



Epitaxial Sr-Bi-Ta Oxide Films of Cubic Fluorite-Like Structure

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Abstract. Epitaxial Sr-Bi-Ta oxide films of a cubic fluorite-like structure were grown by pulsed laser deposition. As the laser fluence increased, the lattice constant decreased. It was revealed that the Ta ion concentration was closely related with the change in the lattice constant. From selected area electron diffraction measurements, it was observed that the films had a superstructure which seemed to come from ordering of metal ions.

Keywords: film, pulsed laser deposition, $\text{SrBi}_2\text{Ta}_2\text{O}_9$, fluorite, X-ray diffraction, selected area electron diffraction

1. Introduction

In recent years, there have been lots of interests in ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) thin films [1]. Since SBT has a high fatigue resistance compared to other ferroelectric materials such as $(\text{Pb,Zr})\text{TiO}_3$, many groups tried to use SBT thin films for nonvolatile random access memory applications [1]. SBT is also known to have good electrical properties, such as a low coercive field and a low leakage current [2]. However, it has a high deposition temperature (typically above 700°C), which can cause severe problems in actual fabrication of real devices. Therefore, reducing the deposition temperature is one of the most important issues in SBT thin film applications. Unfortunately, the efforts to grow the SBT films at low temperature have not been successful, since several phases have been reported to appear at a low temperature [3]. Table 1 shows the summary of phases which have been reported to appear in the low temperature deposited films.

A few groups, including our group, reported that the Sr-Bi-Ta oxide appeared at the low temperature seemed to have a structure very similar to so-called the cubic fluorite [3,4,8]. However, this fluorite-like phase has rarely been investigated and its properties

have not been well understood yet. Moreover, its reported properties were somewhat varied from one group to another. For an example, the reported values for the lattice constants of the fluorite-like phase are varied between 5.37 \AA and 5.446 \AA . Therefore, more systematic investigations on this phase are highly desirable.

To resolve the controversies on existence and properties of the Sr-Bi-Ta oxide films grown at a low temperature [6–8], we systematically investigated the Sr-Bi-Ta oxide films deposited at 550°C . In this paper, we will provide numerous evidences that our Sr-Bi-Ta oxide films are composed of the fluorite-like phase without other impurity phases. We will also report on how laser fluence will affect chemical stoichiometries and lattice constants of the films. In addition, we will show our new finding on an ordering phenomenon in the epitaxial Sr-Bi-Ta oxide film, which was observed by the selected area electron diffraction (SEAD) measurements.

2. Experimental

Epitaxial Sr-Bi-Ta oxide films with the fluorite-like structure were grown by pulsed laser deposition (PLD) on LaAlO_3 (001) substrates with 3rd

Table 1. Reported phases in Sr-Bi-Ta oxide films deposited at low temperature

	Crystal structure	Lattice constant (Å)	Reference	Characteristics
Fluorite	Fcc	$a = 5.446$ $a = 5.4$	[3] [4]	MO_2 ($M = Sr, Bi, Ta$)
Bi-deficient pyrochlore	Cubic	$a = 10.51$	[5]	
Strained $SrBi_2Ta_2O_9$	Orthorhombic	$a = 5.361, c = 26.83$	[6]	$c = 5a, a$ -axis oriented
Impurity phase	Cubic	$a = 5.54$	[7]	δ - Bi_2O_3
Epitaxial Sr-Ta-Bi oxide	Fcc	$a = 5.39$	[8]	Fluorite-like structure

harmonics (wavelength: 355 nm) of a Q-switched Nd:YAG laser. The pulse duration time and the repetition rate of the laser were 6~7 ns and 10 Hz, respectively. The laser beam was focused onto a target through a lens and the distance between the target and the substrate was about 4 cm. To grow the Sr-Bi-Ta oxide films with the fluorite-like structure, a commercially available stoichiometric ceramic target of SBT was used. Before each deposition, the target was polished. This oxide layer was grown at oxygen partial pressure of 200 mTorr and substrate temperature of 550°C. Laser fluence was varied from 1.9 to 4.3 J/cm².

