

Domain structure of orthorhombic (Li,K,Na)NbO₃ ceramics

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The domain structure of orthorhombic Li_{0.02}(K_{0.45}Na_{0.55})_{0.98}NbO₃ [LiKNN] ceramics was investigated. Faceted interfaces and abnormal grain growth was observed in the microstructure of these LiKNN ceramics, which consisted of both large and small grains. A rectangular grain surrounded by faceted grain boundaries was observed, and the bright-field image and SAD pattern indicated that these boundaries belong to {100} planes. 90°, 60°, 180°, and S-type domain walls were observed in the grains as well. In fine grains, simple lamellar twinning was predominant; in coarse grains, twinning with a band structure released the elastic stress.

Key words: KNN, Orthorhombic, Ceramics, Domain, Grain size.

Introduction

(K_{1-x}Na_x)NbO₃ (KNN), a compound of the Morphotropic Phase Boundary (MPB) composition in the (1-x)KNbO₃-xNaNbO₃ solid solution, is recognized as one of a promising host material for preparing lead-free piezoelectrics. Many researchers have attempted to improve their piezoelectric properties by way of the chemical modification of lead-free ferroelectrics [1]. Recently, it has been reported that KNN ceramics obtained by replacing the A and/or B sites give high piezoelectric properties. In particular, a solid solution of KNN with different end members containing Li (such as LiSbO₃ [2, 3, 4], LiNbO₃ [5, 6], LiTaO₃ [7], etc. [8]) has been reported, exhibiting a thickness coupling coefficient of $k_t > 50\%$ and a converse piezoelectric coefficient of d_{33} around 200 pm/V for the Li substituted ceramics.

Intrinsically, these electrical properties are primarily determined by the ferroelectric domain structure and by domain-wall mobility. In order to understand the change in these electrical properties, it is of vital importance to study the relation between the domain structure and grain size [9]. Arlt *et al.* [10] have shown that the equilibrium domain width is dependent on the grain size and decreases for grain sizes (a) < 10 μm, and is effectively constant at a > 10 μm. They explained that the domain size effects gave rise to the high dielectric constant of fine-grained BaTiO₃.

The domain structures of BaTiO₃ and PbTiO₃ have been extensively investigated, due to their simple structure (tetragonal structure) and because of their existence in a ferroelectric state at room temperature. Although several authors have reported the domain structures of a KNbO₃ single crystal, the literature on the domain structures of

polycrystalline orthorhombic KNN is limited. The formation of domains in ceramics is different from that of single crystals because the domain structure of a grain is formed under clamped conditions, whereas that of a single crystal is free.

The low temperature orthorhombic unit cell of KNbO₃ can be described as a distortion of the cubic cell. Commonly, the directions and planes in the orthorhombic phase refer to the axes of the original cube [11]. In the orthorhombic phase, the polarization vector lies along one of the face diagonals of the original cube; a number of domains can exist in the angle between polarization vectors of adjacent domains, being 60°, 90°, 120° and 180° [13, 14].

In this study, the domain structures of orthorhombic KNN ceramics were observed, and the grain size effects on domain patterns were investigated.

Experimental

Li_{0.02}(K_{0.45}Na_{0.55})_{0.98}NbO₃ [LiKNN] ceramics were prepared using a solid state reaction method. The starting materials used in this study were K₂CO₃, Na₂CO₃, Nb₂O₅, Li₂CO₃ of above 99% purity. The powders were mixed in a polyethylene (HDPE) bottle for 24 h using ZrO₂ balls in ethyl alcohol. The mixed powders were calcined at 850 °C for 5 h in air. These powders, milled with a 5 wt% polyvinyl alcohol (PVA) aqueous solution, were uni-axially pressed into disks of 10 mm diameter at a pressure of 100 Mpa and were subsequently sintered at 1050 °C for 5 h in air. The samples were poled by applying a DC field of 40 kV/cm at 120 °C for 30 minutes. The density of prepared samples was measured by the Archimedes method. Crystal structures were determined by XRD analysis. To investigate the piezoelectric properties, the resonant and anti-resonant frequencies were measured by an impedance analyzer (Agilent 4294A) according to IEEE standards. The electro-mechanical coupling factor (kp) and mechanical quality factor (Qm) were then calculated. A commercial Piezo Force

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Microscope (PicoTech, PICOStation) was used to observe surface domain structures on polished samples by contact topography and piezoresponse modes. The scanned head allowed a maximum scan area of $40 \mu\text{m} \times 40 \text{mm}$. Commercially available Pt-coated conductive silicon cantilevers with a tip radius of 40 nm were used. Their spring constants lie between 1.0 and 5.0 N/m with a resonance frequency of approximately 50-70 kHz. The TEM experiment was carried out on a JEM-200CX operated at 200 kV.

