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Effect of non-stoichiometry on ferroelectricity and piezoelectricity in strontium bismuth tantalate ceramics

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Abstract

The effect of non-stoichiometry on the ferroelectricity and piezoelectricity of strontium bismuth tantalate, $SrBi_2Ta_2O_9$, has been studied using ordinarily fired ceramics. $Sr_{1-x}Bi_{2+x}Ta_2O_9$ ($x = 0.0$–0.3) [SBT(x)] ceramics were prepared by a conventional ceramic technique and sintered at 1200 °C. The remanent polarization, P_r, and the electric coercive field, E_c, increase with a change in the composition x. The electromechanical coupling factors (k_p and k_{33}) and mechanical quality factors Q_m increase up to around $x = 0.2$, but decreases at $x > 0.2$ as the composition x increases. The reduction of the piezoelectric properties at $x > 0.2$ is associated with the decrease in the electric resistivity of the SBT(x) ceramics. Both the ferroelectric and piezoelectric properties of the SBT(x) ceramics are basically enhanced by the Bi substitution.

Keywords: Bismuth layered-structure ferroelectrics; Ferroelectric properties; Piezoelectric properties; Tantalates

1. Introduction

Strontium bismuth tantalate ($SrBi_2Ta_2O_9$; SBT), which is one of the bismuth layered-structure ferroelectrics (BLSFs), have been intensively studied for use in non-volatile random access memories (NvRAMs).[1] Since the BLSFs generally show high Curie temperatures, and low dielectric constants ε and losses tan δ, a large anisotropy k_{33}/k_{31} in electromechanical coupling factors, low temperature coefficients of delay, BLSFs ceramics are also expected to be superior piezoelectric materials for use at high temperature and high frequency.

It was reported that the ferroelectric properties of SBT are enhanced by introducing Bi with a vacancy into the Sr-site.[2–4] These reports focused on the relationship between the ferroelectric properties and the crystal structure of SBT. However, there are a few reports regarding the piezoelectric properties of SBT.[5] In our previous report,[6] we successfully improved the piezoelectric properties in the SBT ceramics by introducing non-stoichiometry into the starting materials. The aim of this study is to investigate the influence of non-stoichiometry on the ferroelectricity and piezoelectricity in SBT ceramics. We prepared Sr-deficient and Bi-excess SBT ceramics by a conventional ceramic technique, and examined their ferroelectric and piezoelectric properties.

2. Experimental procedure

Powders of $SrCO_3$, Bi_2O_3 of 99.99% purity and Ta_2O_5 of 99.9% were used. Ceramic samples of $Sr_{1-x}Bi_{2+x}Ta_2O_9$ (SBT(x): $x = 0.0$–0.3) were prepared using a conventional sintering technique. We did not prepare SBT(x) samples with $x > 0.3$ because the SBT single phase with the composition up to $x = 0.3$ was obtained in our previous study.[6] The powders were mixed in acetone, dried, and then calcined at 800 °C for 2 h in air. The calcined powders were heated at 1100 °C for 2 h in air. The phase identification of the SBT(x) powders was performed using a powder X-ray diffraction (XRD) method. The SBT(x) powders were uniaxially pressed into discs or cylinders at 190 MPa. The ceramic samples were prepared by the ordinary fired method at 1200 °C for 2 h. This sintering condition was also determined, based on our previous report.[6] The sintered disk ceramics with an 11.0 mm diameter were polished into a 0.10 mm thick plate for characterization of the dielectric and ferroelectric properties. For

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these ceramics, the electrodes were made on the face of the disks with fire-on Ag paste or sputtered Au films. The frequency dependence of the dielectric constant ε_s and dielectric loss factor tan δ of the SBT(x) ceramics were measured in the frequency range of 10 kHz to 1 MHz using an impedance analyzer (HP4194A). The Curie temperature T_c was also determined. The P (polarization)–E (electric field) hysteresis loops were measured using a standard RT6000 (Radiant Technologies, Inc.) at room temperature in a silicone oil bath.

