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Preparation and electrical properties of $SrBi_2Ta_2O_9$ ceramic

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$SrBi_2Ta_2O_9$ (SBT) ceramic materials were prepared by the conventional mixed-oxide method. Ceramics sintered at different temperatures had distinctly different microstructures. Anisometric plate-like crystalline grains were observed which revealed the layered structure of the material. The variations of the saturation polarization (P_s), remanent polarization (P_r) and coercive field (E_c) with applied field and temperature were studied by hysteresis (P-E) loop measurements. Samples were also DC poled at various temperatures and electric fields, and their permittivity, piezoelectric (d_{33}) and pyroelectric coefficient (p) were measured.

1. Introduction

$SrBi_2Ta_2O_9$ (SBT) is a bismuth-based ferroelectric material which has attracted considerable interest ever since the report that the polarization of SBT films is switchable at low voltage and there is no fatigue with polarization switching [1–7]. This bismuth compound has the general formula $ABi_2B_2O_9$, where A is the divalent metal ion Sr and B is the ion Ta with valence +5. The lattice structure of SBT consists of perovskite (TaO_6) octahedra separated at intervals by bismuth oxide $(Bi_2O_2)^{2+}$ planes. The spontaneous polarization arises from the $(SrTaO_3)^{1+}$ group. Since the $(Bi_2O_2)^{2+}$ layer weakens the dipole interaction of the perovskite "building blocks" the spontaneous polarization lies essentially parallel to the $(Bi_2O_2)^{2+}$ layer, and so the ferroelectric domain configurations in SBT are 180° domains. The deformation of the crystal associated with 180° domain switching is smaller than that associated with 90° domain switching. Moreover, SBT does not contain unstable ions like Ti^{4+} which can change its oxidation state easily, thereby creating oxygen vacancy. These may be the reasons for the good fatigue characteristics of SBT [3]. Most of the reported studies have been concentrated on SBT films [2–7] and there is a lack of data on bulk SBT ceramic material which may be a suitable substrate for growing SBT thin films. In this work, we have studied the polarization, dielectric permittivity, piezoelectric and pyroelectric properties of bulk SBT ceramic.

2. Experimental procedure

The SBT ceramic was prepared by the conventional mixed oxide method using materials (Ta_2O_5, Bi_2O_3 and $SrCO_3$) which are of chemically pure grade. The above chemicals with the stoichiometric ratio of the composition were mixed by ball-milling. The SBT compound was obtained after calcining the mixture at 730°C for 2 hrs. This temperature was selected because too low a temperature would result in incomplete reaction while too high a temperature would cause excessive loss of Bi. X-ray diffraction patterns of the calcined powders were obtained in order to ascertain whether the composition was correct. The Curie transition temperature of the SBT powder was ~340°C, as reflected by the occurrence of an endothermic peak in differential scanning calorimeter (DSC) measurements. The calcined powder was ball-milled again to reduce the particle size, and then mixed with a binder and pressed into disc-shaped samples. The disc sample was heated to about 800°C to remove the binder and then placed in a sealed Al_2O_3 crucible with some SBT powder in it and sintered at 1185–1230°C for one hour.

The fracture surfaces of the sintered samples were examined in a Cambridge Stereoscan 250 MK2 scanning electron microscope (SEM). Hysteresis (P-E) loop measurements were performed using a Radiant Technology RT 66A ferroelectric test system equipped with a Trek P0623A power amplifier. In order to elicit piezoelectric and pyroelectric activities, the ceramic samples were poled by applying electric fields of different magnitudes and at various temperatures in an oil bath. The permittivities of the ceramic before and after poling were measured using a HP 4194A impedance analyzer. The pyroelectric coefficient p was measured using a digital integration method [8] and the d_{33} piezoelectric coefficient was measured using a Pennebaker model 8000 tester from American Piezo-Ceramic Inc. For the poled samples, the dielectric, piezoelectric and pyroelectric properties were measured 24 hrs after poling.

