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ScienceDirect

Acta Materialia 71 (2014) 176–184

Acta MATERIALIA

www.elsevier.com/locate/actamat

Adaptive ferroelectric state at morphotropic phase boundary: Coexisting tetragonal and rhombohedral phases

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Received 4 October 2013; received in revised form 3 March 2014; accepted 3 March 2014
Available online 1 April 2014

Abstract

With a focus on local symmetry, the microstructural basis for high piezoelectric performance in $PbMg_{1/3}Nb_{2/3}O_3$–$xPbTiO_3$ (PMN–PT) ceramics at the morphotropic phase boundary (MPB) composition was investigated by means of convergent-beam electron diffraction analysis and twin diffraction pattern analysis. The local structure was found to consist of coexisting (1 0 1)-type tetragonal nanotwins and (0 0 1)-type rhombohedral nanotwins. A phenomenological theory based on crystallography is proposed to show that such nanoscale coexistence can give rise to an average monoclinic structure through strain accommodation. The average monoclinic structures (Ma and Mc) vary with temperature and composition due to the dependence on temperature and composition of the lattice parameters. Based on in situ X-ray diffraction data, we demonstrate how the polarization rotates across the MPB region in PMN–PT ceramics with varying temperatures and compositions.

Keywords: Piezoelectrics; Morphotropic phase boundary; TEM; Twin boundary; Adaptive phase

1. Introduction

The most useful piezoelectric materials, such as $PbZr_{1-x}Ti_xO_3$ (PZT) [1–3], $PbMg_{1/3}Nb_{2/3}O_3$–$xPbTiO_3$ (PMN–PT) [4–7] and $PbZn_{1/3}Nb_{2/3}O_3$–$xPbTiO_3$ (PZN–PT) [8], display a transition region, referred to as the morphotropic phase boundary (MPB), in their composition–temperature phase diagrams. This has served as the basis for understanding the remarkable electromechanical response in applications [9–11]. In general, the MPB separates the phase of tetragonal (T) symmetry from rhombohedral (R) symmetry [12,13]. It therefore raises the question: how is it possible to smoothly transform from one phase to the other when there is no group–subgroup relationship between T and R? [14]. Probing the microstructure of such a transition from symmetry R to T can be considered to be an effective way to understand the non-group–subgroup transition [15].

We know from symmetry that a non-group–subgroup transition can be mediated by a common subgroup of both T and R [13,14]. Neutron diffraction and X-ray diffraction (XRD) investigations on PMN–PT, PZN–PT and PZT

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http://dx.doi.org/10.1016/j.actamat.2014.03.007
1359-6454/

single crystals and ceramics have shown the presence of a monoclinic (M) phase linking T and R in the MPB region [16,17]. The single M phase is considered a reasonable intermediate phase because the M symmetry (Cm or Pm) is the subgroup of both T symmetry (P4mm) and R symmetry (R3m) [13]. A key feature of this structure is that the polarization vector is no longer constrained to lie along a symmetry axis, as in the R and T structures, but instead can rotate within the monoclinic plane [18]. However, the heterogeneous microstructure in the vicinity of the MPB has been investigated over the last 20 years [19,20] and a number of recent studies have shown that such nanoscaled heterogeneity consists of either R or T symmetry rather than M symmetry [15,21–23]. The evidence for a single M phase, i.e. the appearance of M intensities in diffraction patterns, can also be considered a result of coherence effects amongst the nanoscaled structures [19–24]. The MPB region is thus regarded as inhomogeneous at the nanoscale (with R or T symmetry) but homogeneous at larger scales (with M symmetry) [19,20,23–26].

