Technical report

Piezoelectric Properties of Strontium Bismuth Tantalate $Sr_xBi_{3-x}Ta_2O_9$ Dense Ceramics

Hiroaki TAKEDA, Chie FUJIOKA, Rintaro AOYAGI, Soichiro OKAMURA and Tadashi SHIOSAKI

Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5, Takayama-cho, Ikoma city, Nara 630-0192, Japan

Piezoelectric properties of $Sr_xBi_{3-x}Ta_2O_9$ ($x=0.5-1.0$) [SBT(x)] ceramics were studied for the purpose of discovering bismuth layered-structure ferroelectrics (BLSFs) with large electromechanical coupling factor k_{ij} and mechanical quality factor Q_m. Ordinarily fired (OF) samples were prepared by a conventional ceramic technique and the sintering temperature was varied from 1150 to 1250°C. Before the piezoelectric measurement, an enhancement of the ferroelectric properties of the SBT(x) ceramics by Bi substitution was confirmed. The values of the electromechanical coupling factor with radial-extentional mode k_p for the SBT($x=0.85$) ceramics sintered at 1200°C were found to be the largest ($k_p=10.9\%$) in the SBT(x) system. The piezoelectric and related constants of SBT($x=0.8$) ceramics were also evaluated. The values of k_p (10.6%) and k_{31} (6.8%) with lentgth-extentional mode were higher than those of other OF-BLSFs ceramics with large coupling coefficients, and k_{33} (14.0%) with lentgth-extentional mode were comparable. [Received August 8, 2003; Accepted December 24, 2003]

Key-words : *Strontium bismuth tantalate, Bismuth layered-structure ferroelectrics, Ferroelectricity, Piezoelectricity*

Introduction

Bismuth layered-structure ferroelectrics (BLSFs) are expected to be one series of promising materials that are lead-free electroceramics. The structural formula of the BLSFs is generally described as $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, which consists of pseudo-perovskite $(A_{m-1}B_mO_{3m+1})^{2-}$ layers interleaved with $(Bi_2O_2)^{2+}$ layers along the c-axis. The A site is composed of a mono-, di-, or trivalent metallic ion, and the B site is a tetra-, penta-, or hexavalent metallic ion, where m is the number of BO_6 octahedra in the pseudo-perovskite layers ($m=1$ to 5).[1)] Among the BLSFs, strontium bismuth tantalate ($SrBi_2Ta_2O_9$; SBT) with $m=2$ and bismuth titanate $Bi_4Ti_3O_{12}$ with $m=3$ have been intensively studied for use in nonvolatile random access memories (NvRAMs).[2)-3)] The BLSFs generally show high Curie temperature, and low dielectric constant ε and loss tan δ, large anisotropy k_{33}/k_{31} in coupling factors, low temperature coefficient of delay. Due to these characteristics, BLSFs ceramics are expected to be used in piezoelectric devices under high temperature and high frequency.

It is known that ferroelectric properties of SBT are enhanced by introducing Bi with vacancy into Sr-site.[4)-8)] Shimakawa *et al.*[4)] investigated the crystal structure and ferroelectric properties of SBT and $Sr_{0.8}Bi_{2.2}Ta_2O_9$ and reported that the cation vacancies as well as Bi substitution exist at the Sr site, leading to a higher Curie temperature and greater spontaneous polarization. This enhancement is associated with vacancies at the Sr site in the crystal structure. Onodera *et al.*[5)] and Noguchi *et al.*[6)] confirmed the presence of Sr vacancies in the SBT system by means of a powder diffraction Rietveld analysis. Noguchi *et al.* reported that the maximal value of a spontaneous polarization P_s and a remanent polarization P_r was obtained at $Sr_{0.73}Bi_{2.18}Ta_2O_9$.[7)] Kim *et al.* reported that maximum P_s was observed at $Sr_{0.5}Bi_{2.33}Ta_2O_9$.[8)] Thus, many reports regarding the ferroelectric properties of SBT have been made. However, there are few reports regarding the piezoelectric properties of SBT. To the best of our knowledge, electromechanical coupling factors, k_p and k_t, were observed using SBT ceramics with near stoichiometric composition.[9),10)] It might be expected that the piezoelectric properties of SBT ceramics are improved by introducing Bi with vacancy into the Sr-site.