Results and Discussion

The piezoelectric properties and XRD pattern of samples used in this study are shown in Table 1 and Fig. 1. The X-ray powder diffraction pattern of the solid solution confirmed the formation of the single phase as having a perovskite structure. Ahtee and Glazer [14] reported the crystal structure of KNN in the range of 30-50 mol% KNbO_3 is monoclinic of Pm. However, our Rietveld analysis suggests that the crystal structure of KNN in the range of 40-50 mol% KNbO_3 is a space group Bmm2 and the octahedral tilting angles are changed gradually with the KNbO_3 content. It is difficult to distinguish between the orthorhombic and monoclinic phase for KNN ceramics. Thus, we assumed that the space group of the $\text{Li}_{0.02}(\text{K}_{0.45}\text{Na}_{0.55})_{0.98}\text{NbO}_3$ ceramic was Bmm2, which implied that the domain structure of the $\text{Li}_{0.02}(\text{K}_{0.45}\text{Na}_{0.55})_{0.98}\text{NbO}_3$ ceramic was similar to that of KNbO_3 .

Fig. 2 shows the surface morphology of the $\text{Li}_{0.02}(\text{K}_{0.45}\text{Na}_{0.55})_{0.98}\text{NbO}_3 + 0.5 \text{ wt.}\% \text{ ZnO}$ ceramic. Facet interfaces and abnormal grain growth were observed, which are typical characteristics of KNN ceramics. The domains can be described as twinned areas in the crystal with the domain walls being the twinning planes. The

Table 1. Piezoelectric properties of $\text{Li}_{0.02}(\text{K}_{0.45}\text{Na}_{0.55})_{0.98}\text{NbO}_3 + 0.5 \text{ wt.}\% \text{ ZnO}$ ceramics.

Relative density	96.12%
Electromechanical coupling factor (k_p)	42.5%
Mechanical quality factor (Q_m)	201
Phase transition temperature (T_{0-t})	176 °C

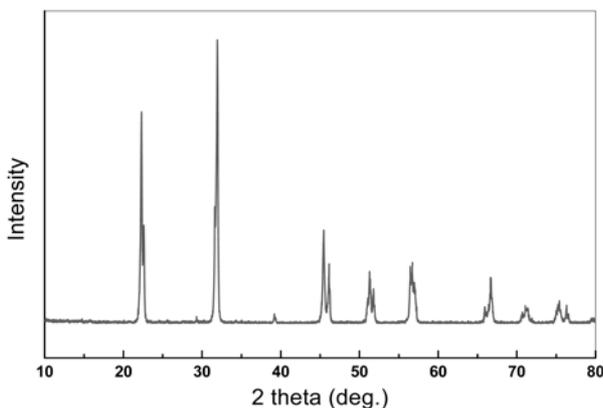


Fig. 1. XRD pattern of a $\text{Li}_{0.02}(\text{K}_{0.45}\text{Na}_{0.55})_{0.98}\text{NbO}_3 + 0.5 \text{ wt.}\% \text{ ZnO}$ ceramic sintered for 5 h at 1050 °C.

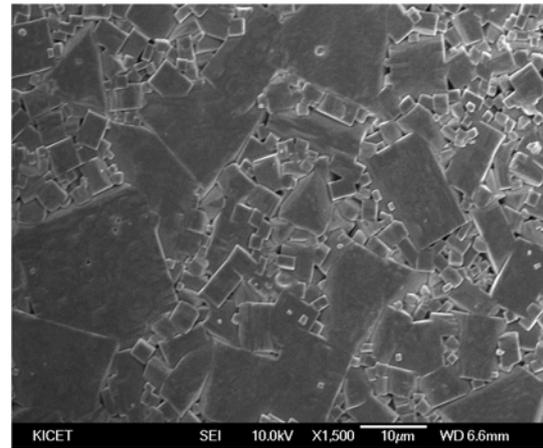


Fig. 2. Surface microstructure of $\text{Li}_{0.02}(\text{K}_{0.45}\text{Na}_{0.55})_{0.98}\text{NbO}_3 + 0.5 \text{ wt.}\% \text{ ZnO}$ ceramics sintered for 5 h at 1050 °C.