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3. Results and discussion

3.1. SEM observations

The SEM micrographs of the fracture surfaces of the SBT samples sintered at 1185°C, 1200°C, 1215°C and 1230°C for 1 hr are shown in Fig. 1a–d, respectively. It is seen that the sample consists of anisometric plate-like crystalline grains whose size increases from less than 10 μm to more than 30 μm as the sintering temperature increases from 1185°C to 1230°C. The crystalline grains seem to be randomly oriented in the SBT sample sintered at 1185°C but there is a certain degree of preferred orientation in the sample sintered at 1230°C. This arises because the grain growth rate is higher in the direction perpendicular to the *c*-axis of the crystal. The anisotropic grain growth is more prominent at higher sintering temperature as the process of mass transfer becomes easier. The densities of all the samples are quite similar, being about 7800 kg/m^3. Although these observed values are slightly higher than the reported density of 7500 kg/m^3 [1], some pores are still observed in the samples.

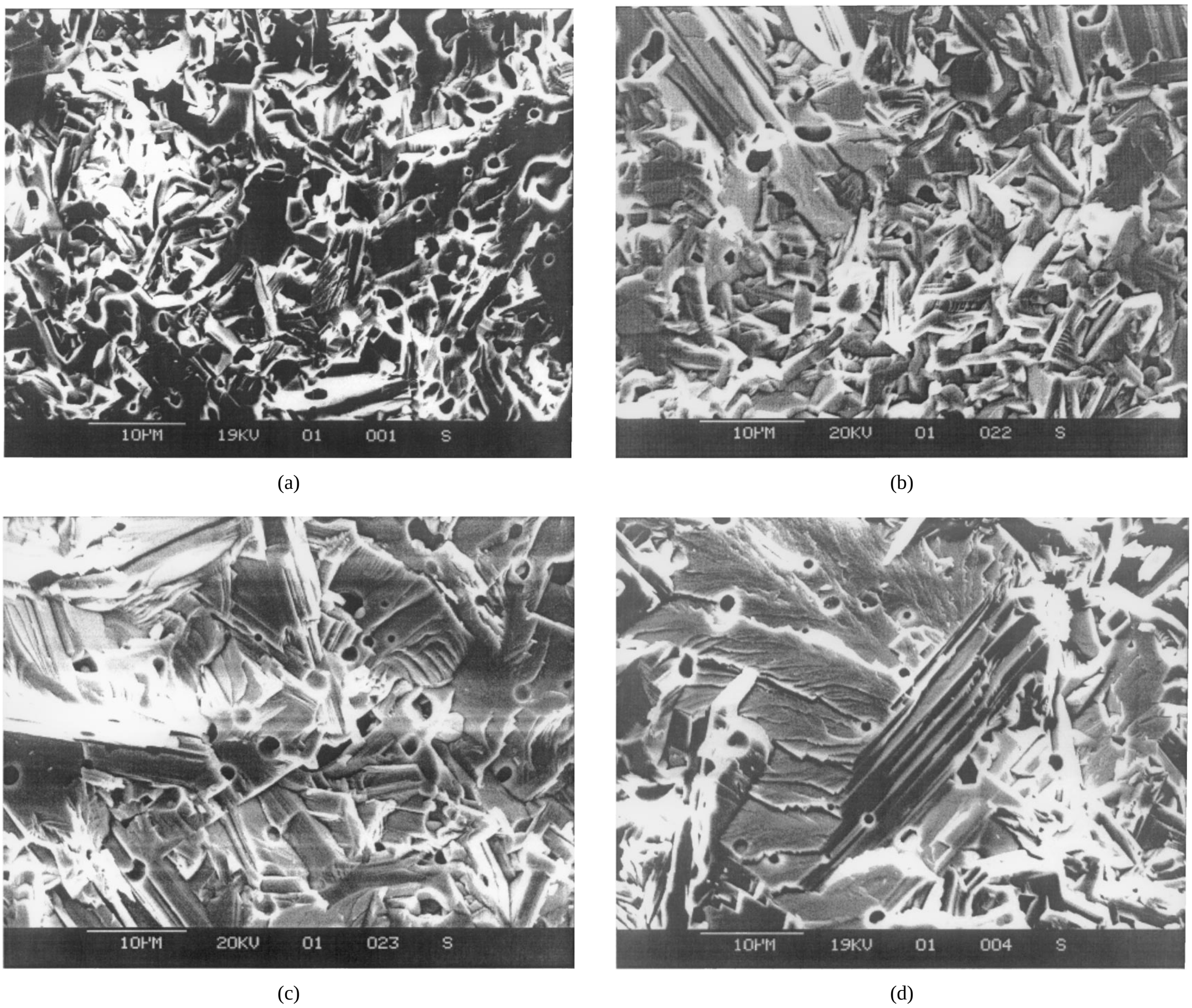
3.2. Hysteresis (P-E) loop measurements

The room temperature P-E loops (with a maximum applied electric field of 6 MV/m) for SBT(1185°C sintered) and SBT(1230°C sintered) are shown in Fig. 2. The P-E loop of 1230°C sintered SBT is more square-like than that of 1185°C sintered SBT. The variations of the saturation polarization P_s, remanent polarization P_r and coercive field E_c with applied field and temperature have been studied by hysteresis measurements and the results are shown in Figs 3, 4 and Table I.