In this paper, we describe the influence of starting materials composition and sintering temperature on piezoelectric properties for SBT ceramics, for the purpose of obtaining a large electromechanical coupling factor k_{ij} and mechanical quality factor Q_m. The ferroelectric properties of the SBT(x) ceramics were also checked before the piezoelectric characterization. We investigated the relationships between piezoelectricity and ferro-(di-)electricity of SBT.

Experimental procedure

Ceramics samples of $Sr_xBi_{3-x}Ta_2O_9$ (SBT(x): $x=0.5$, 0.6, 0.7, 0.75, 0.8, 0.85, 0.9, and 1.0) were prepared using a conventional sintering (ordinarily fired, OF) technique. The mixture of Bi_2O_3, $SrCO_3$ (99.99%), and Ta_2O_5 (99.9%) powders were used as starting materials. The mixtures were calcined at 800°C for 2 h and at 1100°C for 2 h in air. The powders with 1 wt% poly vinyl alcohol as binder were pressed into disc forms at about 190 MPa. The pressed disc samples were sintered at 1150-1250°C for 2 h. Three sintering temperatures (1150, 1200 and 1250°C) were chosen based on the reports that SBT(x) dose not form at 1100°C and considerably decompose at more than 1300°C.[11)] The chemical composition was measured by inductively coupled plasma emission spectrometry (ICP-ES) analysis. The grain morphology of the ceramics was observed by scanning electron microscopy. For a powder X-ray diffraction (XRD) analysis, parts of the ceramic samples were crushed and ground into powder. The phase identification of the SBT powders indicated that we did not obtain the SBT single phase with the composition up to $x=0.7$. Therefore, the SBT(x) ceramics with $0.7\leq x\leq 1.0$ were used for the electrical characterization. The density of the obtained SBT(x) ceramics was measured by the Archimedes method using distilled water, and the relative density ρ was subsequently calculated. For these ceramics, the electrodes were made on both bases of the disks with fire-on Ag paste or sputtered Au films. The changes in ε_s and tan δ in the temperature range from room temperature to 600°C were also investigated using an impedance analyzer (HP4194A). The P (polarization)-E (electric field) hysteresis loops were measured using a standard RT6000 (Radiant Technologies, Inc.) at room temperature. For the piezoelectric measurement, the poling treatment was performed under an electrical field 2–12 kV/mm in silicone oil at 200–260°C for 5 min. The piezoelectric properties of the poled SBT ceramics were measured by a resonance-anti resonance method with an LF impedance analyzer. The electromechanical coupling coefficients were calculated by Onoe's equation[12] using the resonance frequency f_s and antiresonance f_p.

Results and discussion

The ICP-ES analysis showed that this chemical composition of the ceramics agreed with that of the starting powders. With decreasing x, the grains changed from spherical to round cylinder shapes and the grain size increased. The XRD pattern from the polished ceramics surface was the same as that from the crushed powders, and no preferred orientation was observed. **Figure 1** shows the chemical composition (x) and sintering temperature dependence of density of SBT(x) ceramics. On stoichiometric SBT($x=1.0$) ceramics, the density increased with increasing sintering temperature. However, we were not able to obtain dense stoichiometric SBT ceramics. This result agreed with other earlier reports.[6),7)] In refs.,[6),7),9),10)] the dense SBT ceramics with near stoichiometric composition were fabricated by adding small amounts of bismuth oxide into the starting material. In this study, no excess Bi_2O_3 was used in order to characterize the stoichiometric SBT ceramics. The high density ceramics with $\rho \geq 0.94$ was obtained at $x \geq 0.9$. There was no difference in the relative density ρ between ceramic samples sintered at 1150–1250°C.