Structural properties of the films were investigated by X-ray diffraction (XRD) methods using the Cu K_α line. Orientations of the thin films were investigated by the XRD θ - 2θ scan method, and in-plane alignments were investigated by the XRD ϕ scan method. Further structural information was obtained from selective area electron diffraction (SAED) pictures, which were taken by a Philips CM20T/STEM microscope operating at 200 kV. The SAED specimens were prepared using a standard procedure of cutting, gluing, slicing, grinding, and ion milling. And, the SAED patterns were carefully analyzed to investigate structural relations between substrate and grown film. Chemical stoichiometries, i.e., metal ion ratios, of the Sr-Bi-Ta oxide films were measured by an electron probe microanalysis (EPMA), and their surface morphologies were investigated by an atomic force microscope (AFM).

3. Results and Discussion

3.1. Epitaxial Growth of the Films

Figure 1(a) shows the XRD θ - 2θ pattern of the Sr-Bi-Ta oxide films grown on LaAlO₃ (001) substrate at 550°C with the laser fluence of 2.7 J/cm². In addition to LaAlO₃ (001) peaks, there appear two

more peaks which can be indexed as fluorite-like structure (002) and (004) [8]. This shows that the films were highly oriented with their c -axes normal to the substrates. The lattice constant calculated from this XRD data was about 5.37 Å. [We also found that c -axis oriented epitaxial SBT films can be grown at an identical conditions but with a temperature higher than 650°C [8].] Figure 1(b) shows the XRD ϕ scan result of cubic fluorite-like structure {111} reflections. The XRD ϕ scan pattern

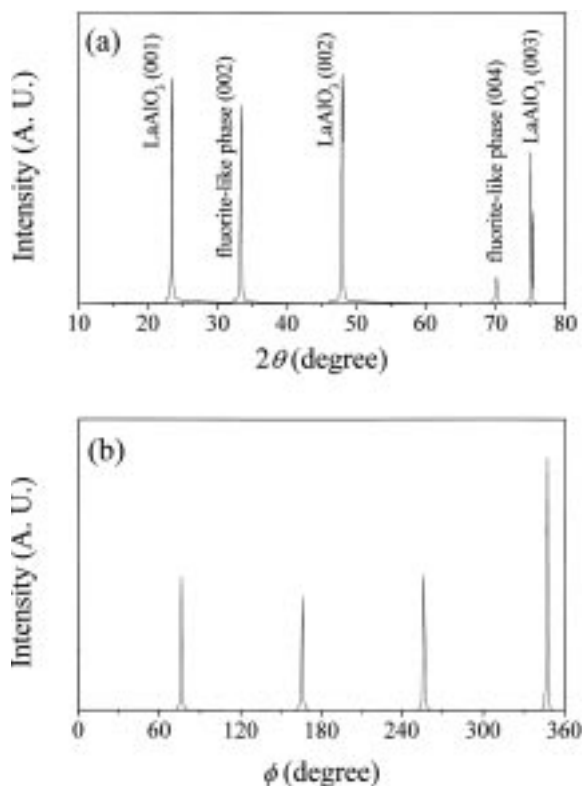


Fig. 1. (a) XRD θ - 2θ scan patterns and (b) XRD ϕ scan pattern of {111} reflection of the films grown on LaAlO₃ (001) substrates at 550°C.

clearly demonstrates a four-fold symmetry. From these results, we can say that the Sr-Bi-Ta oxide film was grown epitaxially.

3.2. Effects of Laser Fluence

To investigate physical properties more systematically, we deposited the Sr-Bi-Ta oxide films under numerous values of laser fluence. Figure 2 shows the XRD patterns of the Sr-Bi-Ta oxide films deposited under laser fluences of 1.9~4.3 J/cm². In spite of the differences in laser fluence, all of the deposited films were found to be epitaxial. The peaks located near the square symbol come from the LaAlO₃ (003) diffraction peak of the Cu K_β line. Estimated lattice constants for the Sr-Bi-Ta oxide films were found to be varied from 5.381 Å to 5.365 Å. As the laser fluence increases, the lattice constant of the fluorite-like phase decreases, as shown in Fig. 3(a).