For the piezoelectric measurement, the SBT(x) ceramics were cut and polished into the appropriate shape for two electromechanical coupling factors (k_p and k_{33}) in the corresponding vibration (radial- and length-extensional) modes. For the k_p and k_{33} modes, we prepared disc (11 mm in diameter and 1.0 mm thickness) and cylinder (2 mm × 2 mm × 5 mm) samples, respectively. We performed the poling treatment of the sample before measurements of the piezoelectric properties. The electric field strength (E_p), temperature (T_p) and time (t_p) for a poling treatment were as follows: E_p = 8–10 kV/cm, T_p = 250 °C, t_p = 5 min for the k_p mode and E_p = 4 kV/cm, T_p = 260 °C, t_p = 5 min for the k_{33}. 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. The dependence of the piezoelectric properties on the poling condition will be reported elsewhere. The piezoelectric properties were investigated using a resonance–antiresonance method with a LF impedance analyzer. The electromechanical coupling coefficients were calculated on the basis of Onoe's equation[7] using the resonance–antiresonance frequency f_s and f_p.

3. Results and discussion

Fig. 1a shows the temperature dependence of the dielectric constant measured at a frequency of 100 kHz for the SBT(x) ceramics. All samples show a peak in the dielectric constants between 300 and 600 °C corresponding to the Curie temperature T_c. Since the peak position of T_c was independent of the measured frequency between 100 kHz and 15 MHz, it was found that no relaxation effect has been observed for the SBT(x) ceramics. Fig. 1b shows the T_c as a function of x. The T_c linearly decreased with an increase in x from 330 °C (x = 0) to 470 °C (x = 0.3). This tendency is consistent with the results reported in Refs. [2–4].

The P–E hysteresis loops of the SBT(x) ceramics were measured at room temperature and the electric field was applied along the direction parallel to the pressing axis. Fig. 2 shows the polarization hysteresis loop at room temperature for the SBT(x = 0.3) ceramics sintered when the drive field (E_m) was about 200 kV/cm. The remanent polarization P_r of 10.2 μC/cm^2 was observed. Well developed P–E hysteresis loops were observed for all samples except for the stoichiometric SBT(x = 0) ceramics. This result is because it is difficult to obtain dense stoichiometric SBT(x = 0) ceramics as

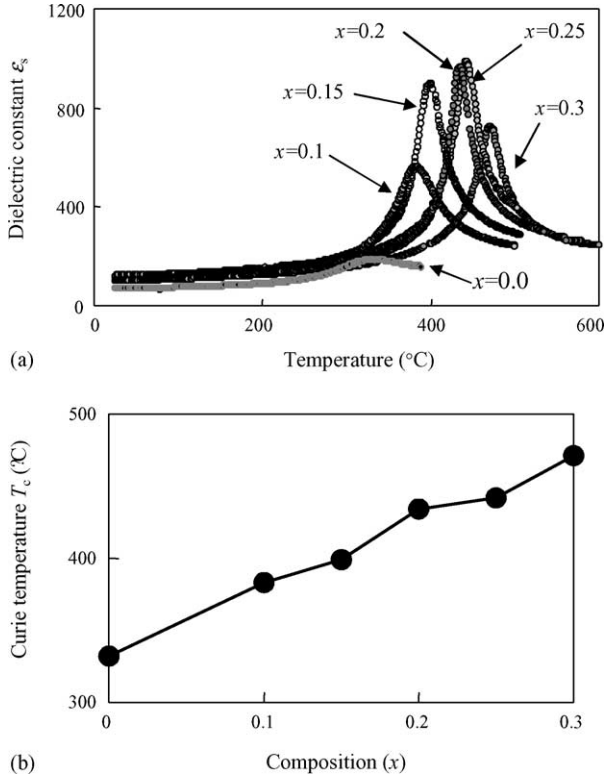

Fig. 1. (a) Temperature dependence of dielectric constant ε_s, and (b) Curie temperature T_c as a function of the composition (x) for SBT(x) ceramics.

discussed in our previous report.[6] The high density ceramics with $\rho \geq 0.93$ was obtained at $x \geq 0.1$.