The composition (x) dependence of Curie temperature (T_c) for SBT(x) was investigated (see **Fig. 2**). The T_c decreased linearly with x and for samples with $x=0.7$ was 140°C higher than that of the stoichiometric SBT($x=1.0$). This tendency is consistent with the results reported in refs..[4),7),8),13)] No difference between the T_C values for the ceramic samples sintered at 1150°C and those at 1250°C was observed.

Well developed *P–E* hysteresis loops were observed for all samples except for the stoichiometric SBT ceramics. **Figure 3** shows the polarization hysteresis loop at room temperature for the SBT($x=0.8$) ceramics when the drive field (E_m) was about 200 kV/cm. $2P_r$ of 21.9 $\mu C/cm^2$ was attained. The composition (x) dependence of the $2P_r$ and coercive field ($2E_c$) for SBT ceramics are shown in **Fig. 4**. The largest $2P_r$ of 21.9

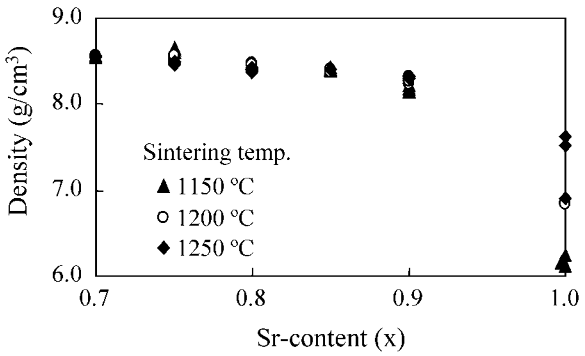

Fig. 1. Density as a function of the composition (x) for SBT ceramics sintered at 1150–1250°C.

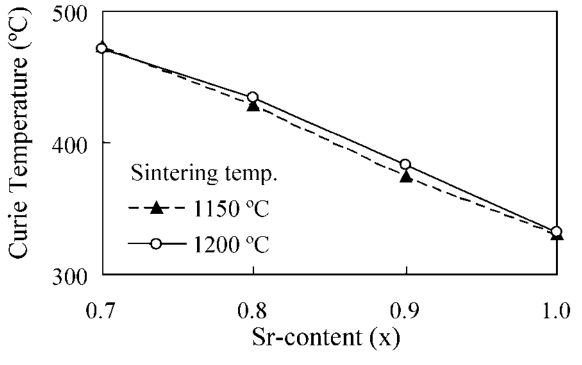

Fig. 2. Curie temperature (T_c) as a function of the composition (x) for SBT ceramics sintered at 1150–1250°C.

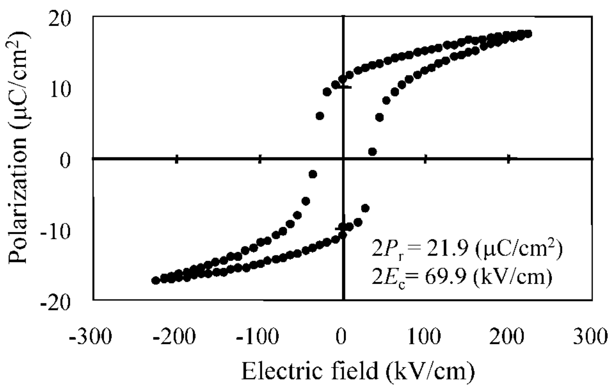

Fig. 3. Polarization hysteresis loops measured using SBT($x=0.8$) dense ceramics at room temperature (25°C).

