Diffuse Phase Transition in Ba(Sn$_x$Ti$_{1-x}$) Ceramics and Thin Films

Takanori Hino *, Teruhiko Sugioka **, Seisyou Tamura ***, Minoru Nishida****, Takao Araki*****

* *Environmental Materials Science and Engineering, Niihama National College of Technology,*
7-1 Yagumo-cho, Niihama-shi, Ehime792-8580, Japan
E-mail: hino@mat.niihama-nct.ac.jp
** *Graduate School of Engineering, Ehime University,*
3 Bunkyo-cho, Matsuyama-shi, Ehime 790-8577, Japan
*** *Advanced Engineering Course, Niihama National College of Technology,*
7-1 Yagumo-cho, Niihama-shi, Ehime792-8580, Japan
**** *Kochi prefectural industrial technology center, 399–3 Nunoshida-chou, Kochi 781-5101, Japan*
***** *Toyo Industrial Creative Center, 2151-10 Oh-Join, Niihama, Ehime792-0060, Japan*

Due to the need to limit the use of Pb in electrical products, dielectric materials based on lead-free perovskite compounds with relaxor behavior are being actively developed. In this study, we carried out an investigation on the perovskite material Ba(Sn$_x$Ti$_{1-x}$)O$_3$, whose B-site ions comprise elements from different periodic table groups but have the same valence state of 4+. We fabricated and evaluated ceramics, single layer solid solution (SS) thin films, and order-controlled superlattice (SL) thin films. The shape of the dielectric anomaly in these materials was demonstrated and the value of parameter γ, calculated from the Curie-Weiss law, was found to be 1.71 for ceramics, 1.86 for SS films and 1.90 for 33% ordered SL films. In addition, the influence of the order-disorder transition on diffuse phase transition (DPT) was clarified.

Keywords: diffuse phase transition, relaxor ferroelectrics, Ba(Sn$_x$Ti$_{1-x}$), order degree, artificial superlattice thin films

1. Introduction

A(B'B'')O$_3$ perovskites, such as the compounds Pb(Mg$^{2+}_{1/3}$Nb$^{5+}_{2/3}$)O$_3$ (PMN) [1] and Pb(Zn$^{3+}_{1/2}$Nb$^{5+}_{1/2}$)O$_3$ (PZN) [2], that contain lead and have B-site ions from two different periodic table groups with different valence states, have been actively studied as ferroelectric materials exhibiting relaxor behavior. The relaxor phenomenon gives rise to a large dielectric constant over a wide temperature range due to the disorder of the electric dipole polarization caused by fluctuation of the crystal phase in the compound [3]. Setter et al. also suggested that this phenomenon can be controlled by changing from the ordered to the disordered structure in Pb(Sc$^{3+}_{1/2}$Ta$^{5+}_{1/2}$)O$_3$ (PST) along the <111> direction of the crystal [4].

However, from an environmental point of view, the use of Pb in electric products is undesirable, and ferroelectrics based on lead-free perovskites with relaxor behavior are being actively investigated. Recently, relaxor behavior in the ferroelectric Ba(Zr$_x$Ti$_{1-x}$)O$_3$ (BZT), whose B-site ions are from the same periodic table group and have a valence state of 4+, was reported [5-7]. On the other hand, Ba(Sn$_x$Ti$_{1-x}$)O$_3$ (BTS) has also attracted attention as a candidate material for relaxor ferroelectrics [8-14]. Perovskite structures in which the B-site ions have the same valence state cannot become naturally ordered due to the absence of a charge difference between the ions, and usually take on a disordered state. From a study of superlattices, it was found that the degree of order in the arrangement of B-sites is a dominant factor influencing the relaxor phenomenon [15]. However, further clarification of this effect is required.

In the present study, we investigated the relaxor behavior in BTS ferroelectrics, whose B-site ions are from different periodic table groups but have the same valence state of 4+. The dielectric properties of BTS (x=0.05~0.25) thin films were investigated and compared to those of ceramics produced by solid-state synthesis. The shape of the dielectric anomaly in the paraelectric phase in the ceramics, solid-solution single-layer thin films (SS films) and order-controlled superlattice thin films (SL films) was also investigated based on the value of the γ parameter calculated from the Curie-Weiss law. The degree of diffuse phase transition (DPT) in the SL films was also investigated by using quadric law.