It was revealed that the change of the lattice constant was closely related with relative metal ion

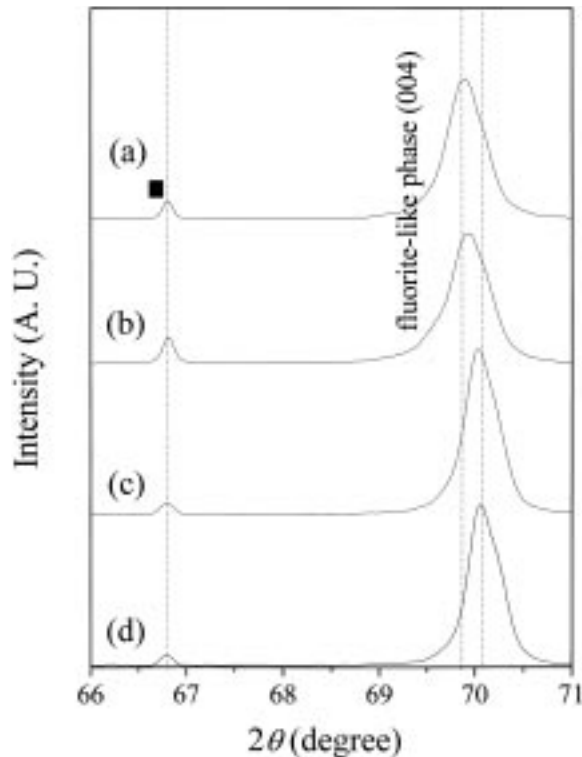


Fig. 2. XRD θ - 2θ scan patterns of the films grown on LaAlO₃ (001) substrates with the laser fluence of (a) 1.9 J/cm², (b) 2.7 J/cm², (c) 3.5 J/cm², and (d) 4.3 J/cm².

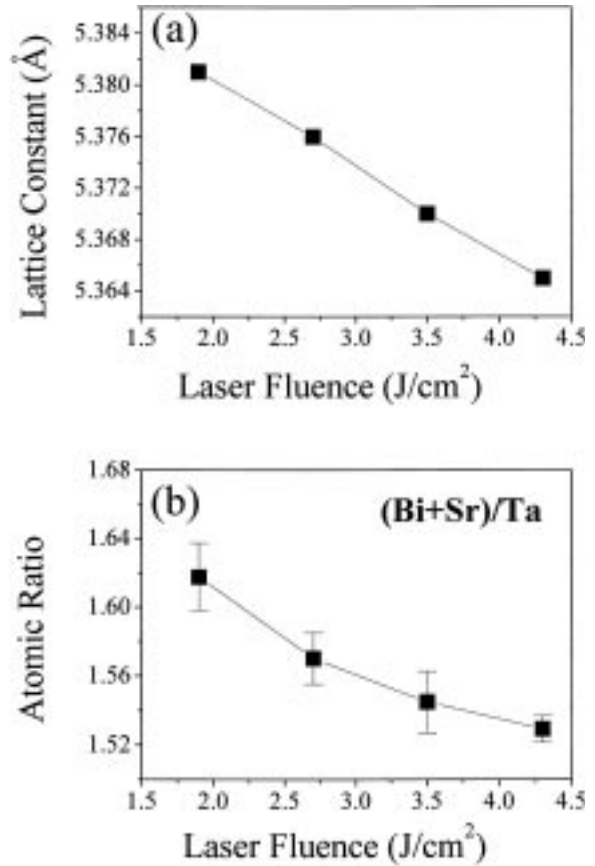


Fig. 3. Dependence of (a) the lattice constants and (b) the (Bi + Sr)/Ta ion ratios on the laser fluence.

ratio in the Sr-Bi-Ta oxide films. Figure 3(b) shows the relative change of (Bi + Sr) ions compared with Ta ions, which was measured from EPMA. As the laser fluence increases, the relative concentration of (Bi + Sr) ions decreases. The lattice constant change, shown in Fig. 3(a), can be ascribed to different ionic sizes of the metal ions in the cubic fluorite structure. Generally, the ideal cubic fluorite structure, whose chemical formula is MO₂ (M = metal ions), should have one equivalent metal site. Since the Ta⁵⁺ ion is much smaller than the Bi³⁺ and the Sr²⁺ ions [10], the increase of the Ta⁵⁺ ion concentration will effectively provide the decrease in the lattice constant.