An adaptive state, formed via strain accomodation, has been proposed to show that the average M symmetry found for the MPB could be considered a result of coherence effects of R (or T) nanodomains [21,25–29]. Three types of adaptive states with M symmetry are known, namely, Ma, Mb and Mc [30]. The former two Ma, Mb (Cm) states are obtained by shearing primitive unit cells along the pseudo-cubic $(1\,1\,0)_{pc}$ plane, the polarization $[uuv]$ of which is confined to the pseudo-cubic $(1\,-1\,0)_{pc}$ plane with $u > v$ and $u < v$, respectively, as schematically shown in Fig. 1a [30,31]. The other Mc (Pm) phase results from shearing primitive unit cells along the pseudo-cubic $(1\,0\,0)_{pc}$ plane. The polarization along $[u0v]$ is thus constrained to lie within the $(0\,1\,0)_{pc}$ plane, as shown in the schematic in Fig. 1a [30,31]. Transmission electron microscopy (TEM) experiments and lattice parameter analysis based on XRD in PMN–PT and PZN–PT have identified that the average symmetries of (0 0 1)-type R nanotwins [27,29], (1 1 0)-type R nanotwins [27,29] and (1 0 1)-type T nanotwins [21,24–26,32,33] are Ma, Mb and Mc symmetries, respectively.

The average structure can be any, or some combination, of the states Ma, Mb and Mc depending on temperature [34–36], composition [37,38], electric [8,36,39] and stress [31,36,40] fields. However, the local structure has so far been shown to be either nanoscaled R or T twins in the vicinity of the MPB in PMN–PT, PZN–PT and PZT piezoelectric materials [15,21,22,24]. Thus, it is still unclear how the M adaptive states (Ma, Mb or Mc) with distinct local structures transform from one structure to the other. This is especially the case for transformations between Ma and Mb with local R symmetry and Mc with local T symmetry.

A number of studies have indicated that local R and T structures can coexist within the microstructure. For example, the thermodynamics of coexistence of T and R heterophase polydomains at the MPB in ferroelectric films has been considered within the theory of elastic domains [41,42]. The volume fractions of the phases and different twin components have been obtained as functions of misfit strain and film orientation by applying an external field [41,42]. Recent high resolution XRD and TEM observations on epitaxial $BiFeO_3$ films have shown that R and T twins can coexist in the MPB region of $BiFeO_3$ [43,44]. In the case of very low domain wall energy and fine domains, the average symmetry of $BiFeO_3$ is monoclinic [31,45]. The large electromechanical response may be understood on the basis of electric field or strain-driven inter-conversion between R and T coexisting phases near the MPB [43,44]. These results imply that the microscopic origin of high electromechanical response in PZT, PMN–PT and PZN–PT near the MPB may be attributed to phase

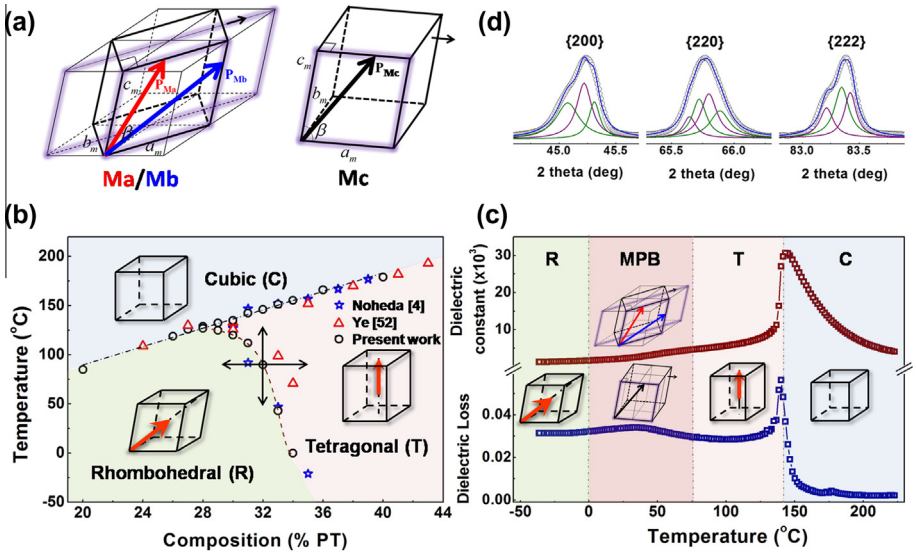

Fig. 1. (a and b) Phase diagram of PMN–xPT near the MPB composition. (c and d) Dielectric permittivity (ε) vs. temperature (T) curves for PMN–32PT. Three kinds of adaptive states with M symmetry, namely, Ma, Mb and Mc, can be found around the MPB region.