2. Experiment procedures

BTS ceramics and deposition targets with composition ratios of x=0.05, 0.10, 0.15, 0.20, and 0.25 were prepared by a conventional solid-state synthesis technique. High purity BaTiO$_3$ and BaSnO$_3$ powders were weighed according to their composition ratio and mixed in alcohol. After drying, the powders were calcined at 1373 K for 12 hours. The calcined powders were milled with a mortar grinder and pressed uniaxially at 20 MPa into 2-mm-thick pellets, which were then sintered at 1673 K for 12 hours in air. The density of 92% sintered ceramics was obtained.

Table 1 Target composition for PLD and degree of order.

target composition		order degree
$Ba(Sn_{2x-y}Ti_{1-2x+y})O_3$	$Ba(Sn_yTi_{1-y})O_3$	
$Ba(Sn_{0.15}Ti_{0.85})O_3$	$Ba(Sn_{0.15}Ti_{0.85})O_3$	0 % (solid solution)
$Ba(Sn_{0.1}Ti_{0.9})O_3$	$Ba(Sn_{0.2}Ti_{0.8})O_3$	33 % (super lattice)
$BaTiO_3$	$Ba(Sn_{0.3}Ti_{0.7})O_3$	100 % (super lattice)

SS films with a thickness of 200 nm were prepared by pulsed laser deposition using a KrF excimer laser. The composition of the films was adjusted using Vegard's law. The rotating targets were irradiated by the laser at a fluence of 3.0 J/cm^2 and a pulse frequency of 2 Hz. Films were deposited on Nb-doped SrTiO$_3$(111) substrates at a temperature of 973 K in an O$_2$–8%O$_3$ atmosphere with a gas pressure of 1 Pa.

Two kinds of SL films were also fabricated by the alternate laser ablation of two different targets under the same conditions used for the SS films. The SL films were deposited using a $Ba(Sn_{2x-y}Ti_{1-2x+y})O_3$ and $Ba(Sn_yTi_{1-y})O_3$ target as shown in Table 1. The degree of order (S) was calculated using Eq. (1).

$$S = \frac{y - x}{x} \times 100 \qquad (1)$$

These structures were produced by repeated deposition until 21 layers were formed. The crystal structures of the SS and SL films have been described in a previous report [16].

The capacitance and dielectric loss tangent (tan δ) were measured using an LCR meter (HP4284A) in the frequency range 1 kHz to 1 MHz and at temperatures ranging from 100 to 400 K. Electrical measurements were conducted using a top electrode / ferroelectrics / a bottom electrode configuration. The platinum electrodes were deposited by sputtering through a metal shadow mask with an area of 0.25 mm^2. The electrode distance for the sintered compacts and the thin films was 2 mm and 200 nm respectively. In the case of films, the Nb-SrTiO$_3$ substrate that has electrically conductive by adding Nb can be used as a bottom electrode.
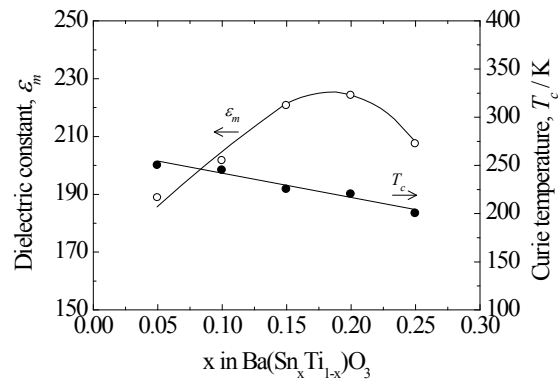
3. Results and discussions

