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Dielectric and Piezoelectric Properties of Nonstoichiometric $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ Ceramics

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Abstract. Nonstoichiometric $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN) ceramics were prepared by a solid state reaction method. X-ray diffraction analysis showed that single-phase of Bi-layered perovskite was obtained. With different Sr/Bi content ratios of SBT and SBN, Curie temperature (T_C), electromechanical factor (K_p) and mechanical quality factor (Q_m) were measured. T_C of SBN (SBT) rose from 414°C (314°C) to 494°C (426°C) when Sr/Bi content ratio was increased from 0.55/2.3 to 1.2/1.8. In the most Sr-deficient/Bi-excess ratio of 0.55/2.3, the maximum values of Q_m were obtained approximately 1013 and 3325 for SBT and SBN, respectively.

Keywords: Bi-layered perovskite, Curie temperature, electromechanical factor, mechanical quality factor

1. Introduction

Many lead-based perovskite ferroelectric materials such as PZT [$Pb(Zr,Ti)O_3$] have been widely used dielectric or piezoelectric materials in electronic ceramics applications. However, lead (Pb) leads to serious environmental pollution and lots of 90 degree domains generated on the ferroelectric phase transition. Poling with very high electric field is required for piezoelectric and ferroelectric applications. The development of Pb-free and 90 degree domain-free materials is required. For this reason, bismuth layer ferroelectrics which have been studied for ferroelectric random access memories applications (FRAMs) were considered to be candidate materials [1–10].

Bismuth layered ferroelectric materials such as $SrBi_2Ta_2O_9$ (SBT) or $SrBi_2Nb_2O_9$ (SBN) ceramics are represented by $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, $m = 2$, [11] and generally have higher Curie temperature (T_C) than PZT. Ferroelectric properties such as the remanent polarization (P_r) and T_C have been found to depend on the Sr/Bi content ratio. It was reported that the nonstoichiometric compositions with Sr-deficient/Bi-excess have better ferroelectric properties than the stoichiometric compound [12, 13]. Bismuth layer structured ferroelectrics such as SBT and SBN ceramics are adequate for the fine tolerance oscillator applications since piezoelectric properties of these materials have a lower electromechanical factor and a higher mechanical quality factor than PZT [5].

In this work, different Sr/Bi ratio compositions of $Sr_{0.55}Bi_{2.3}Ta_2O_9$, $Sr_{0.7}Bi_{2.2}Ta_2O_9$, $SrBi_2Ta_2O_9$, and $Sr_{1.2}Bi_{1.8}Ta_2O_9$ for the SBT and $Sr_{0.55}Bi_{2.3}Nb_2O_9$, $Sr_{0.7}Bi_{2.2}Nb_2O_9$, $SrBi_2Nb_2O_9$, and $Sr_{1.2}Bi_{1.8}Nb_2O_9$ for the SBN ceramics were prepared. The effects of nonstoichiometry on the crystal structure, T_C, dielectric and piezoelectric properties were investigated.

2. Experimental

In this study, $SrBi_2Nb_2O_9$ and $SrBi_2Ta_2O_9$ ceramics were prepared by a solid state reaction method. The starting raw materials were SrO(Aldrich 99%), Bi_2O_3(Aldrich 99%), Nb_2O_5(Aldrich, 99%), Ta_2O_5(Aldrich, 99%). The powders were weighed and mixed by ball milling with methanol for 24 hours. After drying at 80°C and they were calcined at 900–1000°C for 2 hours. The calcined powders were mixed with 10wt% polyvinylalcohol as a binder for 24 hours and dried again. They were pressed into pellets with 8 mm

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in diameter and 1 mm thick uniaxially. The pellets were sintered for 1 hour at 1150–1250°C. For the research on ferroelectric properties, all of the ceramic pellets were electroded by silver paste on both surfaces and cured at 650°C for 30 min. For piezoelectric measurements, samples were poled by applying a *dc* electric field of 3.5 kV/mm for 30 min in silicone oil at above 110°C.

