Investigation of lead-free piezoceramics $\text{Bi}_{0.5}(\text{Na}_{1-x}\text{K}_x)_{0.5}\text{TiO}_3$ with scanning probe microscope

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Abstract. Lead-free piezoceramics $\text{Bi}_{0.5}(\text{Na}_{1-x}\text{K}_x)_{0.5}\text{TiO}_3$ ($x=0.00$~$1.00$) has been investigated by using scanning probe microscope with lock-in technique. Superior to other bulk measurements, this technique gives not only the topological but the piezo/ferroelectric properties without any convolutions. By the appropriate selection of lock-in channel and spectra analysis, we can get the trend of the magnitude and phase of polarization with different $x$ value. And this enables us to find the morphotropic phase boundary successfully.

Ferroelectric materials have a spontaneous polarization and in which the direction of the polling can be changed by an external electric field. In addition, all of ferroelectric materials show the piezoelectric effect. By these unique properties, it has attracted widespread attentions for the application. The switchable remnant polarization can be applied to ferroelectric memory devices and the piezoelectricity has been used for mechanical sensors and actuators.

As is well known, the most widely used piezoelectric/ferroelectric material is $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) ceramics which has various advantages for the application. It has high transition temperature (Curie temperature, $T_c$), high piezoresponse and high electromechanical coupling factor. What is better, the fabrication of PZT needs relatively low temperature and low cost. Nevertheless, PZT has a critical drawback, that is, it contains lead which has been expelled from many applications owing to its...
toxicity. Thus many researchers have made efforts to seek for lead-free piezo/ferroelectrics as an alternative for PZT [1, 2].

\( \text{Bi}_{0.5}(\text{Na}_{1-x}\text{K}_x)_{0.5}\text{TiO}_3 \) (BNKT-x), as one of the candidate for lead-free piezoceramics, is promising material exhibiting good piezoelectricity, high electromechanical coupling factor, high \( T_c \) and low sintering temperature. BNKT, just as PZT, is composed of two different structures, rhombohedral \( \text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3 \) (BNT) and tetragonal \( \text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 \) (BKT) structure [3, 4]. It is well known that many physical properties of piezoceramics reach their maximum or minimum at the morphotropic phase boundary (MPB) where the two structural phases coexist [5, 6].

The ways to find MPB of hetero-structural material are rather experimental than theoretical. As same with PZT, BNKT shows maximal physical properties around the MPB. Thus, the MPB of a piezoceramics has been found through measurement of enhancement of dielectric and piezoelectric properties [7, 8]. And many researches revealed that the MPB of BNKT exists around \( x=0.15-0.20 \). In this study, instead of conventional bulk measurement, we investigate piezoelectric and ferroelectric properties of BNKT ceramic using scanning probe technology, especially around MPB and suggest a new way of finding MPB with a probe microscope.

The BNKT, was prepared by a conventional ceramic fabrication technique. Reagent-grade \( \text{Bi}_2\text{O}_3 \), \( \text{Na}_2\text{CO}_3 \), \( \text{K}_2\text{CO}_3 \) and \( \text{TiO}_2 \) powders were ball-milled with zirconia balls for 20 hours. The mixed powders were dried and calcined at 800 \(^\circ\text{C}\) for 2 hours. The calcined mixtures were compacted into disk samples with a pressure of 50 MPa, and sintered at 1150\(^\circ\text{C}\) for 2 hours in the ambient air. The samples were polished and thermally etched at 1150\(^\circ\text{C}\) for 1hour.

Experiment has been performed using a commercial atomic force microscope Autoprobe CP (Park Scientific Instrument) with a lock-in amplifier SR830 (Standford Research). An ac modulation voltage is applied between the tip and the bottom of sample, and then we obtain a domain image as well as surface morphology simultaneously using a lock-in technique [9].

