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Structured diffuse scattering and the fundamental 1-d dipolar unit in PLZT $(Pb_{1-y}La_y)_{1-\alpha}(Zr_{1-x}Ti_x)_{1-\beta}O_3$ (7.5/65/35 and 7.0/60/40) transparent ferroelectric ceramics

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ABSTRACT

The observation via electron diffraction of relatively sharp, $\mathbf{G}\pm\{111\}^*$ sheets of diffuse intensity arising from the large amplitude excitation of inherently polar, transverse optical modes of distortion in $[(Pb_{1-y}La_y)_{1-\alpha}\square_\alpha][(Zr_{1-x}Ti_x)_{1-\beta}\square_\beta]O_3$ (PLZT), 7.5/65/35 and 7.0/60/40, samples close to the morphotropic phase boundary in this system shows that the fundamental dipolar units in these materials correspond to highly anisotropic $\langle 111\rangle$ chain dipoles formed from off-centre Pb/La and coupled Ti/Zr displacements. The correlation length along the chain of these 1-d dipoles can, in principle, be determined from the width of the observed $\{111\}^*$ diffuse sheets in reciprocal space and is estimated to be at least 2–3 nm. The primary role of the dopant La ions appears to be to set up random local strain fields preventing the condensation of long wavelength homogeneous strain distortions of the unit cell thereby suppressing transverse correlations of the fundamental $\langle 111\rangle$ chain dipoles and the development of macro-, or even nano-scale, ordered ferroelectric domain state/s in the absence of an applied external electric field.

1. Introduction

Ever since the early pioneering work of Smolenskii [1], ferroelectric/relaxor ferroelectric systems exhibiting frequency dependent, rounded, broad peaks in dielectric permittivity as a function of temperature, have been of intense and continuing interest [1–6]. This is both because of a fundamental interest in the physical mechanism underlying "diffuse phase transitions" (DPTs) but most directly because of the huge range of applications of such systems (e.g. as electrostrictive and/or piezoelectric actuators and sensors [7–10], as electro-optic, elasto-optic and photorefractive elements [9], as light shutters, coherent modulators and image storage devices [10] etc.).

The $Pb[(Zr_{1-x}Ti_x)]O_3$ (PZT) and $[(Pb_{1-y}La_y)_{1-\alpha}\square_\alpha][(Zr_{1-x}Ti_x)_{1-\beta}\square_\beta]O_3$ (PLZT), $y(1-\alpha)=2\alpha+4\beta$, systems, particularly for compositions close to the so-called morphotropic phase boundary (MPB) separating the "rhombohedral" and tetragonal ferroelectric phase fields therein, represent two of the most important and widely studied of such systems [1,10–25]. This is largely because many of the properties of interest, such as the dielectric constant, remanent polarization as well as electromechanical and piezoelectric coupling coefficients etc. are typically maximized along, or close to, the MPB [10–14]. Early on, the addition of relatively small amounts of La to the basic PZT system was found to significantly improve various dielectric, ferroelectric and piezoelectric properties, in particular it enabled optically transparent samples to be produced [10–14].

In this paper, we focus on a characteristic, highly structured, diffuse intensity distribution and its relationship to the elementary dipolar unit in two particular optically transparent PLZT samples close to the reported MPB in the PLZT system, namely PLZT (7.5/65/35, corresponding to $y=0.075$, $x=0.35$ and overall composition $(Pb_{0.905}La_{0.073}\square_{0.022})(Zr_{0.645}Ti_{0.347}\square_{0.007})O_3$ assuming $\alpha/\beta=3$, as suggested in [10] for $x\sim0.35$) and PLZT (7.0/60/40, corresponding to $y=0.070$, $x=0.40$ and overall composition $(Pb_{0.911}La_{0.069}\square_{0.021})(Zr_{0.596}Ti_{0.377}\square_{0.007})O_3$, again assuming $\alpha/\beta=3$). The former is nominally just on the "rhombohedral" side of the MPB and the latter just on the "tetragonal" side of this phase boundary (see e.g. Fig. 2 of [10]). Both samples are optically transparent and no well-defined macroscopic or striated nano-scale ferroelectric domain textures are observed in bright field (BF) transmission electron microscope (TEM) images of either sample.

Typically, with increasing La content, the cubic paraelectric to rhombohedral ferroelectric phase transition temperature (at T_m) characteristic of the end member PZT (0/65/35 and 0/60/40) samples systematically decreases while the associated permittivity peak systematically broadens until clear frequency dependent

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dielectric behaviour is apparent for $y > \sim 0.06$–0.07 [17,18]. For lower La concentrations, apparently homogeneous ferroelectric domains on the macro-scale (i.e. micron) are apparent in BF TEM images. For $y \sim 0.06$, however, this large scale domain contrast largely disappears to be replaced by a much finer scale (tens of nm's) "striated" domain contrast [17,18]. For $y < 0.06$–0.07, however, only a very fine scale mottled contrast ($\sim$ a few nm's) reported to arise from polar nano-regions (PNRs) remains [17,18]. From the structural point of view, for La content increasing from zero up to ~ 0.06–0.07, the rhombohedral unit cell dimension and volume as well as the rhombohedral distortion angle (the deviation from 90°) systematically decrease until the latter becomes very difficult to detect for $y > \sim 0.06$–0.07 (see e.g. Fig. 2 of [13]). At and above this La content, i.e. near the reported MPB, the average structure unit cell becomes highly stress-sensitive [13] and metrically extremely close to cubic (often labelled "pseudo-cubic", see e.g. [21]) at all temperatures, both above and below the remaining now significantly broadened and frequency-dependent peak in the dielectric permittivity at T_m (see e.g. the powder XRD traces of the PLZT (7.5/65/35) and (7.0/60/40) samples shown in Fig. 1 and the measured dielectric permittivity versus temperature behaviour of the PLZT (7.0/60/40) sample shown in Fig. 2).