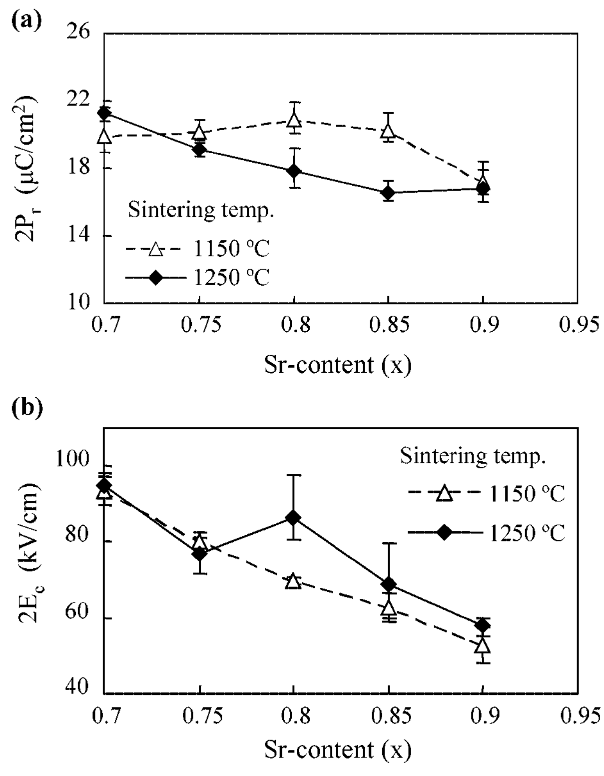

Fig. 4. (a) Remanent polarization $2P_r$ and (b) coercive field $2E_c$ as a function of the composition (x) for SBT ceramics sintered at 1150 and 1250°C.

and 21.3 μC/cm^2 was attained for the SBT($x=0.8$) samples sintered at 1150°C and the SBT($x=0.7$) sample at 1250°C, respectively. The $2P_r$ for the samples sintered at 1250°C decreased monotonically with x. On the other hand, the $2P_r$ value for the samples sintered at 1150°C increased up to $x=0.8$ and then decreased. The decrease in x resulted in a gradual increase in the $2E_c$ value from 55 to 94 kV/cm. The large $2P_r$ was attained for SBT with the cation vacancy and/or Bi incorporation into the Sr site, and this $2P_r$ value was twice as large as that of SBT. This result is the same as those reported using a thin solid film[14)] and ceramics.[4),8)] The enhancement of the spontaneous polarization P_s of SBT was theoretically explained from the results of crystal structure analysis.[4)–8)] Incidentally, Shyu *et al.*[15),16)] prepared the stoichiometric SBT ceramic by sintering at 1000–1300°C, and showed that the maximum density and $2P_r$ were obtained for the sample sintered at 1300 and 1200°C, respectively. Although the change in $2P_r$ basically follows that of P_s, it is difficult to find the dependence of sintering conditions on ferroelectric properties of the SBT ceramics.

The piezoelectric properties of the SBT ceramics with radial-extensional mode (k_p mode) were investigated using a disk sample with an 11 mm in diameter and 1.0 mm thickness at room temperature. In stoichiometric SBT, we did not obtain clear resonance and anti-resonance frequency. If the ideal poling state is achieved, the impedance phase angle θ approaches 90° in the frequency range between f_s and f_p. The maximum phase angle θ observed was around 40°. Although we increased the electric field to increase the phase angle θ, the samples were electrically broken down and high accuracy frequency data could not be obtained. On the other hand, clear amplitudes and phases were observed in the other compositions. **Figure 5** shows the frequency dependence of the impedance $|Z|$ and phase θ measured in the k_p mode of the SBT($x=0.8$) sample. The phase angle of the impedance was limited to around 85°. The calculated electromechanical coefficient k_p and mechanical quality factor Q_m were 10.6% and 5400, respectively.