Figure 4 shows the AFM image of the Sr-Bi-Ta oxide films deposited with various laser fluences. It is clearly observed that the surface morphology changes systematically with the laser fluence. As the laser fluence increases, the film surface becomes smoother. When the laser fluences were 1.9, 2.7, 3.5, and

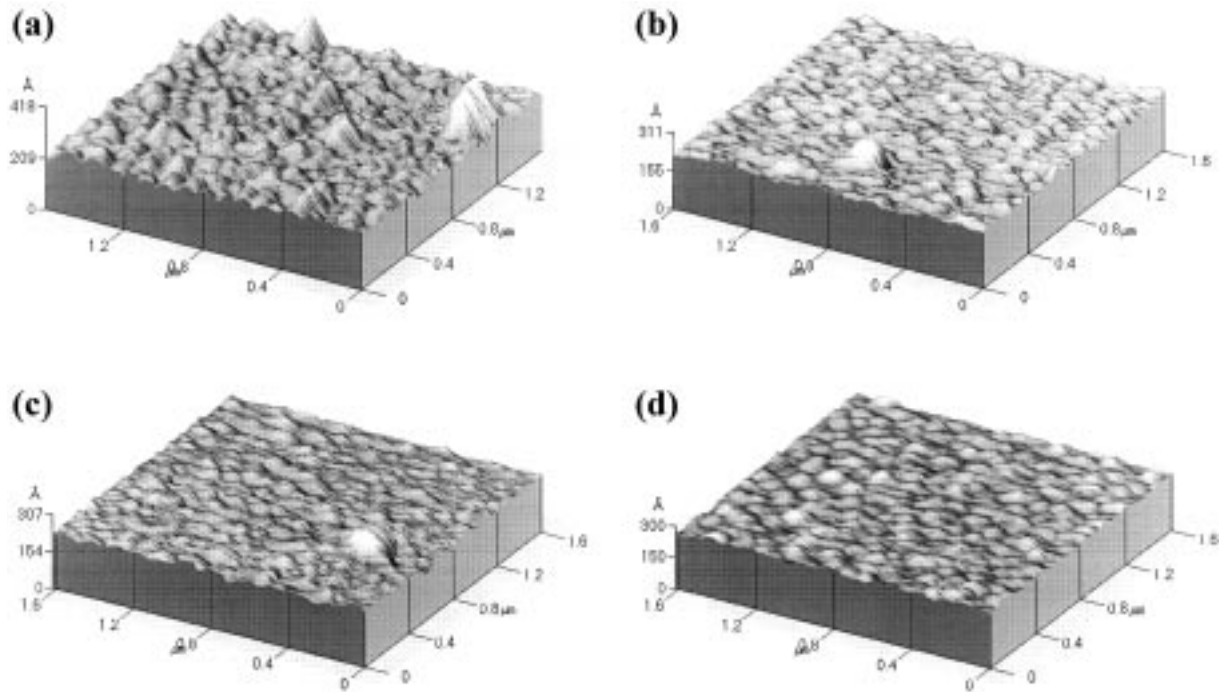


Fig. 4. AFM images of a cubic fluorite-like Sr-Bi-Ta oxide film deposited with the laser fluence of (a) 1.9 J/cm^2 , (b) 2.7 J/cm^2 , (c) 3.5 J/cm^2 , and (d) 4.3 J/cm^2 .

4.3 J/cm^2 , the root mean square roughnesses were 19.4, 12.3, 9.46, and 7.17 \AA , respectively. The origin of the morphology dependence on the laser fluence is not clear at this moment.

3.3. Effect of Post-Annealing

This fluorite-like phase is found to be quite stable up to 650°C and can be transformed into a layered perovskite SBT phase by post-annealing at a higher temperature [9]. Understanding such a transformation is really important in some real processing techniques, such as chemical vapor deposition, where the deposition is typically made at a low temperature and a further thermal annealing is required at a higher temperature. In order to obtain more insights on the transformation, we performed post-annealing experiments.

Figure 5 shows the XRD θ - 2θ patterns of the films which were post-annealed at various temperatures for 1 h in an oxygen atmosphere. As shown in Fig. 5(b), the film annealed at 650°C didn't show a large change in the crystal structure, except its c -axis lattice

constant was decreased from 5.37 \AA to 5.34 \AA . As the annealing temperature increased, the films were turned into the layered perovskite SBT phase. Figure 5(c) shows that, in the film annealed at 750°C , most of the fluorite-like phase materials were transformed into the layered perovskite phase. However, the XRD pattern also shows that a small amount of the fluorite-like phase still exists. As shown in Fig. 5(d), all the peaks from the fluorite-like phase disappeared for the film annealed at 800°C , and the film was transformed into a c -axis oriented polycrystalline SBT film. From these results, we can conclude that the fluorite-like phase is stable up to 650°C and that it can be transformed into SBT at a higher temperature.