orthorhombic structure leads to more complicated patterns of domain distribution than those of tetragonal structures composed of only two types of domain walls, a 90° and 180° domain wall. In the case of a 90° domain in the orthorhombic structure, the domain walls are oriented parallel to the $\{001\}_{pc}$ planes, whereas in the case of 60° domains, their orientation is parallel to the $\{110\}_{pc}$ planes. The subscript pc indicates that the orientations refer to the original cubic cell [11]. In addition to these commonly observed walls, an S wall can appear in a Bmm2 crystal structure such as in KNbO_3 and KNN [11, 12]. As a consequence of the crystallographic analysis, domain walls with three types of angles are present in KNN. A domain wall with an angle of 18.4° was assigned to the S-type walls (120° domain walls) of the $(331)_{pc}$ plane [1, 13], while each domain wall with 90° and 45° was assigned to the 90° (the $(100)_{pc}$ plane) and 60° (the $(110)_{pc}$ plane) domain walls, respectively [1, 15].

In order to analyze the domain structure of ceramics, it is important to investigate the orientation of the grains. Fig. 3 shows a transmission electron micrograph of a

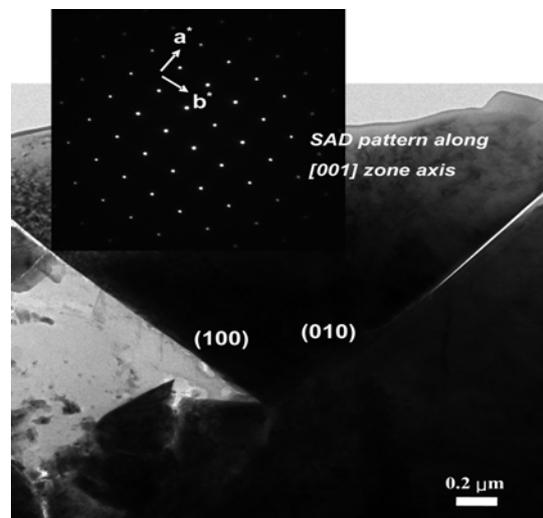


Fig. 3. TEM bright field image and SAD pattern of a grain with faceted boundaries.

rectangular grain surrounded by faceted grain boundaries and a SAD pattern along the [001] zone axis. Both the bright-field image and the SAD pattern indicate that the faceted boundaries of the rectangular grain belong to {100} planes.

An Atomic Force Microscope (AFM) micrograph and the Piezo Force Microscope (PFM) image of a rectangular grain are shown in Fig. 4. As noted earlier, 90° domain walls, 60° domain walls and S-type walls may be identified by the angle between a domain wall and a grain boundary. 60° and 90° domain walls and S-type walls intersect the grain boundaries ({100} planes) with an incline of 0° or 90°, 45° and 18.4°, respectively. All were observed together in a grain as shown in Fig. 4.

Numerous polycrystalline ceramics, which undergo ferroelectric phase transitions have a simple lamellar twinning or a banded twin structure. In fine-grained ceramics, the deformed grains adjust in two dimensions by simple lamellar twinning; in coarse-grained ceramics, the twinning with a band structure allows for grain adjustment in the third dimension [16]. Fig. 5 shows simple lamellar twinning in a 10 × 14 μm grain. The 90° and 180° domains are distributed predominantly, and the width of the 90° domain

is 200 nm. The domain size in ferroelectric materials is a state of equilibrium between the energy of the domain walls and the energy of those electric and elastic fields created by the spontaneous polarization and strain. Arlt [16] suggests that the twin width (*d*) depends on the grain size (*g*), $d \propto g^{1/2}$. This relationship holds for all types of simple lamellar twinning in ceramics, in which the twin wall energy and the elastic deformation energy determine the minimum. It does not depend on the type of interface which separates the twins. This relationship has been confirmed in fine-grain BaTiO₃ ceramics for grain sizes between 1 and 10 μm, which may be valid for KNN ceramics. In a coarse KNN grain, the banded twin structure was observed as shown in Fig. 6. The banded twin structure has the ability to transform to the simple lamellar twin structure by stress relief [16]; it can be understood that the banded twin structure contains a higher elastic energy than that of the simple lamellar twin structure since the absolute strain energy increases with grain size ($g \propto g^3$). Banded twin structures were also observed in a 10 × 13 μm grain. It is assumed that the boundary in grain size between the simple lamellar twin structure and the banded twin structure is in the range of 10-13 μm.