Figure 6 shows the influences of the sintering temperature and starting material composition on the electromechanical coupling factor k_p (Fig. 6a), the mechanical quality factor Q_m (Fig. 6b), and phase θ (Fig. 6c). Besides our results, we plotted the data of near stoichiometric SBT ceramics sintered at 1260°C for 2 h after ref. 9. Similar changes in the k_p, Q_m and θ values against the composition x were observed in the ceramics sintered at 1150–1250°C. All values (k_p, Q_m and θ) for the samples sintered at 1200°C were higher than those for the samples sintered at 1150°C, and were the same as those for the samples sintered at 1250°C. In Fig. 6a, the k_p increased up to $x=0.85$ as the composition x increased, and thereafter fell off. The largest k_p of 10.8% was obtained for the SBT($x=0.85$) ceramics sintered at 1200°C, whereas that for the near stoichiometric SBT ceramics was 9.46%.[9)] This result revealed that the cation vacancy and/or Bi incorporation in the Sr site of SBT improved not only the ferroelectric property but also the piezoelectric one. In Fig. 6b, the small deviation of Q_m against the composition x was observed for the ceramics sintered at 1200 and 1250°C. On the other hand, the Q_m value for the ceramics sintered at 1150°C increased with x within the region investigated. In Fig. 6c, the phase θ increased up to $x=0.8$, and thereafter was constant at approximately 84°. This suggested that the almost ideal poling state of the SBT(x) ceramics is achieved above $x=0.8$. It is known that both the k_p and Q_m factors depend on the density and poling state of the ceramics. No obvious difference in the density of the prepared

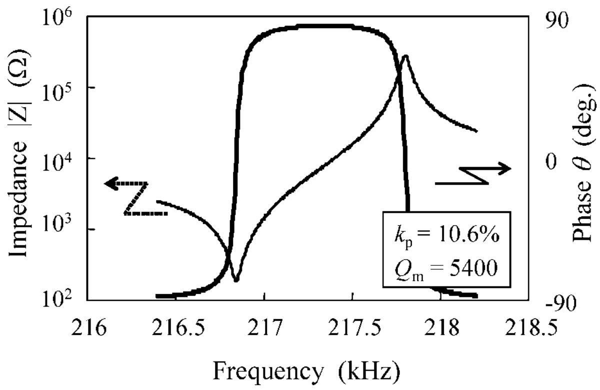

Fig. 5. Frequency dependence of impedance $|Z|$ and phase θ measured at room temperature in radial-extentional mode k_p for SBT ($x=0.8$) ceramics sintered at 1200°C.

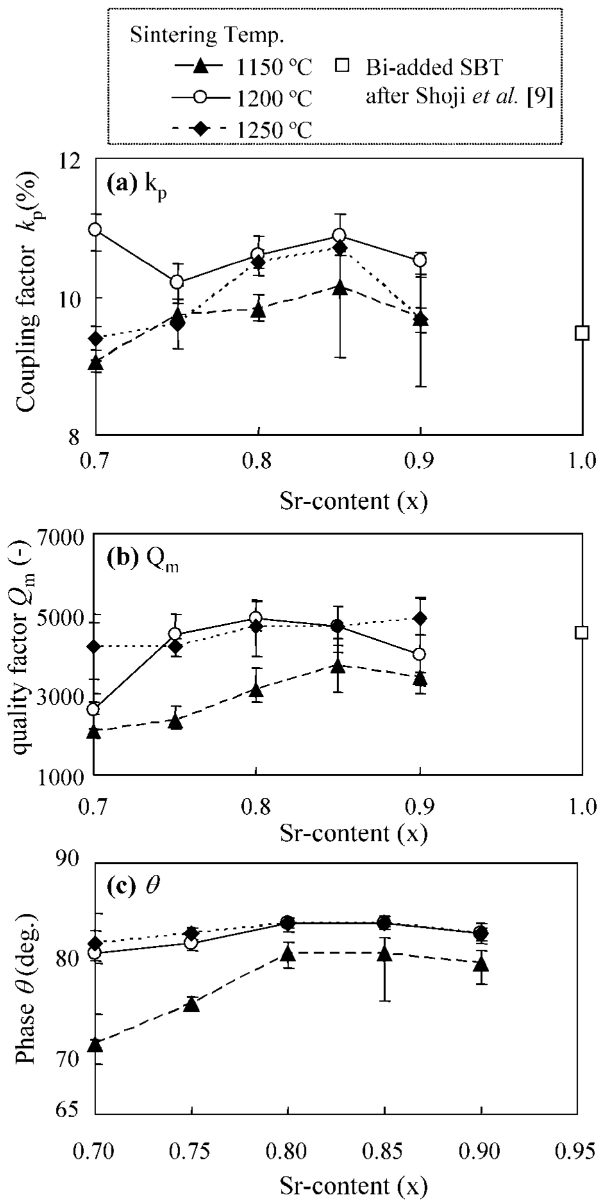

Fig. 6. (a) Electromechanical coupling factor in radial-extentional mode k_p, (b) mechanical quality factor Q_m and (c) phase θ as a function of the composition (x) for SBT ceramics sintered at 1150–1250°C.