The composition (x) dependence of the P_r and coercive field (E_c) for the SBT(x) ceramics is shown in Fig. 3. The increase in x resulted in a gradual increase in the E_c value from 27 to 38 kV/cm. The large P_r was attained for SBT with the cation vacancy and/or Bi incorporation into the Sr-site. This result is the same as those reported in Ref. [4]. The enhancement of the spontaneous polarization P_s and enlargement of the E_c

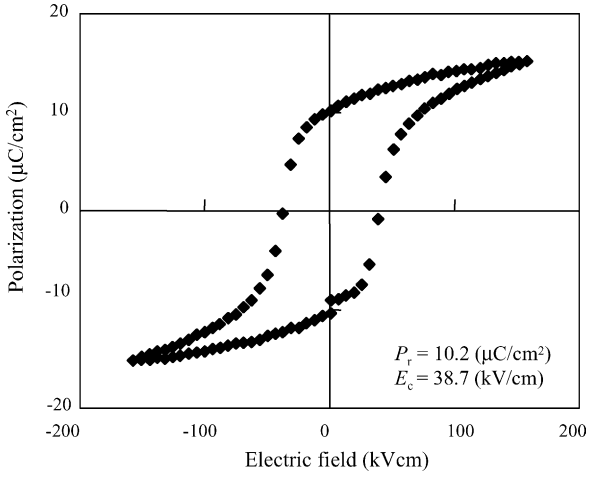

Fig. 2. Polarization hysteresis loop measured using SBT(x = 0.3) dense ceramics at room temperature (25 °C).

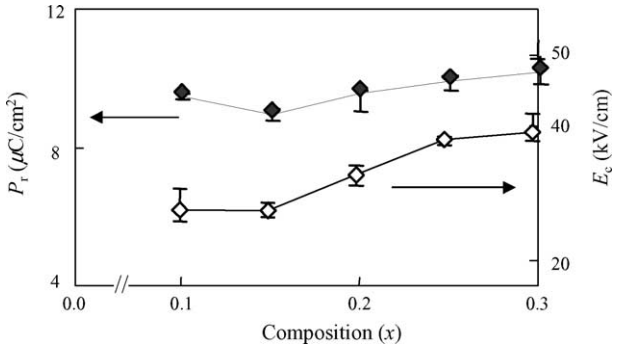

Fig. 3. Remanent polarization P_r and coercive field E_c as a function of the composition (x) at room temperature (25 °C).

value in the SBT(x) was favorably explained from the results of X-ray and/or neutron crystal structure analysis.[2–4]

Fig. 4 shows the frequency dependence of the impedance, $|Z|$, and the phase, θ, in the k_{33} mode for the SBT($x = 0.2$) ceramics. 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 phase angle θ observed on the samples was around 85°. The calculated k_{33} value of 13.8% was near the maximum value of the isomorphic BLSF ceramics fabricated by an ordinary firing method.

Fig. 5 shows the influences of the sintering temperature and starting material composition on the electromechanical coupling factors k_p and k_{33} (Fig. 5a), the mechanical quality factor Q_m (Fig. 5b), and phase θ (Fig. 5c). In Fig. 5c, we omitted the θ and k_{33} data for SBT($x = 0.0$) ceramics because $\theta < 0°$ and the k_{33} values are very small. Similar changes in the $k_p(k_{33})$, Q_m and θ values versus the composition x were observed in the SBT(x) ceramics. In Fig. 5a, k_p and k_{33} increased to $x = 0.15$ and 0.25 as the composition x increased, and thereafter decreased, respectively. The highest k_p of 10.8% was obtained for the SBT($x = 0.15$) ceramics and the highest k_{33} of 14.2% was for the SBT($x = 0.25$) ones. These results indicated that the incorporation of Bi atoms

