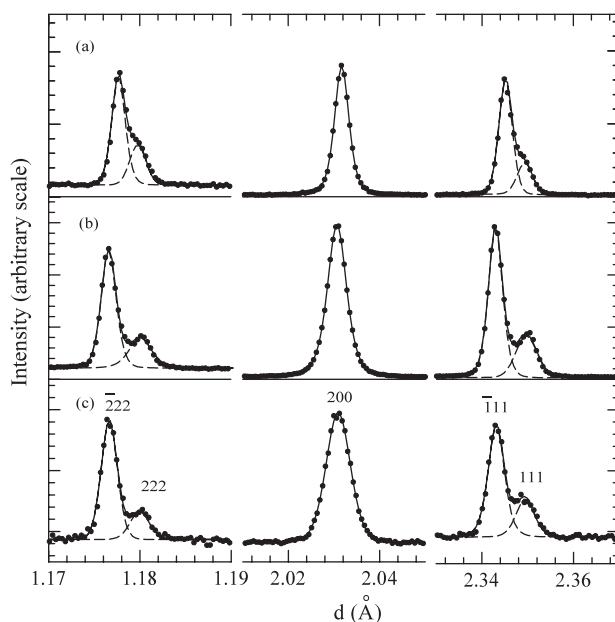
Figure 2. 200, 111 and 222 reflections of room temperature (a) and 4.2 K ((b), (c)) neutron powder diffraction patterns recorded from PZN crystals. Peaks recorded using both <143 μm ((a),(b)) and 1–2 mm crystals (c) are shown. The lines show fits to one (200) and two (111, 222) Pearson VII functions illustrating the absence of an observable cubic (X-phase) contribution.

ratio 3:1 and 200 remains unsplit. These visual observations were confirmed by fitting Pearson VII functions to the reflections shown in figure 2, where it may be seen that the addition of more than a few per cent of a cubic phase would seriously degrade the fit. Our major conclusion is that, with the crystals used in this investigation, no evidence for the cubic X-phase was observed.

Using 10 keV x-rays with a penetration depth of 13 μm and 67 keV x-rays with a penetration depth of approximately 400 μm, the rhombohedral surface layer of crystals showing the X-phase effect was estimated by Xu *et al* to be 10–50 μm deep [11]. The crystals used here were either <143 μm or 1–2 mm in diameter. Assuming the maximum skin depth and a 1–2 mm cube crystal, the interpretation of Xu *et al* would suggest a cubic (X-phase) volume fraction of 73–85%. Given the penetrating nature of neutron diffraction, any cubic core to the crystals would be very obvious in the diffraction patterns. It was initially somewhat surprising that the neutron diffraction results differ so greatly from the x-ray results. The explanation of this difference requires a more careful consideration of the x-ray experimental arrangement and results.

The data of Xu *et al* [11] were recorded as longitudinal scans about the 111 Bragg reflection. A true single crystal would show only one peak under these conditions. In contrast, un-poled ferroelectric 'single' crystals contain many domains that form during cooling from the high-temperature cubic phase into the lower-temperature ferroelectric phase. In rhombohedral structures, this leads to splitting of the 111 peak in the ratio 3:1 as was observed for example in our neutron powder diffraction data (figure 2). Xu *et al* [11] clearly expected that (i) their PZN crystals, if rhombohedral, would contain a statistically random collection of the four domain types 111, $\bar{1}$11, 1$\bar{1}$1 and 11$\bar{1}$, and (ii) that the x-ray beam was sufficiently large to sample many domains. Indeed, this is what was observed by Xu *et al* at the sample surface when low-energy x-rays were used, as may be seen in figure 1. As expected, the reflections are

somewhat broadened due to inter-domain strains. With the high-energy x-rays, only a single narrow reflection was observed (figure 1) and the conclusion drawn by Xu *et al* was that the crystal was internally cubic, which they named the X-phase. This conclusion is based *solely* on the assumption that the diffraction shows contributions from *all* types of domains.

The other, more likely explanation is that in the subsurface of the crystal, within the region sampled by the x-ray beam, *one* domain orientation has become dominant over regions of crystal larger than the x-ray beam. Instead of representing a cubic structure, the X-phase is merely *one* of the four rhombohedral variants. Inter-domain strains are absent because of the larger domain size and therefore a single narrow Bragg reflection is observed. This explanation also accounts for the fact that the X-phase reflection observed (figure 1, see also figure 2 of [11]) is positioned exactly under one of the rhombohedral 'surface' reflections, 111 (figure 1). A cubic interior would lead to a reflection positioned *between* the two rhombohedral reflections as was demonstrated in earlier work by Xu *et al* using data recorded in the genuine cubic high-temperature state [10]. A material such as we propose would give a perfectly normal rhombohedral *powder* diffraction pattern (such as we observe) because of the large number of randomly oriented crystals. The situation with the other compositions studied in [11] is less clear, although a comment by Xu *et al* that the work of Forrester *et al* [9] on PZN–4.5% PT was affected by shallow penetration is incorrect as that work was undertaken in transmission using neutron diffraction.

Whether the centres of as-grown PZN crystals routinely have larger domain sizes in which one orientation becomes dominant remains to be determined. It is possible that crystals used for the X-phase observations were a special case because they were dimensionally anisotropic and had 'undergone many heating and cooling cycles' [11]. This may have caused their internal domain size to increase and extend beyond the dimensions of the synchrotron beam (not given in [11]) and/or their domain population to become highly skewed to favour one orientation. Similar behaviour is quite common, for example, in the 'training' of two-way shape memory alloys [13]. Even with our more conventional explanation of the X-phase observations, the existence of single crystals with very different surface and internal domain populations is nonetheless intriguing and potentially useful.

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