3.4. Ordering in Sr-Bi-Ta Oxide Film of Cubic Fluorite-Like Structure

To obtain further insights on the crystal structure, we performed SAED measurements. Figure 6(a) shows the SAED pattern of the Sr-Bi-Ta oxide film post-annealed at 650°C for 1 h. Figures 6(b) and 6(c) show the SAED patterns of the bare LaAlO_3 substrate and

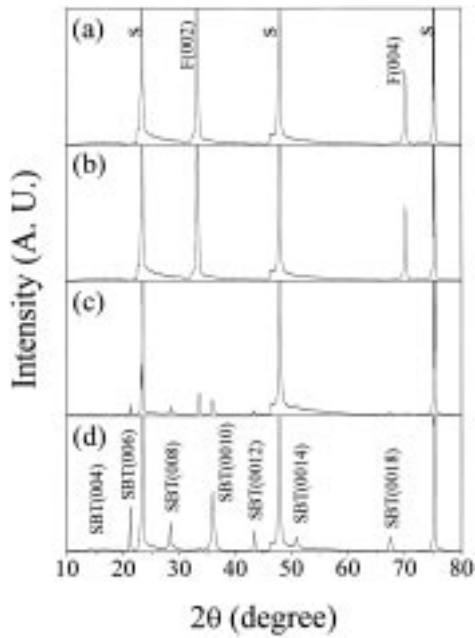


Fig. 5. XRD θ - 2θ scan patterns (a) of as-grown film, and after annealing for 1 h at (b) 650°C, (c) 750°C, and (d) 800°C.

the film with the substrate, respectively. From these diffraction patterns, it is clearly seen that the Sr-Bi-Ta oxide film is epitaxially grown with a face-centered cubic (fcc) structure. The epitaxial relation is such that the [100] direction of the Sr-Bi-Ta oxide film is parallel to LaAlO_3 [110], which is in agreement with the XRD ϕ scan result, shown in Fig. 1 (b).

In addition to the diffraction peaks which come from the face-centered cubic structure, we could observe some additional superstructure peaks. It can be easily realized by comparing Fig. 6 (a) with the diffraction pattern of the ideal fcc structure, shown in Fig 6(d). The superstructure peaks appear in the directions of $\{1/2, 1/2, 1/2\}$ and $\{1, 0, 0\}$. The former peaks are much stronger than the latter peaks. The superstructure peaks seem to come from an ordering of the metal ions [11]. The ordering distance is about two times larger than the corresponding lattice constant.

The origin of this ordering is not clear at this moment. One possibility is that there exists an intrinsic defect fluorite structure where the metal ions are