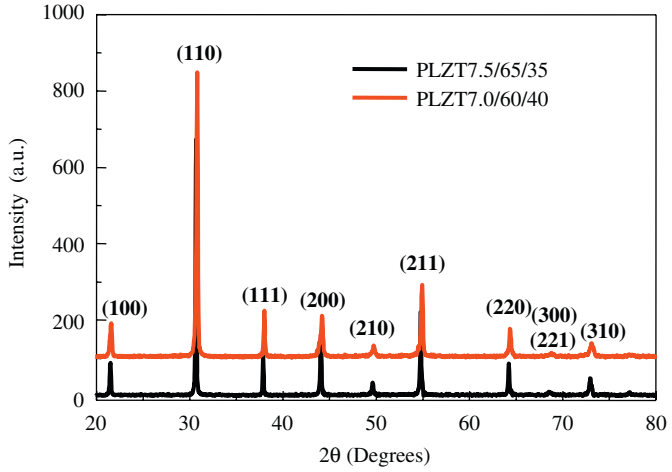

Fig. 1. XRD patterns of the PLZT (7.5/65/35) (lower) and (7.0/60/40) samples (upper) obtained using Cu$K\alpha_1$ radiation on a Siemens D-5000 diffractometer.

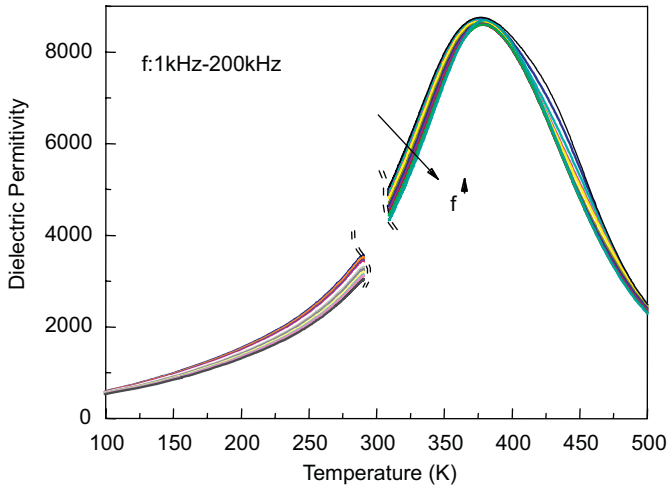

Fig. 2. The measured dielectric permittivity versus temperature behaviour of the PLZT (7.0/60/40) sample for frequencies ranging from 1 to 200 kHz.

The nature and distribution of the PNRs in these PLZT samples close to the MPB and their relationship to the accompanying maximization of the dielectric, electromechanical and piezoelectric properties of these materials [10–25] is still not at all well understood. The purpose of the current paper is to report the results of a detailed electron diffraction investigation of PLZT (7.5/65/35) and PLZT (7.0/60/40) samples close to the MPB searching for evidence of PNRs. Given that a highly structured diffuse intensity distribution first reported to exist in rhombohedral PZT (but to virtually disappear in the vicinity of the MPB [23]) has only very recently been demonstrated to arise from the fundamental 1-d dipolar unit in PZT i.e. from coupled off-centre displacements of Pb and Zr/Ti ions relative to the oxygen substructure [24], it is particularly important to establish whether or not this characteristic diffuse scattering is or is not also present in our PLZT samples close to the MPB.

2. Experimental

2.1. Sample fabrication

The PLZT 7/60/40 ceramic was fabricated via a two-step annealing process using high purity PbO, La_2O_3, ZrO_2 and TiO_2 as raw starting materials. Powders of the appropriate stoichiometry (including a 2.5% excess PbO to allow for the high temperature volatility of PbO) were first ball milled together for 24 h then heat treated at 950 °C for 2 h. Pellets were then made under a pressure of 280 MPa. A stacked arrangement of these pellets interspersed with PLZT powder of the same composition was then placed in an alumina crucible with a lid. This crucible was then placed into a tube furnace and annealed at 1000–1150 °C for 1 h at a low pressure, followed by a second annealing at 1250 °C for 5 h under an oxygen atmosphere. The density of the resultant sample was 99.5% of theoretical density. The PLZT (7.5/65/35) was prepared in the same manner as above except that the second of the above annealings was carried out in a hot-press furnace to further increase the resultant density, to 99.9%.

2.2. X-ray powder diffraction

X-ray powder diffraction patterns of both samples were collected on a SIEMENS D-5000 diffractometer using Cu$K\alpha_1$ radiation. For higher resolution, powder XRD data were also obtained using a Guinier–Hägg focusing camera with Cu$K\alpha_1$ radiation. Silicon (NBS 640) was used as an internal standard for accurate determination of unit cell parameters, refined using the "Unitcell" software package [26].

2.3. Electron diffraction

Electron diffraction at room temperature was carried out in a Philips EM 430 TEM operating at 300 kV on crushed portions of both samples dispersed onto holey carbon coated copper grids. The typical diameter of the area from which the selected area electron diffraction patterns (EDPs) shown in Figs. 3 and 4 below were obtained was $\sim 0.5\,\mu m$.

2.4. Dielectric property measurements

A high quality transparent pellet of the PLZT (7.0/60/40) sample with a diameter of 10 mm, thickness of ~ 1 mm and relative density of 99.5% was coated with silver paste for dielectric measurement using a high precision LCR meter (HP4284A) and