X-ray diffraction (XRD, APD System, Philips) was used to determine the formation of the Bi-layered perovskite phase. With different Sr/Bi content ratios, grain morphologies and sizes were investigated using a scanning electron microscope (SEM, Hitachi, S-2400). Resonance-antiresonance frequencies and static capacitance at 1 kHz were measured, using an impedance analyzer (HP 4194A). From these results, K_p and Q_m were calculated. Dielectric constants were measured at various frequencies from 100 Hz to 10 MHz in the temperature range from 30 to 700°C and variation of T_C with different Sr/Bi content ratios was investigated.

3. Result and Discussion

Figure 1 shows XRD patterns of the SBT and SBN ceramics in the 2θ range from 10° to 80°. As shown in the XRD peaks of all samples, the layered perovskite (115) peak was found and no secondary phase was detectable. Furthermore it was found that there was no appreciable influence of Sr/Bi content ratio on the crystal structure of the SBT and SBN ceramics. Figure 2

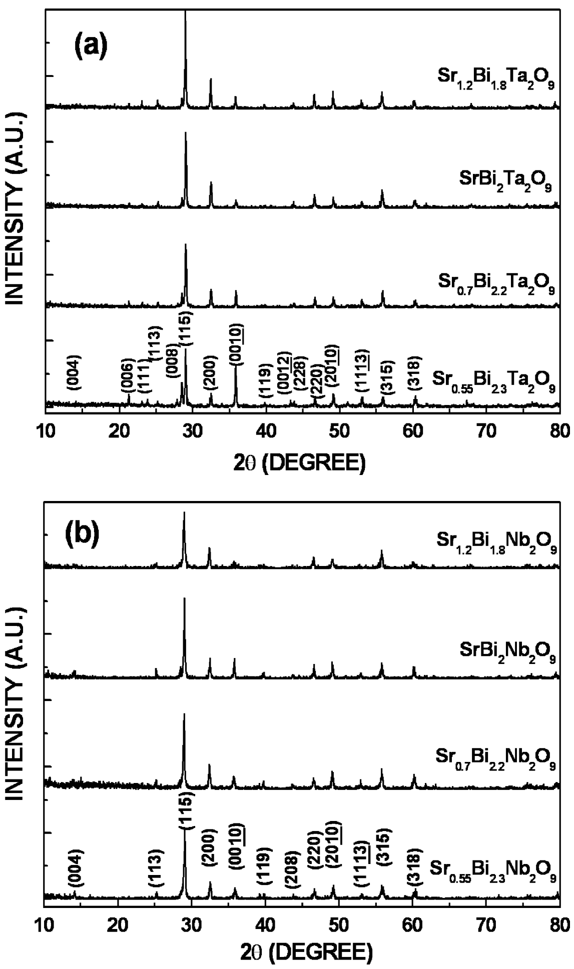

Fig. 1. (a) X-ray diffraction patterns of the $Sr_{1\pm x}Bi_{2\pm y}Ta_2O_9$ ceramics and (b) X-ray diffraction patterns of the $Sr_{1\pm x}Bi_{2\pm y}Nb_2O_9$ ceramics.