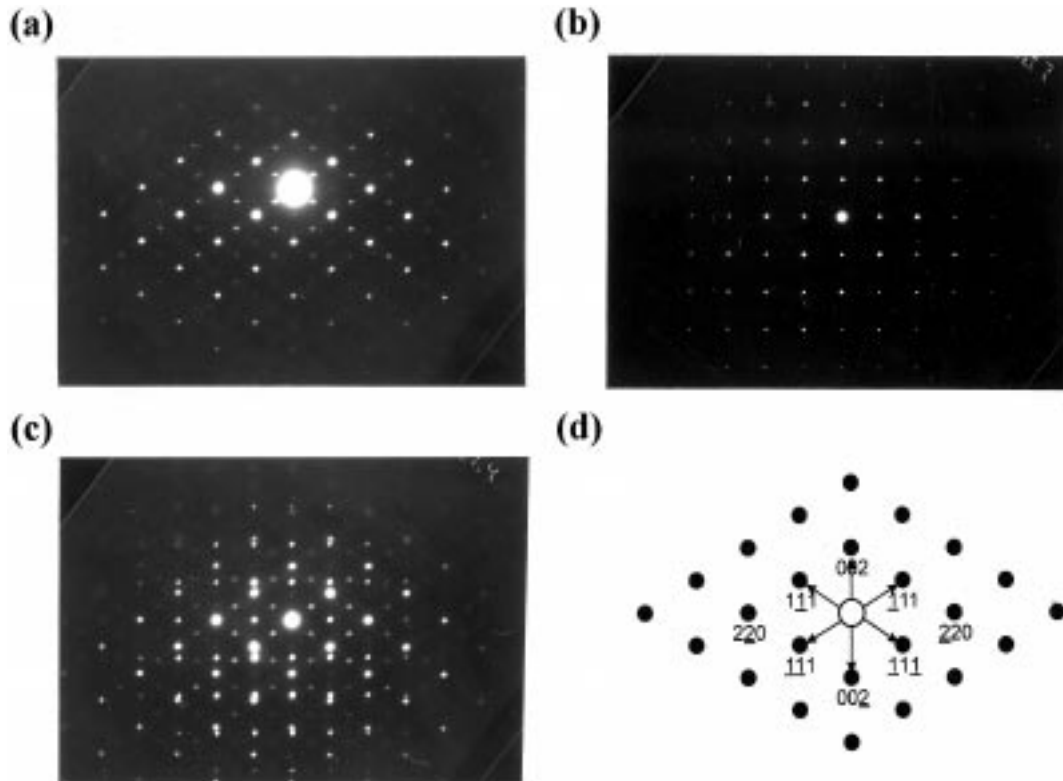


Fig. 6. SAED pattern of (a) the fluorite-like phase film, (b) LaAlO_3 substrate and (c) the film with the substrate after annealing at 650°C for 1 h. (d) SAED pattern of ideal face-centered cubic structure.

ordered. Using an extended edge X-ray absorption fine structure spectroscopy, Hartmann et al. [12] claimed that the oxygen environment for the Ta ion should be closely related to that of the TaO₆ octahedra of the SBT. Since the Ta ion is much smaller than other metals, such a claim seems to be plausible. The other possibility is that such a metal ion ordering do occur during the annealing process. We also observed similar superstructure peaks in the SAED pattern of an as-grown epitaxial Sr-Bi-Ta oxide thin film. However, the superstructure peaks are somewhat weaker than those in Fig. 6(a). At this moment, it is not certain whether this superstructure is an intrinsic phenomenon of the fluorite-like phase or an ordering effect during heat treatments. Further experiments are now in progress.

4. Summary

We grew epitaxial Sr-Bi-Ta oxide thin films of a fluorite-like structure on LaAlO₃ (001) substrates by the pulsed laser deposition method. The lattice constant of the fluorite-like phase decreases as the laser fluence increases, which is closely related to size differences of the metal ions. From SAED patterns, it was also observed that the fluorite-like phase had a superstructure whose ordering distance was two times larger than its lattice constant.

Acknowledgments

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Reference

1. C.A.P. Araujo, J.D. Cuchiaro, L.D. McMillian, M.C. Scott, and J.F. Scott, *Nature*, (London) **374**, 627 (1995).
2. K. Ammanuma, T. Hase, and Y. Miyasaki, *Appl. Phys. Lett.*, **66**, 221 (1995).
3. T. Ami, K. Horonaka, C. Isobe, N. Nagel, M. Sugiyama, Y. Ikeda, K. Watanabe, A. Machida, K. Miura, and M. Tanaka, *MRS Symp. Proc.*, **415**, 195 (1996).
4. T. Osaka, A. Sakakibara, T. Seki, S. Ono, I. Koiwa, and A. Hashimoto, *Jpn. J. Appl. Phys.*, **37**, 597 (1998).
5. M.A. Rodriguez, T.J. Boyle, B.A. Hernandez, C.D. Buchheit, and M.O. Eatough, *J. Mater. Res.*, **11**, 2282 (1996).
6. J.H. Cho, S.H. Bang, J.Y. Son, and Q.X. Jia, *Appl. Phys. Lett.*, **72**, 665 (1998).
7. J. Lettieri, C.I. Weber, and D.G. Schlom, *Appl. Phys. Lett.*, **73**, 2057 (1998).
8. S.J. Hyun, B.H. Park, S.D. Bu, J.H. Jung, and T.W. Noh, *Appl. Phys. Lett.*, **73**, 2518 (1998).
9. S.J. Hyun, B.H. Park, S.D. Bu, and T.W. Noh, *J. Korean Phys. Soc.*, **35**, S573 (1999).
10. R.D. Shannon, *Acta Cryst.*, **23**, 751 (1976).
11. J.Y. Gu, K.H. Kim, J.S. Ahn, T.W. Noh, J.S. Lee, Y.W. Jeong, and H.J. Lee, *J. Korean Phys. Soc.*, **31**, 512 (1997).
12. A.J. Hartmann, C.D. Gutleben, G.J. Foran, C.P. Whitby, C. Isobe, K. Watanabe, and J.F. Scott, *Ferroelectric Lett.*, **23**, 75 (1997).