Table 1. Piezoelectic and Related Constants of SBT(x=0.8) Ceramics Sintered at 1200°C

ρ_0 (g/cm^3)	8.5	$\varepsilon_{11}{}^T/\varepsilon_0$	108
σ^E	0.19	$\varepsilon_{33}{}^T/\varepsilon_0$	113
d_{31} (pC/N)	6.0	g_{31} (10^{-3}V·m/N)	6.0
d_{33}	13.0	g_{33}	12.9
d_{15}	10.2	g_{15}	10.7
k_p (%)	10.6	$Q_m(k_p)$	5400
k_{31}	6.8	$Q_m(k_{31})$	4100
k_{33}	14.0	$Q_m(k_{33})$	3600
k_{15}	7.8	$Q_m(k_{15})$	5300
N_p (Hz·m)	2490		
N_{31}	1950		
N_{33}	1880		
N_{15}	1280		

samples was observed as shown in Fig. 1. The variation of k_p was very similar to that of θ. Here, as seen in Fig. 4, $2P_r$ and $2E_c$ decreased in rough proportion to x. It was suggested that the reduction of θ occurred because the poling treatment performed in this study was insufficient due to higher $2E_c$ at $x<0.8$. We expect the larger k_p at $x<0.8$ if the poling state is improved. For the improvement, the poling under higher temperature, namely, rising in temperature of the silicon oil is the most effective. In this study, the maximum temperature was set at 260°C for safety reasons because the fire point of the silicon oil is 300°C. Furthermore, all values (k_p, Q_m and θ) did not change for the ceramics poled over 230°C. The dependence of the poling condition will be reported elsewhere.

Table 1 shows piezoelectric and related constants of SBT (x=0.8) ceramics sintered at 1200°C. The ceramics with this composition was selected because many researchers reported the ferroelectric properties in the SBT system. The values of k_p and k_{31} (length-extensional mode) are higher than those of the OF-BLSFs ceramics with the large coupling coefficients (m=2 : $Na_{0.5}Bi_{2.5}Ta_2O_9$,[17] m=3 : $Bi_4Ti_3O_{12}$,[18] m=4 : $Na_{0.5}Bi_{4.5}Ti_4O_{15}$[18),19)] and $CaBi_4Ti_4O_{15}$[20)]). Moreover, the values of k_{33} (length-extensional mode) and Q_m are comparable to the highest ones of the BLSFs. The application of the hot-forged technique is effective in producing the grain-oriented BLSFs ceramic and enhance the coupling factors, ex. $PbBi_2Nb_2O_9$ and $Bi_4Ti_3O_{12}$.[17] By means of this technique, the SBT(x=0.8) ceramics may also show a superior material for use in piezoelectric devices.

Conclusions

$Sr_xB_{3-x}Ta_2O_9$ ($x=0.5-1.0$) ceramics were prepared by a conventional ceramics technique. The influence of the starting material compositions and sintering temperature on the ferroelectric and piezoelectric properties was investigated. The enhancement of remanent polarization $2P_r$ and electromechanical coupling factors k_{ij} were found for SBT ceramics with the cation vacancy and/or Bi incorporation into the Sr site. The largest k_p was obtained for the SBT(x=0.85) ceramics of which the almost ideal poling state is achieved. The piezoelectric properties of the SBT(x=0.8) ceramics were superior to those of the other bismuth layered-structure ferroelectric ones.

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