3.1 Dielectric properties of ceramics and SS films

Figure 1 shows the dielectric constant and the Curie temperature of the BTS ceramics as a function of the composition ratio. The dielectric constant was found to increase with BaSnO$_3$ content, and was largest at a composition ratio between 0.15 and 0.20. For composition ratios above 0.20, the dielectric constant decreased. It has been reported that BTS ceramics have a pinching composition close to x=0.15 [17], so the dielectric constant became largest at the pinching composition ratio. The existence of a pinching effect suggests the possibility of the co-existence of multiple phases. The Curie temperature was found to decrease linearly with increasing BaSnO$_3$ content, and had a value
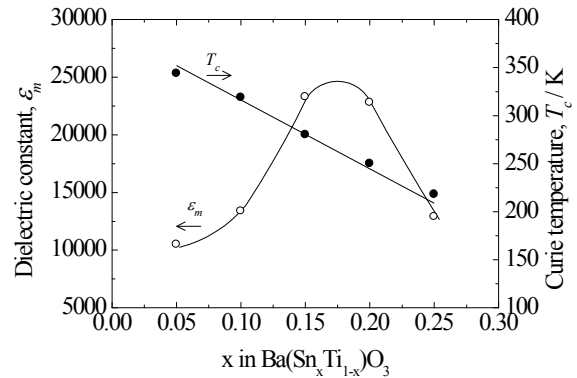
Fig. 1 Dielectric properties of ceramics, measured at 100 kHz. Open circles represent the dielectric constant and closed circles represent the Curie temperature.

Fig. 2 Dielectric properties of SS films, measured at 100 kHz. Open circles represent the dielectric constant and closed circles represent the Curie temperature.

of 280 K at x=0.15. These results agree with previous reports for BZT [18], although the pinching effect for BTS occurred at a lower temperature than for BZT. Thus, the use of Sn^{4+} as a shifter dopant leads to a larger effect on the Curie temperature than that for Zr^{4+}.

Figure 2 shows the dielectric constant and the Curie temperature of the BTS SS films as a function of the composition ratio. Although the dielectric constant behaved similarly to that for ceramics, the Curie temperature, which decreased rapidly with increasing composition ratio, was lower than that for the ceramic material, and reached a value of 230 K for x=0.15. In these materials the (111) plane is occupied by B-site ions, and the added Sn^{4+} ions have a large effect on the dielectric properties. Films grown on SrTiO$_3$(111) also have a large lattice strain, causing a shift in the Curie temperature to lower values [18].

3.2 XRD of BTS

Figure 3 shows the XRD pattern of sintered ceramics used for target. The position of diffraction angle shifted to lower angle depend on composition x. Figure 4 shows the spacing of (111) plane (d(111) value) of ceramics and films calculated from diffraction angle of BTS(111) peak. In figure 4, the d(111) value obtained from JCPDS for BaTiO$_3$ and BaSnO$_3$ were also described. These d(111) values linearly increased with increasing Sn concentration in BTS.
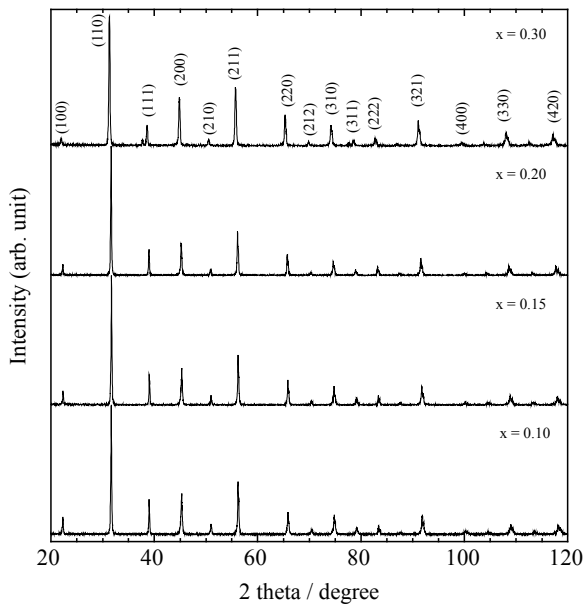
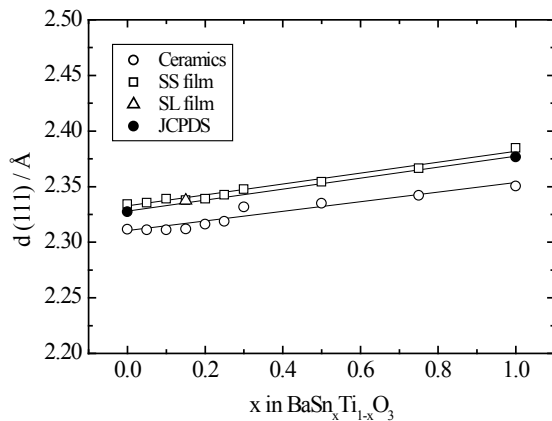**Fig. 3** X-ray diffraction patterns of sintered BTS ceramics.

