Characterization of ferroelectric domains in morphotropic potassium sodium niobate with scanning probe microscopy

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(Received 26 April 2007; accepted 26 May 2007; published online 19 June 2007)

Lead-free piezoceramic potassium sodium niobate in its morphotropic composition was synthesized with abnormal grain growth. Ferroelectric domain patterns were imaged with piezoresponse force microscopy. Analysis of the domain structure at the morphotropic phase boundary revealed a coexistence of tetragonal and orthorhombic polarized domains in a single grain. © 2007 American Institute of Physics. [DOI: 10.1063/1.2750395]

Recently the search for lead-free ferroelectrics has been intensified in order to replace lead zirconate titanate (PZT) ceramics as high-performance piezoelectric materials because of certain legal restrictions\textsuperscript{1} on the use of toxic lead. The most promising lead-free candidate seems to be the potassium sodium niobate (KNN) family, which was proposed by Saito \textit{et al.} in 2004.\textsuperscript{2} Since then a number of publications concerning KNN have been published considering the processing and electrical properties.\textsuperscript{3–8} In our work we present the ferroelectric domain structure of KNN in its morphotropic composition, which is crucial for the understanding of its nanoscale properties and for the further improvement of its overall piezoelectric properties.

Ceramic powders with the composition $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_3$ were synthesized by mixing the corresponding carbonate and oxide raw powders. The attritor-milled, dried, and sieved powders were calcined at 750 °C for 5 h and afterwards milled, dried, and sieved again. Green bodies prepared by uniaxial and cold-isostatic pressing were sintered at 1075 °C for 1–8 h in air. With the given parameters abnormal grain growth occurred during sintering, which resulted in grains larger than 50 μm. This was necessary, because conventionally prepared KNN ceramics contain grains with maximum sizes of only 5 μm. Grains of that size or smaller have only a few domains and therefore do not show a domain structure suitable for analysis.

Our x-ray diffraction analysis of KNN samples indicate that the composition $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O_3$ is within the tetragonal/orthorhombic morphotropic phase boundary (MPB), as found in Ref. \textsuperscript{2}. Samples with a small grain size are predominantly orthorhombic with a distortion of approximately 1% to the cubic phase, but with increasing annealing time and abnormal grain growth, the ratio of the tetragonal/orthorhombic phase content increases significantly.

While the existence of domains in KNN has already been indicated by TEM studies,\textsuperscript{9} our domain structure of a large KNN grain, shown in Fig. 1, was imaged with piezoresponse force microscopy (PFM). This scanning probe microscopy (SPM) technique is a very powerful tool for imaging ferroelectric domain structures, which has been demonstrated by imaging ferroelectric domains in various ferroelectric materials, e.g., PZT and BaTiO$_3$.\textsuperscript{10–13} With our setup (Dimension 3000, nanoscope IV, Veeco instruments) the polished surface of a KNN ceramic was scanned with a conductive SPM probe (PPP-EMF Nanosensors, Switzerland; length: 228 μm, thickness: 2.0 μm, width: 27 μm, resonance frequency: 70 kHz, spring constant: 2.8 N/m) in

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![FIG. 1. (Color online) PFM images in three-dimensional (3D) relief structure. (a) $P_{||}$: in-plane PFM and (b) $P_{\perp}$: out-of-plane PFM.](image-url)
order to collect images of the topography, the y component $P_y$ (in-plane PFM signal), and the z component $P_z$ (out-of-plane PFM signal) of the spontaneous polarization vector $\mathbf{P}_s$.

In both images especially in the $P_y$ image, which shows a better signal to noise ratio due to specific measuring conditions, a distinct domain pattern is observed. Domain walls are usually restricted to certain crystallographic orientations depending mostly on the crystallographic structure of the compound.\textsuperscript{14,15} At the MPB of KNN we have to consider both tetragonal and orthorhombic structures. In the tetragonal system there are six $\mathbf{P}_z$ with the following directions: [100], [100], [010] (cf. right unit cell of Fig. 2), [010], [001], and [001]. There exist only six different crystal planes that can form domain walls between two adjacent domains with rectangular arranged polarization vectors. If pseudocubic axes are used, which is done here and in the following discussion for simplicity, these 90° domain walls are given by the six crystallographic planes of \{110\} [e.g., (110), drawn in the center unit cell of Fig. 2]. Additionally, there also exist 180° domain walls, which are restricted only to be parallel to $\mathbf{P}_s$ and therefore do not necessarily consist of crystallographic planes.\textsuperscript{16}

The orthorhombic system provides twelve possible $\mathbf{P}_z$ in all \{110\} directions, which are [110], [101] (cf. left unit cell of Fig. 2), [101], [011], [110], [101], [101], [011], [011], and [110]. The angles between two polarization vectors for KNN can be 180° and 90° as in a tetragonal system or 120° and 60°, as described in Refs. 17 and 18 for orthorhombic KNbO$_3$ crystals. Uncharged domain walls, at which adjacent polarization vectors are arranged “head to tail,” are limited to \{100\} planes for 90° and \{110\} for 120° domain walls. For 60° domain walls the indices depend on piezoelectric and/or electrostrictive coefficients.\textsuperscript{14} 180° domain walls are again restricted only to be parallel to the respective polarization vectors.