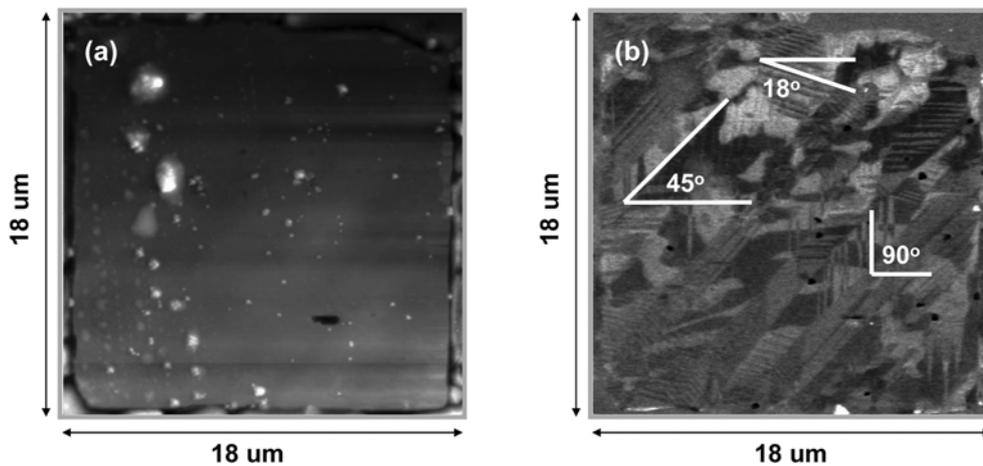


Fig. 4. (a) Topograph and (b) PFM image of a LiKNN ceramic showing the orientations of domain walls with {100} grain boundaries.

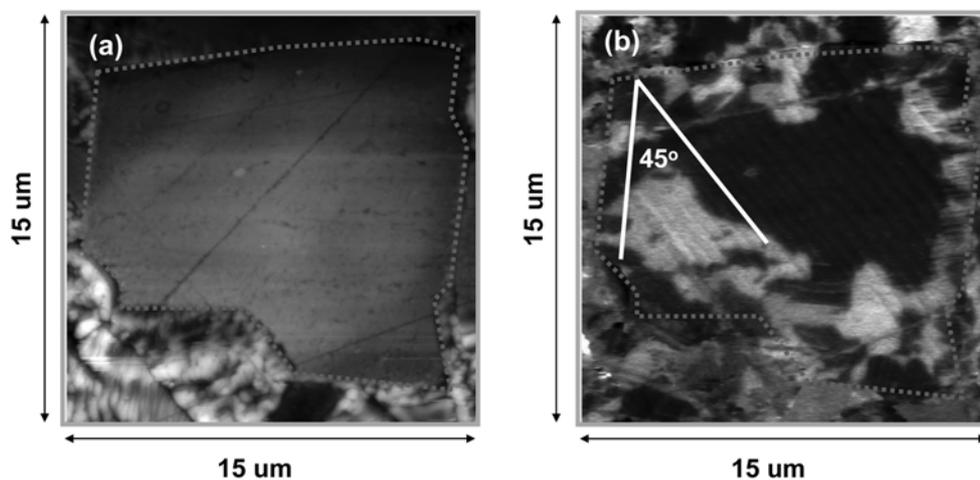


Fig. 5. Simple lamellar twinning (a) Topograph and (b) PFM image.