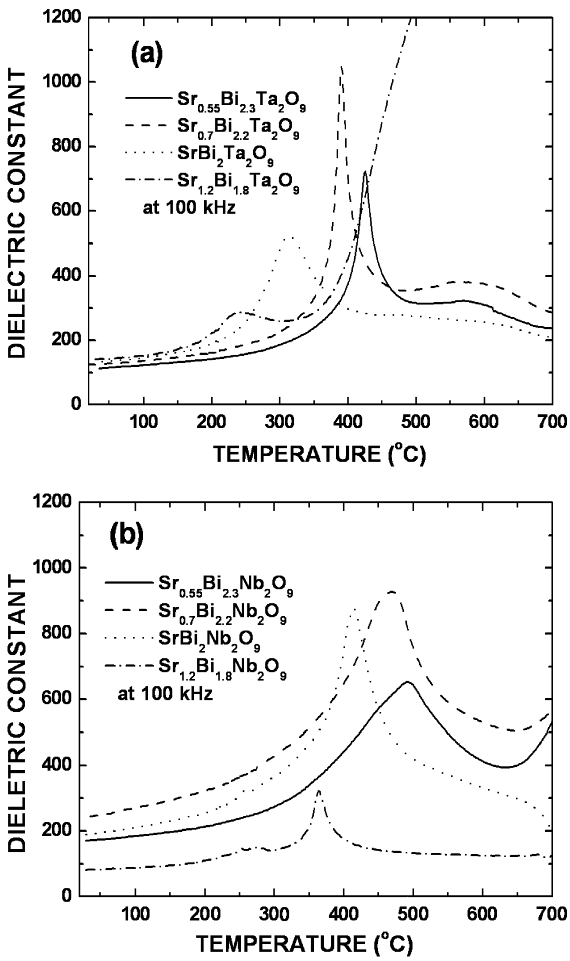

Fig. 2. (a) Dielectric constant of $Sr_{1\pm x}Bi_{2\pm y}Ta_2O_9$ ceramics as a function of temperature measured at 100 kHz and (b) Dielectric constant of $Sr_{1\pm x}Bi_{2\pm y}Nb_2O_9$ ceramics as a function of temperature measured at 100 kHz.

Table 1. Ferroelectric and piezoelectric characteristics of SBN and SBT ceramics.

	$Sr_{1\pm x}Bi_{2\pm y}Nb_2O_9$				$Sr_{1\pm x}Bi_{2\pm y}Ta_2O_9$			
Sr/Bi ratio	0.55/2.3	0.7/2.2	1.0/2.0	1.2/1.8	0.55/2.3	0.7/2.2	1.0/2.0	1.2/1.8
T_C (°C)	494	470	414	364	426	390	314	244
K_p (%)	3.7	4.2	4.7	8.1	3.4	4.6	8.7	2.9
Q_m	1013	918	771	185	3325	2246	390	2066
ε(at RT)	171	245	192	82	112	126	133	141
$\tan\delta$ (at RT)	0.95	1.5	1.2	1.5	1.0	0.9	1.2	0.1

shows the dielectric constant of SBT and SBN samples as a function of temperature, at a frequency of 100 kHz. It is seen that T_C is dependent on Sr/Bi content ration. Figure 2(a) shows the temperature dependence of dielectric constant for $Sr_{1\pm x}Bi_{2\pm y}Ta_2O_9$ samples. Curie temperature of stoichiometric $SrBi_2Ta_2O_9$ was measured as 314°C and broad peak was obtained. On the other hand, others have sharp peak and T_C of $Sr_{0.55}Bi_{2.3}Ta_2O_9$ and $Sr_{0.7}Bi_{2.2}Ta_2O_9$ was decreased from 426°C to 390°C when Bi^{3+} content was increased. Figure 2(b) shows the temperature dependence of dielectric constant for $Sr_{1\pm x}Bi_{2\pm y}Nb_2O_9$ samples. T_C of stoichiometric $SrBi_2Nb_2O_9$ was measured as 414°C and T_C of $Sr_{0.55}Bi_{2.3}Ta_2O_9$ and $Sr_{0.7}Bi_{2.2}Ta_2O_9$ was obtained 494°C to 470°C, respectively. Increase of Bi^{3+} content ratio was showed relaxor properties [14]. The increase in T_C is caused by O-Ta(Nb)-O chain in perovskite structures and it can be associated with the larger distortion of oxygen octahedral. At nonstoichiometric composition, substitutions of two Bi^{3+} for three Sr^{2+} generate vacant cation sites for charge neutrality. Consequently, the excess Bi^{3+} atom would occupy vacant A site (Sr^{2+}) of perovskite so that the increase of Curie temperature would be expected by increase of distortion.