Fig. 4 The spacing of (111) plane of BTS.

Fig. 5 Temperature dependence of dielectric constant in (a) 100% ordered SL film and (b) 33% ordered SL film.

The gradient of these straight lines was almost the same. So we could also assume that a homogeneous target was obtained for each composition. Since thin films with the target composition can be formed according to Vegard's law, the PLD method is suitable for forming thin films of complex oxides ceramic. The d (111) value of the films was larger than that of target. The lattice of the films was expanded to <111> direction by compressive strain due to lattice mismatch at the interface.

3.3 Dielectric properties of SL films

The SL films were prepared with an average composition of x=0.15, which is the composition ratio where the ceramics and the SS films exhibited the highest dielectric constant. The effect of the degree of order on the relaxor behavior has been previously examined, and it was found that 35% is the optimum degree of order for PST (x=0.5) [4], whereas 25% is optimum for BZT (x=0.2) [19]. Therefore, a degree of order of 33% for the BTS (x=0.15) SL films was decided upon, and the dielectric properties were compared to the 100% ordered films.

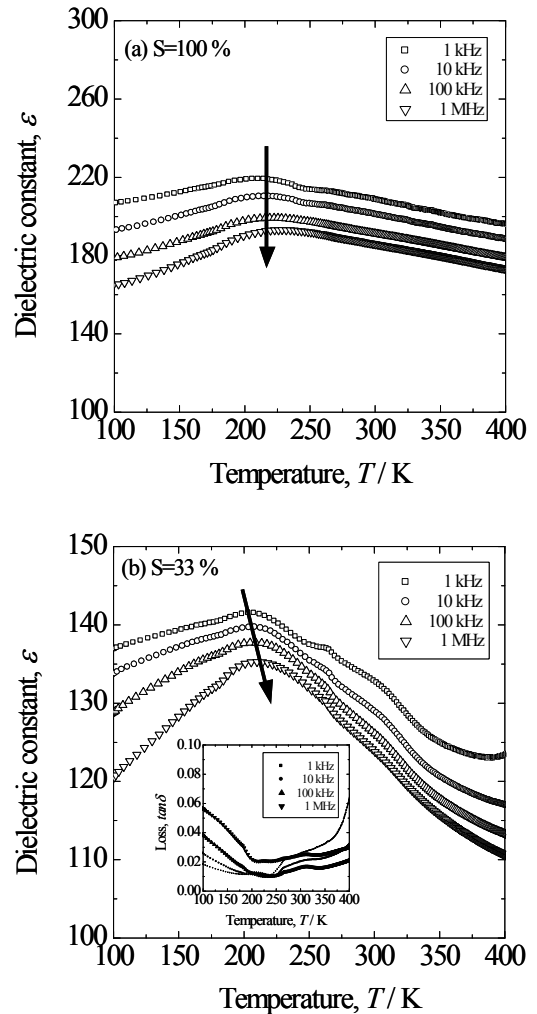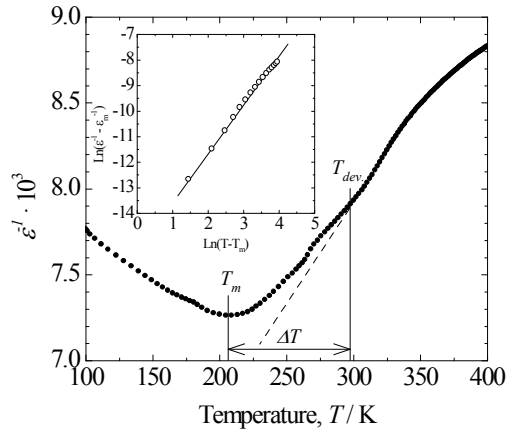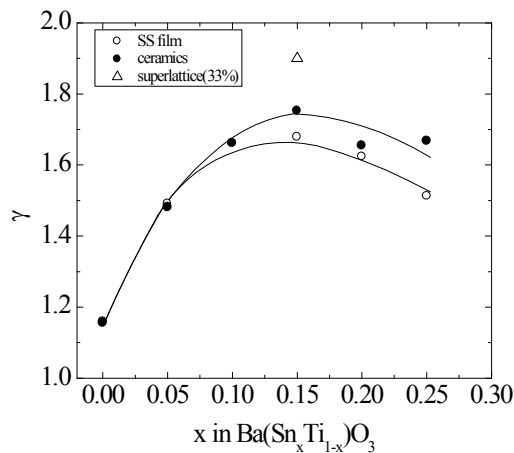Figure 5 shows the temperature dependence of the dielectric constant for the SL films measured at 1, 10, 100, and 1000 kHz. The dielectric constant of the 100% ordered film is seen to be larger than that of the 33% ordered film. Because the difference in composition between the layers is large when the degree of order is 100%, each interface is affected by the lattice strain. It has previously been shown that the dielectric constant increases with increasing lattice strain [18]. A broad phase transition is observed for the 33% ordered film, indicating that diffuse phase transitions occur in this film. The arrows in the figure indicate the frequency dispersion of the dielectric constant. For the 100% ordered film, an inflection point is found at 210 K, which is close to the Curie temperature of the SS films. However, no broad phase transition or frequency dispersion is observed. For the 33% ordered film, on the other hand, the inflection point shifts to higher temperature with increasing frequency. Such frequency dispersion is one of the characteristics of relaxor materials [20]. The dielectric loss as a function of temperature is also shown in the figure, and was less than 0.05 for all measurement frequencies.