For analysis of the KNN domain structure presented in Fig. 1, we take a closer look at the very well defined periodic pattern slightly left of the center of the image. This pattern contains two broad strips of domains with a substructure of narrow V-shaped domains. A sketch of this structure with the results of the following characterization of the pattern is given in Fig. 3. The two broad strips have $P_y$ [Fig. 1(a)] and $P_z$ [Fig. 1(b)] components of opposite sign and, as a result, are assigned with opposing $\mathbf{P}_s$. The domains are separated by a 180° domain wall parallel to the vectors. By assuming that this domain wall is formed by a \{100\} plane, for example, (010), it is obvious that these big domains are separated by (110) domain walls from the narrow V-shaped domains, in our example, (110) and (110). The angle between these two planes which is close to 90° shows that the imaged surface plane is almost parallel to (010) and that the $\mathbf{P}_s$ of the broad strips are [101] and [101] of the orthorhombic system. The $P_y$ and $P_z$ components of the narrow V-shaped domains are approximately zero and as a result the polarization must be in the $P_x$ direction. It is not possible to assign an orthorhombic $\mathbf{P}_s$ to these domains; whereas assigning [010] from the tetragonal system fits perfectly well, considering that at the MPB both systems can exist side by side and that in both crystallographic systems \{110\} planes are permissible domain walls. It must be noticed that even though some of our assumptions could be wrong, the domain pattern can only be explained if $\mathbf{P}_s$ from both the orthorhombic and the tetragonal sets are used. In Fig. 4 it can be seen that the analyzed domain structure of Fig. 1 is a typical pattern, which does not arise due to unusual circumstances such as, for example, local strains, because the analyzed pattern is repeated at the right border of the image (encircled area).\textsuperscript{18}

The (110) and the (110) planes, which form the domain walls between the tetragonal and the orthorhombic polarized domains, are of special interest. The tetragonal $\mathbf{P}_s$ [010] shows an angle of 54.7° and the orthorhombic $\mathbf{P}_s$ [101] shows an angle of 35.3° towards the domain wall (Fig. 2) and similar to all other $\mathbf{P}_s$ in Fig. 3 they are arranged head to tail. In order to estimate the residual surface charge on the domain wall the polarization data from KNbO$_3$ (Ref. 19) is used. For the norms of the $\mathbf{P}_s$ we get $|P_x^{\text{orth}}[101]|$ = 32.5 C m$^{-2}$ and $|P_x^{\text{tet}}[010]|$ = 30 C m$^{-2}$. Projecting these $\mathbf{P}_s$ on the (110) domain wall gives a residual net charge of 6 C m$^{-2}$. For KNN the net $P_x$ is likely to be of the same

Fig. 2. Three unit cells of a perovskite with (110) domain wall separating the proposed tetragonal (right unit cell) and orthorhombic phases (left unit cell) in KNN.
order and could even be zero, but unfortunately there is no data available yet.

The detailed orientation of all \{100\} and \{110\} planes was calculated using the knowledge of the postulated orientation of the (010), (110), and (110) planes of the above analyzed domain structure of Figs. 1–3. Measuring the angles between the (110) and (010) planes and between the (010) and (110) planes giving 42.5° and 43.5°, respectively (see Fig. 4), is sufficient to calculate the intersection of all domain walls with the sample surface, as shown in detail in Ref. 20. Mathematically this is performed by a rotation \( R_i(\psi, \theta, \varphi) \) (\( \psi, \theta \), and \( \varphi \) being the Euler angles) of the orthogonal crystallographic system \( e_i \) into the orthogonal surface plane system \( e_j \) \((i=1-3)\). The sample surface is defined as the (001) plane in the surface plane system. The result gives \( \theta=158.5° \) and \( \varphi=7.5° \), whereas \( \psi \) corresponds to the rotation around the [001] axes in the surface plane system and can be set to zero as the measured angles between the planes are independent of \( \psi \). The orientation of the intersecting line of the \{100\} and \{110\} planes was plotted and matched to some domain walls of the pattern in Fig. 4. There are some small deviations between the calculated and imaged domain walls which we mainly attribute to the cubic unit cell which was used in the calculation instead of the approximately 1% distorted unit cells of the tetragonal or orthorhombic crystal structures. Not all the imaged domain walls could be attributed to calculated planes, which means that they are either 60° (orthorhombic system) or 180° domain walls, or, in particular, charged 180° domain walls that are not restricted at all. However, the calculation verifies the structure given in Fig. 3 and aids to further understanding of the pattern.

We were able to image domains in KNN with PFM. From x-ray diffraction analysis, we know that our KNN consists of tetragonal and orthorhombic phases. Knowing this we were able to analyze a domain pattern as an interwoven structure of coexisting tetragonal and orthorhombic domains in one grain. Our evaluation proposes that tetragonal and orthorhombic domains are separated by \{110\} planes. This applies to the extraordinary ferroelectric properties of KNN and other materials at their MPBs. Our analysis is not an unambiguous proof of the structure but it gives a consistent interpretation of the domain structure imaged with PFM. Open issues are whether the tetragonal/orthorhombic domain walls are charged or not. Other parts of the imaged domain structure should be analyzed in more detail as well. On the other hand we would like to point out that no analysis of a domain structure of a ferroelectric material near the MPB—including PZT materials—has been done before. This insight should provide a basis for the understanding of KNN domain patterns, for the theoretical understanding of MPBs, and should therefore aid the developing of KNN as a ferroelectric material.