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Interplay of strain mechanisms in morphotropic piezoceramics

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Abstract—A large number of transducers, ultrasonic motors or actuators are based on lead zirconate titanate (PZT) piezoceramics, with compositions near the morphotropic phase boundary (MPB) where the relevant material properties approach their maximum. Since the best piezoelectric properties, in particular the highest recoverable strains, are observed for these MPB compositions with phase coexistences, a separate analysis of each phase is mandatory. Here we present a sophisticated method to correlate the macroscopic strain observations to mechanisms on the atomic scale. The technique allows a quantification of all contributing strain mechanisms such as lattice strain, domain switching and phase transition for each phase. These results indicate that the major strain contribution is of structural instead of microstructural origin and the electric field induced phase transition occurs through polarisation rotation. Such a mechanism could be generalised in other MPB piezoceramics and will be useful to design and optimise the next generation of high performance piezoelectric materials.

Keywords: PZT; Piezoelectricity; Neutron diffraction; Electric field; Rietveld refinement

1. Introduction

Large piezoelectric response, which is generally observed in morphotrophic phase boundary compositions (MPB), for which two crystal structures are energetically comparable, results in the creation of a large strain in response to an external electric field [1]. Prototypical MPB solid solution systems are relaxor-$PbTiO_3$ based ferroelectrics such as $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3 - xPbTiO_3$ (PZN-PT) [2] and $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3 - xPbTiO_3$ (PMN-PT) [3] and lead free piezoelectrics such as $(1-x)(Na_{1/2}Bi_{1/2})TiO_3 - xBaTiO_3$ [4,5], which can either be obtained as single crystals or as piezoceramics, and more importantly commercial piezoelectric ceramics like $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) which are the basis of most actuator devices [6].

In contrast to polycrystalline piezoelectric materials, the strong piezoelectric response observed in single crystals is found to be structurally intrinsic in nature [7]. For the polycrystalline state of the technologically important PZT system, the origin of the high piezoelectric response is either proposed to be due to (1) an extrinsic complex microstructural domain reorientation between the rhombohedral (*R*3*m*) and tetragonal (*P*4*mm*) phases adjacent to the MPB [8,9] or to (2) the existence of a low symmetry monoclinic structure (*Cm*) [10,11], which can give rise to a polarisation rotation mechanism [12–14]. The latter intrinsic structural hypothesis was originally obtained based on a first principles study [15] on the simple $BaTiO_3$ perovskite, for which the rhombohedral – orthorhombic (low symmetry) – tetragonal phase transition sequence is observed experimentally. In order to determine the origin of the large piezoelectric response in MPB PZT only a combined *in situ* structural and microstructural study as a function of applied electric field can provide the appropriate information to understand the behaviour of this material under the conditions of use in technological applications.

In the past decade *in situ* and *in operando* techniques for the investigation of piezoceramics advanced significantly. X-ray and neutron diffraction studies enable structural changes to be correlated with macroscopic properties [16–19]. Unfortunately, the geometry used for combined microstructural-structural studies [16,18], i.e. with the

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incident beam fixed at 90° to the electric field, does not allow information to be obtained along the crystallographic c-direction aligned along E from the piezoceramic crystallites which are not in the appropriate diffraction conditions. In order to overcome this technical problem, we obtained diffraction data by rotating the field vector E (i.e. the sample) over ω with respect to the incident beam k_i (Fig. 1).

The strain mechanisms of piezoceramics were identified as lattice strain [16,20], domain switching [19,16,20] and, for morphotropic compositions, a field induced structural phase transition [21–23]. Field induced converse piezoelectric effect and remanent lattice strain result in shifts of Bragg reflection positions and indicate the expansion or compression of the unit cells. The field induced domain switching results in a texturing along the electric field vector that affects the Bragg reflection intensities. The field induced phase transition is a reversible switching between the two coexisting phases at the phase boundary and results in a change of reflection intensity of the respective phases. The field induced responses can be differentiated in structural contributions, such as converse piezoelectric effect or phase transitions, and in microstructural contributions, such as domain switching and stress–strain interactions. Since the electric field is uniaxial, all three strain mechanisms strongly depend on the orientation of the crystallites with respect to the electric field. Therefore, a comprehensive analysis is only possible with a study of a large number of sample orientations.