Fig. 6 The inverse dielectric constant as a function of temperature for the 33% ordered SL film measured at 1 kHz. The inset shows the plot of $ln(\varepsilon^{-1}-\varepsilon_m^{-1})$ as a function of $ln(T-T_m)$. The solid line is fitted using Eq. (3).

Fig. 8 The inverse dielectric constant as a function of $(T-T_m)^2$ for the 33% ordered SL film measured at 1 kHz. The solid line is fitted using Eq. (4).

Fig. 7 Dependence of γ on BTS composition, where closed circles represent ceramics, open circles represent SS films, and the triangle represents the 33% ordered SL film.
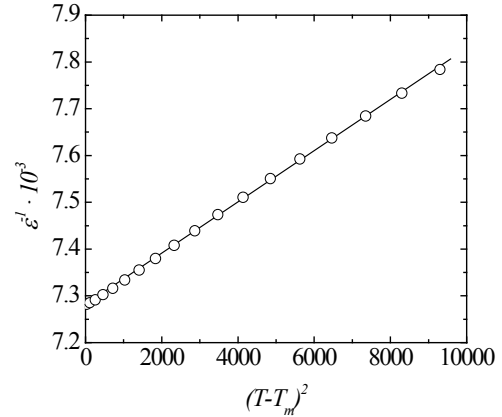
The SL films fabricated in this study were good ferroelectrics with low leakage currents.

3.4 Diffuseness of the phase transition

The dielectric characteristics of relaxor ferroelectrics are well known to deviate from the typical Curie-Weiss law and can be described by a modified Curie-Weiss relationship. Smolenskii [21], Kirillov and Isupov [22] have developed theoretical approach for quantitative description of the relaxor behavior. They suggested that the local temperatures distribution in the relaxor material with microscopic compositional fluctuations is given by a Gaussian function around the Curie temperature. Then, the deviation from Curie-Weiss relationship caused with the relaxor ferroelectrics is represented by the following equation.