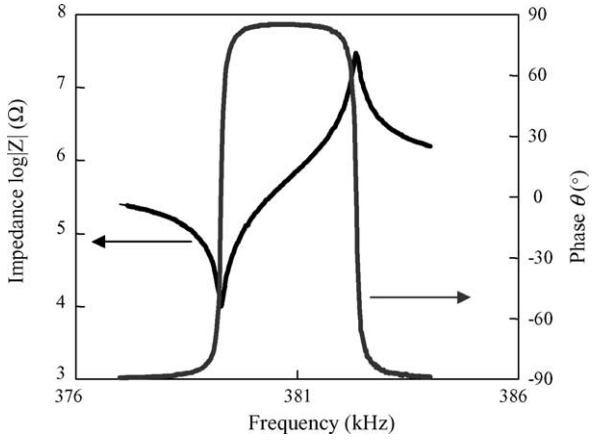

Fig. 4. Frequency dependence of impedance $|Z|$ and phase θ measured at room temperature in length-extensional mode k_{33} for SBT($x = 0.2$) ceramics.

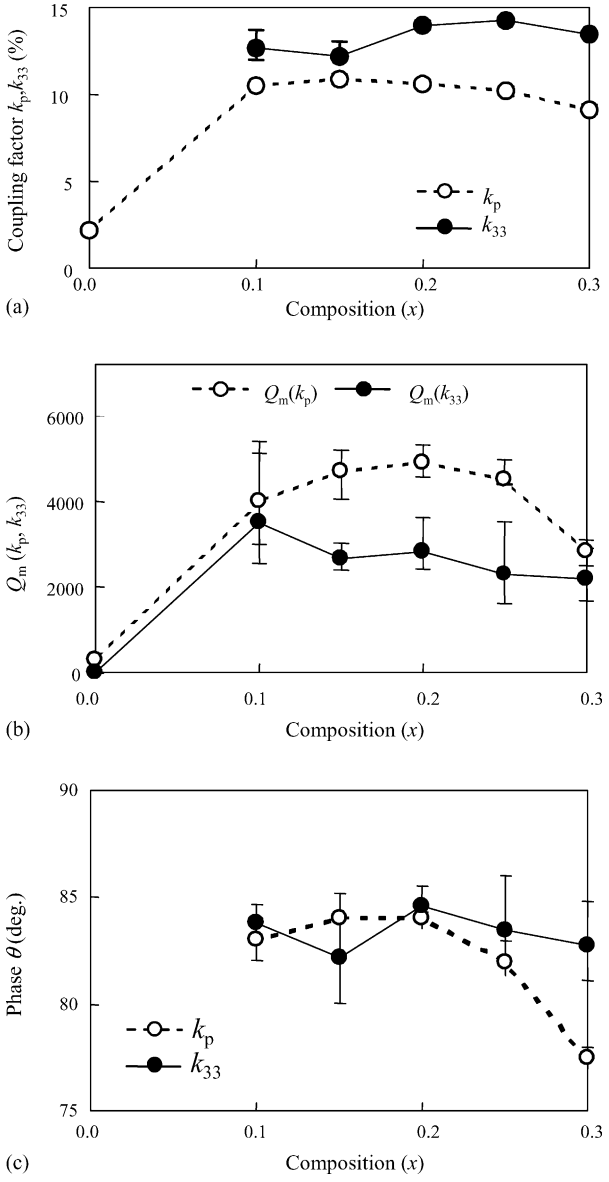

Fig. 5. (a) Electromechanical coupling factors (k_p and k_{33}), (b) mechanical quality factors Q_m, and (c) phase θ as a function of the composition (x) for SBT(x) ceramics.

with a vacancy into the Sr-site improved not only the ferroelectric property but also the piezoelectric one. In Fig. 5b, the Q_m in k_p and k_{33} modes increased up to $x = 0.20$ and 0.10 with a change of the composition x, and then decreased, respectively. The highest Q_m of 4900 in the k_p mode was obtained for the SBT($x = 0.20$) ceramics and the highest one in the k_{33} mode of 3500 was for the SBT($x = 0.10$) ones. In Fig. 5c, the maximum θ values in both the k_p and k_{33} modes was observed at $x = 0.20$. The variation in the $k_p(k_{33})$ and Q_m values was very similar to that of θ. It is known that both the coupling factors and Q_m factors depend on the density and poling state of the ceramics. No difference in the density of the prepared samples was found in this study except for the SBT($x = 0.0$) ceramics. Therefore, it was expected that the