However, application of an electric field results in the creation of a large strain as previously mentioned and great attention must be paid in order to take into account the overall scattering geometry between the electric field and the incident incoming beam. In order to accurately determine both, the large texture effect and the piezoelectric effect, the scattering contributions of all crystalline directions have to be measured. Using a specific setup, we recently determined the crystal structure of PZT as a function of the electric field by synchrotron X-ray diffraction, which was consistent with a reversible tetragonal-to-monoclinic phase transition [21]. These results were confirmed through cycling and the progressive damping of the phase transformation was proposed to account for the structural origin of the ferroelectric fatigue [24]. Here we probe both structural and microstructural contributions in PZT piezoceramics using neutron scattering and we will show without any ambiguity that the greatest contribution to the piezoelectric strain is structural and not microstructural, i.e. 80% and 20% of the response respectively. This result has strong implications for MPB and non MPB systems and should be taken into account in order to design and optimise materials with large piezoelectric response.

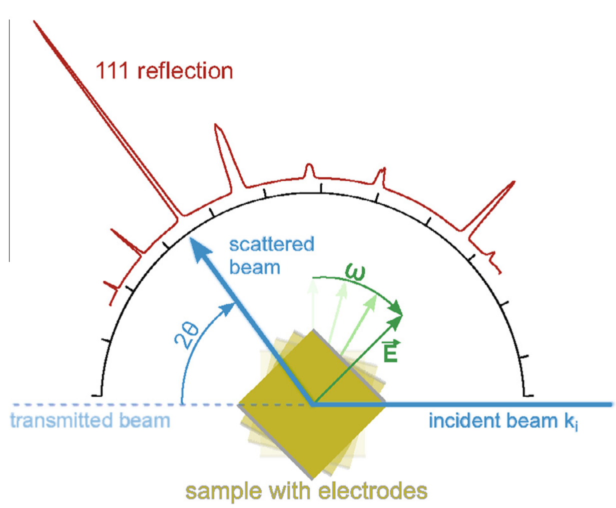

Fig. 1. Experimental setup for analysing all strain mechanisms in one diffraction experiment.

2. Experimental

2.1. Measurement

Since the vast majority of technically relevant compositions exhibit phase coexistences, special requirements are necessary for a successful X-ray or neutron diffraction analysis. In order to resolve the coexisting and highly correlated phases a high angular resolution is mandatory. At the same time a high Q-range is necessary to obtain enough information to correctly determine the orientation distribution function (ODF) of the textured material. The requirements could be achieved with neutron diffraction measurements at the high-intensity diffractometer D20 [25] (Institute Laue-Langevin, Grenoble). Data were collected at a monochromator take-off angle of 90° using wavelengths of 1.54423(9) Å for a high Q-range and 2.41821(19) Å for high angular resolution. For each wavelength, a series of 13 complete diffraction patterns (detector angle 5°–150°) were collected with different orientations of the electric field with respect to the incident beam by moving the ω-sample table in 15° steps. By this means, the relative orientation between the electric field vector and the scattering vectors of the individual reflections was varied. The investigations were carried out on commercially available soft doped samples of PIC151 (PI ceramics, Lederhose, Germany), based on the lead zirconate titanate system and technically applied in actuator applications.

2.2. Analysis

Data analysis was carried out using the software package MAUD (Materials Analysis Using Diffraction) [26]. MAUD allows full pattern Rietveld refinements including full texture analysis for multiple phases. Therefore, all data sets with different wavelengths and sample orientations contribute to the refinement. By assigning the Euler angles of the experiment to each diffraction pattern, the orientation dependent information can be exploited. For this additional information the extended Williams–Imhof–Matthies–Vinel (E-WIMV) algorithm was used for texture refinement [27] and the weighted strain orientation distribution function (WSODF) strain model for refinement of the field induced lattice strain [28]. A two phase structure model of $P4mm$ and $R3m$ allowed a modelling of both the remanent and the applied field state.

The analysis is based on the simultaneous fit to the data collected at different orientations of the electric field. Recently this approach was applied for $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3 - x(Ba_{0.7}Ca_{0.3})TiO_3$ [18] and $(Bi_{1/2}Na_{1/2})TiO_3 - 6\%BaTiO_3$ [29]. Although these studies were capable of analysing all strain mechanisms they were either performed on a single phase material [18] or did not calculate the macroscopically observed strain values [29]. The data collection using two wavelengths offers data sets