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T-T_m)^\gamma}{C} \tag{2}$$

Here γ and C are assumed to be constant, and $1 \leq \gamma \leq 2$. The parameter γ gives information on the shape of the

anomaly in paraelectric phase. Eq. (2) can also be written as follow.

$$ln\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m}\right) = \gamma \, ln(T - T_m) - ln\, C \tag{3}$$

When $\gamma=1$, the ideal Curie-Weiss law is observed, which is the case for normal ferroelectrics, whereas $\gamma=2$ corresponds to ideal relaxor ferroelectrics which have diffuse phase transition (DPT) [23].

Figure 6 shows the inverse dielectric constant as a function of temperature for the 33% ordered SL film measured at 1 kHz. The inset shows the relationship between $ln(\varepsilon^{-1}-\varepsilon^{-1}_m)$ and $ln(T-T_m)$. A $T_{dev.}$ is a temperature at which dielectric constant starts to deviate from Curie-Weiss law. Here, ΔT $(=T_{dev}-T_m)$ was 90 K, which is consistent with the reported values for Ba(Zr, Ti)O$_3$. A γ value of 1.90 was obtained by fitting the experimental data based on Eq. (3).

Figure 7 shows the value of γ for the ceramics and thin films as a function of the composition ratio. In the case of x=0.00, γ is 1.16, which is close to the value for normal ferroelectrics. It becomes higher as the BaSnO$_3$ content is increased, reaching a maximum of 1.75 for the ceramics and 1.68 for the SS films. These values were close to those previously reported for BZT (x=0.15~0.35), which are in the range 1.62 to 2.01 [24-27].

The γ value for the 33% ordered SL film was higher than for ceramics and SS films. Since the value was also close to 2.0, it can be concluded that the accurate control of order using the super lattice technique can give rise to more relaxor like behavior. The γ value of the 100% ordered SL films could not be accurately calculated since the inflection points were not clear, but it was approximately 1.48.

The γ parameter alone cannot demonstrate the relaxor behavior. The degree of DPT is also related with the width of the dielectric anomaly. Uchino and Nomura [28] reported that not all diffuse phase transitions obey the eq. (2) exactly, and improved the quadric law represented as follow.

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^2}{2\varepsilon_m\sigma^2} \qquad\qquad (4)$$

In this equation the diffuseness parameter is σ that describes in the denominator. The γ parameter accounts for the shape of the dielectric anomaly in the paraelectric phase but the diffuseness parameter is σ.

The degree of DPT based on the parameter σ can be determined from the slope of ε^{-1} versus $(T-T_m)^2$ as shown Figure 8. Although the slope calculated from Eq. (4) was 5.5×10^{-8} close to the reported value [29, 30] and the parameter σ was 257 K for 33% ordered SL film, was found to be higher than the reported value for other of relaxor ferroelectric materials [31]. These means that 33% ordered BTS SL film has wide DPT. Hence, it can be concluded that a degree of order of 33% is necessary to produce relaxor behavior in BTS SL films.

4. Conclusions

We studied the relaxor behavior in BTS ceramics, SS films, and SL films, which cannot become naturally ordered due to the absence of a charge difference between their B-site ions. The degree of order in the controlled SL films was discussed on the basis of the γ value calculated from the Curie-Weiss law and modified quadric law.

The Curie temperature was found to decrease linearly with increasing $BaSnO_3$ content, and Sn^{4+} was found to have a very large effect as a shifter dopant. BTS solid solution have largest dielectric constant at the composition of x=0.15. The degree of order controlled SL films were obtained with the average composition of x=0.15. The dielectric loss was less than 0.05, so that the SL films were good ferroelectrics with low leakage currents. The γ value was found to be close to 2.0 for 33% ordered SL film. A broad phase transition and frequency dispersion were also observed. The value of σ, which elucidate the degree of DPT, was significant higher than the value of reported other relaxor ferroelectrics. It was confirmed that clear relaxor behavior was exhibited by the 33% ordered SL film. In summary, the degree of order in BTS was successfully controlled and the influence of the order-disorder transition on relaxor behavior was clarified.

Acknowledgments

References

[1] G. A. Smolensky and A. I. Agranovskaja, Sov. Phys. Tech. 3 (1958) 1380.

[2] J. Kuwata, K. Uchino, S. Nomura: Ferroelectrics 22 (1979) 863.