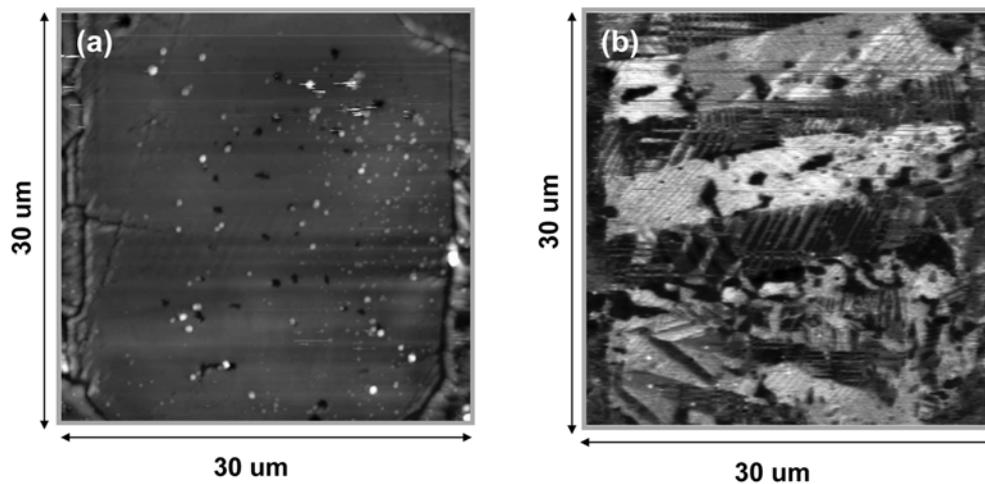


Fig. 6. Banded twin structure (a) Topograph and (b) PFM image.

We are also attempting to investigate the grain size effect on the domain size in KNN ceramics. Since different domain sizes exist in a grain, and the domain width was revealed according to the angle between the polarization direction and surface orientation, it was difficult to determine the domain size accurately. However, it was obvious that the domain size decreased with a decrease in the grain size as for BaTiO₃ or PbTiO₃.

Conclusions

A Li_{0.02}(K_{0.45}Na_{0.55})_{0.98}NbO₃ ceramic was prepared using a solid state reaction method. A rectangular grain surrounded by faceted grain boundaries was observed and the bright-field image and SAD pattern indicated that the faceted boundaries of a rectangular grain belong to {100} planes. All the 90° domain, 60° domain, 180° domain and S-type walls were observed in a grain. In fine grains, simple lamellar twinning is predominant; in coarse grains, twinning with a banded structure releases the elastic stress.

Acknowledgments

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References

1. S. Wada, K. Muraoka, H. Kakemoto, T. Tsurumi and H. Kumagai, *Mater. Sci. and Eng. B* 120 (2005) 186-189.
2. Y.H. Kim, D.Y. Heo, W.P. Tai and J.S. Lee, *J. Korean Ceram. Soc.* 45 (2008) 363-367.
3. G. Zang, J. Wang, H. Chen, W. Su, C. Wang, P. Qu, B. Ming, J. Du, L. Zheng, S. Zhang and T.R. Shrout, *Appl. Phys. Lett.* 88 (2006) 212908.
4. J. Wu, D. Xiao, Y. Wang, W. Wu, B. Zhang, J. Li and J. Zhu, *Scripta Materialia* 59 (2008) 750-752.
5. Y. Wang, J. Wu, D. Xiao, J. Zhu, P. Yu, L. Wu and X. Li, *J. Alloys Comp.* 459 (2008) 414-417.
6. Y. Guo, K. Kakimoto and H. Ohsato, *Appl. Phys. Lett.* 85 (2004) 4121-4123.
7. Y. Guo, K. Kakimoto and H. Ohsato, *Mater. Lett.* 59 (2005) 241-244.
8. F. Rubio-Marcos, P. Ochoa and J.F. Fernandes, *J. Eur. Ceram. Soc.* 27 (2007) 4125-4129.
9. S.B. Ren, C.J. Lu, J.S. Liu, H.M. Shen and Y.N. Wang, *Phys. Rev. B* 54 (1996) 14337-14340.
10. G. Arlt, D. Hennings and G. de With, *J. Appl. Phys.* 58 (1985) 1619-1625.
11. K.G. Deshmukh and S.G. Ingle, *J. Phys. D: Appl. Phys.* 4 (1971) 124-132.
12. A. Bellou and D.F. Bahr, *Materials Characterizations* 59 (2008) 688-692.
13. E. Wiessendanger, *Czech. J. Phys. B* 23 (1973) 91-99.
14. M. Ahtee and A.M. Glazer, *Acta Cryst. A* 32 (1976) 434-446.
15. J. Fousec, *Czech. J. Phys. B* 21 (1971) 955-968.
16. G. Arlt, *J. Mater. Sci.* 25 (1990) 2655-2666.