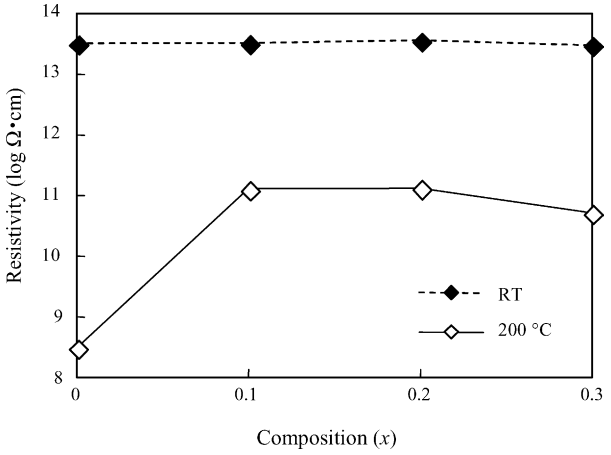

Fig. 6. Resistivity at room temperature and 200 °C as a function of the composition (x) for SBT(x) ceramics.

reduction in θ occurred because the poling treatment in this study was insufficient due to a higher E_c at $x > 0.2$ or other phenomena. We measured the P–E hysteresis loops of the SBT(x) ceramics at 200 °C near T_p. In this measurement, a very small variation in E_c (12–14 kV/cm) was observed from $x = 0.0$–0.3. These E_c value also were low enough to apply the poling treatment.

Fig. 6 shows the composition (x) and temperature dependences of the electric resistivity in the SBT(x) ceramics. The resistivity of all the SBT(x) ceramics decreased from room temperature (25 °C) to 200 °C over a 10^2 order. The resistivity at 25 °C was independent of the composition (x). On the other hand, the variation in the resistivity at 200 °C was very similar to that of θ. In Fig. 6, the resistivity at 200 °C increased up to $x = 0.20$ as the composition x increased, and thereafter decreased. The low resistivity of the SBT($x = 0.0$) ceramics was due to the low density of the ceramic samples. The density of the other SBT(x) ceramics was the same. The ferroelectric property was enhanced with the increasing x, as shown in Fig. 3. Therefore, we regarded that the decrease in the resistivity, i.e., the change in the conductivity, for the SBT(x) ceramics at $x > 0.2$ made the poling treatment insufficient and then lowered the piezoelectric properties. In this study, we prepared SBT(x) ceramics with the nominal starting composition of $Sr_{1-x}Bi_{2+x}Ta_2O_9$. Considering charge neutrality, a very small amount of Bi_2O_3 should exist in the ceramic samples except for $x = 0.0$, but we did not detect any impurities using the X-ray diffraction technique. Noguchi et al.[4] synthesized SBT ceramics with the nominal starting composition of $Sr_{1-z}Bi_{2+z}Ta_2O_9$ and found impurity phases for the samples with $z > 0.15$ by Rietveld analysis. The existence of the impurity phases probably lowered the resistivity of the SBT($x > 0.2$) ceramics. We concluded that the piezoelectric properties of the SBT(x) ceramics are enhanced by Bi substitution, as is the case for the ferroelectric properties. It is expected that higher k_p and k_{33} at $x > 0.2$ are obtained if the poling state is improved.

4. Conclusions

SBT(x) ceramics with $x = 0.0$–0.3 were synthesized using a conventional ceramics technique under the sintering conditions of 1200 °C and 2 h, based on our previous report.[6] We focused the influence of non-stoichiometry on the ferroelectric and piezoelectric properties in SBT(x). An enhancement of the remanent polarization $2P_r$ with increasing x was confirmed. The maximum electromechanical coupling factors (k_p and k_{33}) and mechanical quality factors Q_m were obtained for an SBT(x) at around $x = 0.2$. The reduction of the piezoelectric properties at $x > 0.2$ was found. We regarded that this phenomenon was due to the decrease in the electric resistivity of the SBT(x) ceramics, and then concluded that the piezoelectric properties of the SBT(x) ceramics are basically enhanced by Bi substitution.

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