[3] L. E. Cross: J. Appl. Phys. 34 (1995) 2525.

[4] N. Setter and L. E. Cross, J. Appl. Phys. 51 (1980) 4356.

[5] P.W. Rherig, S.E. Park, S.T. McKinstry, G.L. Messing, B. Jones, T.M.Shrout, J. Appl. Phys. 86 (1999) 1657.

[6] J. Ravez, C. Broustera and A. Simon, J. Mater. Chem. 9 (1999) 1609.

[7] Z. Yu, C. Ang, R. Guo, and A. S. Bhalia, J. Appl. Phys. 92 (2002) 2655.

[8] J. Cieminski, H. Beige, J. Phys. D, Appl. Phys. 24 (1991) 1182.

[9] T. B. Wu, C. M. Wu, M. L. Chen, Appl. Phys. Lett. 69 (1996) 2659.

[10] S. Halder, P. Victor, A. Laha, S. Bhattacharya, S. B. Krupanidhi, G. Agarwal, A. K. Singh, Solid State Communications 121 (2002) 329.

[11] J.W. Zhai, B. Shen, X. Yao, L.Y. Zhang, J. Am. Ceram. Soc. 87 (2004) 2223.

[12] L. Geske, V. Lorenz, T. Müller, L. Jäger, H. Beige, H. Abicht, V. Mueller, J. Eur. Ceram. Soc. 25 (2005) 2537.

[13] I.A. Souzaa, A. Z. Simoesa, S. Cavab, L. S. Cavalcantec, M. Cilensea, E. Longoa, J. A. Varela, J. solid state chem. 179 (2006) 2972.

[14] Song Sannian, Zhai Jiwei, Yao Xi, Solid State Sciences 9 (2007) 1049.

[15] Y. Hotta, G. W. Hassink, T. Kawai and H. Tabata, Jpn. J. Appl. Phys., 42 (2003) 5908.

[16] T. Hino, M. Nishida, T. Araki, T. Ohno, T. Kawahara, M. Murasugi, H. Tabata and T. Kawai, J. Laser Micro/Nanoengineering, 2 (2007) 166.

[17] N. S. Novosiltsev and A. L. Khodakov, Sov. Phys. Tech. Phys. 1 (1956) 306.

[18] T. Hino, N. Matsumoto, T. Takahashi, M. Nishida and T. Araki, J. Mat. Sci. Sco. Jpn., 45 (2008) 229.

[19] H. Tabata, Y. Hotta, A. Doi and T. Kawai, J. Surf. Sci. Soc. Jpn., Vol. 26, No. 4, (2005) 200.

[20] L. E. Cross, Ferroelectrics 76 (1987) 241.

[21] G. A. Smolenski, J. Phys. Soc. Jpn., 28 (1970) 26.

[22] V.V. Kirillov, V.A. Isupov, Ferroelectrics 5 (1973) 3.

[23] K. Uchino and S. Nomura, Ferroelectr. Lett. Sect., 44 (1982) 55.

[24] T. Badapanda, S.K. Rout, S. Panigrahi, T.P. Sinha, Current Appl. Phys. 9 (2009) 727.

[25] O.P. Thakur, C. Prakash, A.R. James, Journal of Alloys and Compounds 470 (2009) 548.

[26] X.G. Tang, K. H. Chew, H. Chan, Acta Materialia 52 (2004) 5177.

[27] X.P. Jiang, M. Zeng, H. Chan, C. L. Choy, Mater. Sci. Eng. A 438 (2006) 198.

[28] K. Uchino, S. Nomura, L. E. Cross, S. L. Jang, R. E. Newnham, J. Appl. Phys. 51 (1980) 1142.

[29] Tanmoy Maiti, R. Guo, and A. S. Bhalla, J. Appl. Phys. 100, (2006) 114109.

[30] A.A. Bokov, Z. G. Ye, Solid State Communications 116 (2000) 105.

[31] A. A. Bokov, Y.-H. Bing, W. Chen, and Z.G. Ye, S. A. Bogatina, I. P. Raevski, S. I. Raevskaya, and E. V. Sahkar, PHYSICAL REVIEW B 68, (2003) 52102.