Figure 3 shows electromechanical factor (K_p) and mechanical quality factor (Q_m) of $Sr_{1\pm x}Bi_{2\pm y}Ta_2O_9$ and $Sr_{1\pm x}Bi_{2\pm y}Nb_2O_9$ ceramics as functions of Sr/Bi content ratio. K_p of SBT and SBN obtained about 3–9% lower values than PZT but Q_m obtained higher value. In the case of SBN, the value of K_p increase and the value of K_p decrease as amount of Bi^{3+} is increased. On the other hand, in case of SBT, the value of K_p has a maximum value at stoichiometric composition and the value of Q_m has a maximum value, 3320 at Sr/Bi = 0.55/2.3. In comparison with PZT, this has relatively very high value. SBT and SBN ceramics for fine tolerance oscillator applications has enhanced

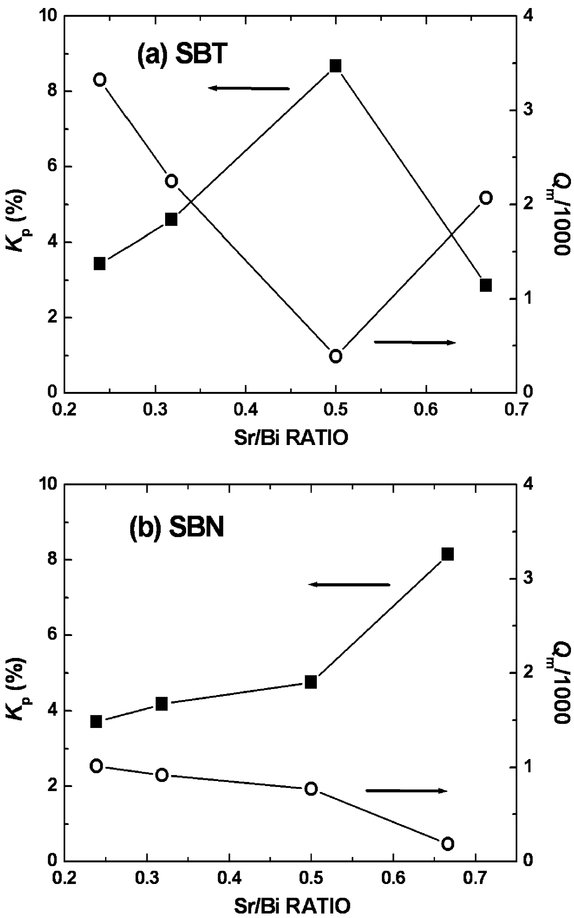

Fig. 3. (a) K_p and Q_m of $Sr_{1\pm x}Bi_{2\pm y}Ta_2O_9$ ceramics as functions of Sr/Bi content ratio and (b) K_p and Q_m of $Sr_{1\pm x}Bi_{2\pm y}Nb_2O_9$ ceramics as functions of Sr/Bi content ratio.

properties when Sr-deficient/Bi-excess. Especially, because Sr-deficient/Bi-excess phase shows higher T_C, it is expected to have low temperature dependence of resonance frequency [5]. Table 1 shows ferroelectric and piezoelectric characteristic of SBN and SBT ceramics.

4. Conclusions

Ferroelectric $Sr_{1\pm x}Bi_{2\pm y}Ta_2O_9$ and $Sr_{1\pm x}Bi_{2\pm y}Nb_2O_9$ ceramics were prepared by a solid reaction method, and dielectric and piezoelectric properties were investigated. A single phase Bi-layered perovskites were formed in all ceramics samples by XRD. As increasing Sr/Bi content ratio, T_C of $Sr_{0.55}Bi_{2.3}Nb_2O_9$ decreased from 494°C to 364°C for $Sr_{1.2}Bi_{1.8}Nb_2O_9$. And T_C of $Sr_{0.55}Bi_{2.3}Ta_2O_9$ decreased from 426°C to 244°C for $Sr_{1.2}Bi_{1.8}Ta_2O_9$. As for piezoelectric properties, the value of K_p decreased with Sr/Bi content ratio. On the other hand, the value of Q_m increased and had a maximum value, at Sr/Bi = 0.55/2.3.

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