The local polarization measured through lock-in amplifier can be written as \( P = Pe^{i\theta} \); the magnitude \( P \) exhibiting the quantities of ferroelectricity/piezoelectricity such as the remnant/saturated polarization and the piezoresponse can be seen in amplitude image obtained from the absolute value channel of lock-in amplifier. And \( \theta \) measured in phase image denotes the qualities of physical properties such as the average angle of polarization and the phase alignment of electric dipoles.

When the tip is highly biased, most of dipoles near the surface are polarized in the normal direction of the surface and the characteristic of polarization differs with one another as the composition \( x \) varies. Figure 1 shows selected images of BNKT obtained by highly biased tip. Figure 1 (a), (b) and (c) are topographic images of BNKT-0.10, 0.17 and 0.25 respectively, showing grain size increases slightly with \( x \).
Figure 1. Topographic image of BNKT-0.10 (a), 0.17 (b) and 0.25 (c) and the corresponding amplitude $P$ images (d), (e) and (f). Scan size 25 $\mu m^2$, tip bias 100V.

The corresponding amplitude images are shown in Fig. 1 (d), (e) and (f) which follow same structure as is shown in topography owing to the grain boundaries. The significant distinctions among these samples are shown in Fig. 2 (a), the spectra of amplitude images. The peak positions of the BNKT move to right as $x$ increase up to $x=0.17$ while it becomes low after $x$ passes 0.17. This reveals that the local polarization of BNKT-0.17 is the highest, and implies that its composition ratio is the nearest to the MPB. As is shown in Fig. 2 (b), the plot of most probable value of $P$, there is noticeable enhancement of polarization around $x=0.17$.

Selected phase images for BNKT-15, 17 and 20 obtained by high voltage tip are shown in Fig. 3 (a), (b) and (c). Because most of electric dipoles are aligned along the direction of field, the phase signal therefore seems to be coherent. Though the degree of coherence seems to be almost same at these images, the spectra of phase images as shown in Fig. 3 (d), (e) and (f) show some differences. Depending on the composition, the width and the height of the distribution differ while the peak
positions are almost same. When these spectra are overlapped, these distinctions are clearly shown (Fig. 4 (a)). While the distribution becomes narrower for the samples of smaller x than 0.17, it begins to spread out crossing x=0.17. This indicates that the individual dipoles are aligned well around x=0.17 and suggests again that the MPB is near by x=0.17. Figure 4 (b), the plot of the full width at half maximum (FWHM), certifies this expectation.

Figure 3. Phase images of BNKT-0.15 (a), 0.17 (b) and 0.20 (c). Scan size 25 μm², tip bias 100V. Corresponding spectra of phase images (d), (e) and (f) show the distribution of BNKT-0.17 takes narrow shape (e) while the others are not.

Figure 4. (a) Phase distributions for selected samples. The distribution curve for x=0.17 takes the sharpest shape and as the composition goes away from x=0.17, the distribution becomes broad. (b) FWHM of θ distribution reveals that the phase of the electric dipole is most coherent at x=0.17.

Most of ferroelectric properties are compatible with piezoelectric properties. Thus, ferroelectric writing capability, the typical ferroelectricity, is expected to be excellent around MPB. To examine the property, we scanned the area of 4 μm² with negatively biased tip and wrote a square of 1 μm² inside of the area with positive bias. Figure 5 (a), (b) and (c) are the results of this procedure on x=0.00, 0.17 and 0.20, respectively. As is clearly shown, only the BNKT-0.17 shows distinguished contrasts (Fig. 5 (b)) while the others show faint boundaries (Fig. 5 (a) and (c)).
In conclusions, we investigated lead-free piezoceramics BNKT-x using probe microscope with high-voltage tip. By appropriate selection of lock-in channel and spectra analysis, we can get the trend of the magnitude and phase of polarization with different x value and this reveals the existence of the MPB around x=0.17. Though the scanned area is less than 30 $\mu$m$^2$, any statistical errors are not found and the result agrees well with former results. Superior to conventional bulk measurement, this method provides additional information of the sample such as surface morphology and ferroelectric writing capability.

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