As shown in Fig. 3, P_s, P_r and E_c at both 23°C and 100°C increase as the applied field increases, but the increase is less significant at 100°C. At low applied field (3.8 MV/m), the temperature dependence of P_r is weak, but P_s increases while E_c decreases as the temperature increases (see Fig. 4). At an applied field of 6 MV/m, P_s increases slightly while both P_r and E_c decrease with increasing temperature (see Table I). At 23°C and at this applied field, $P_s = 5.5 \times 10^{-2}$ C/m^2, which is close to the theoretical value of 5.8×10^{-2} C/m^2 [1]. The decreases in P_r and E_c indicate that domain reversal is easier at higher temperature. It is also seen from Table I that the sample sintered at higher temperature (1230°C) has lower P_s and P_r but higher E_c, which result from the larger size and preferred orientation of the crystallites.

3.3. Permittivity measurements

The permittivities ε at 23°C of unpoled SBT sintered at 1185°C and 1230°C are shown as functions of frequency in Fig. 5. ε for SBT (1230°C sintered) is smaller

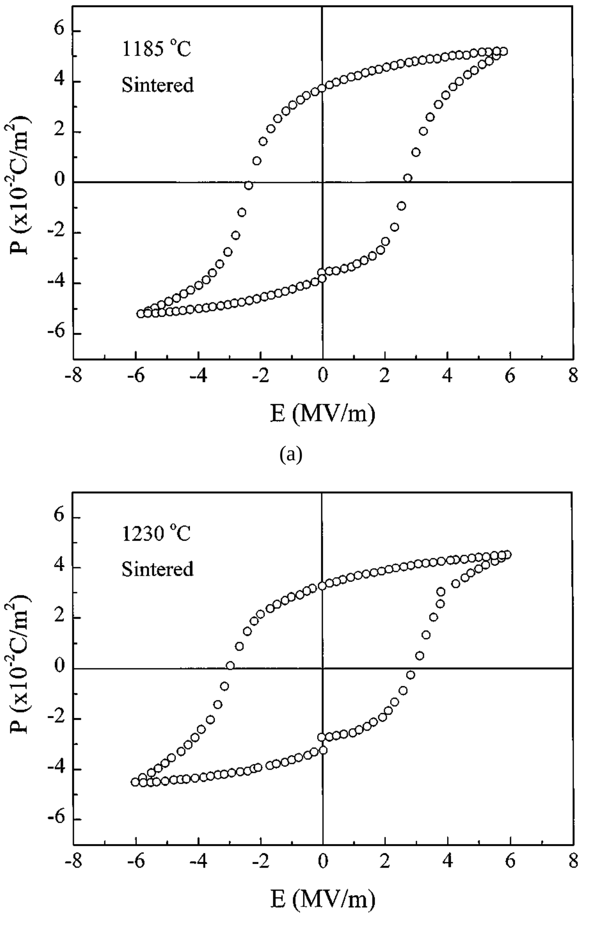


(a) (b) (c) (d)

Figure 1 SEM micrographs of the fracture surface of SBT ceramic samples sintered at (a) 1185°C, (b) 1200°C, (c) 1215°C and (d) 1230°C.

TABLE I P_s, P_r and E_c for SBT sintered at 1185°C and 1230°C

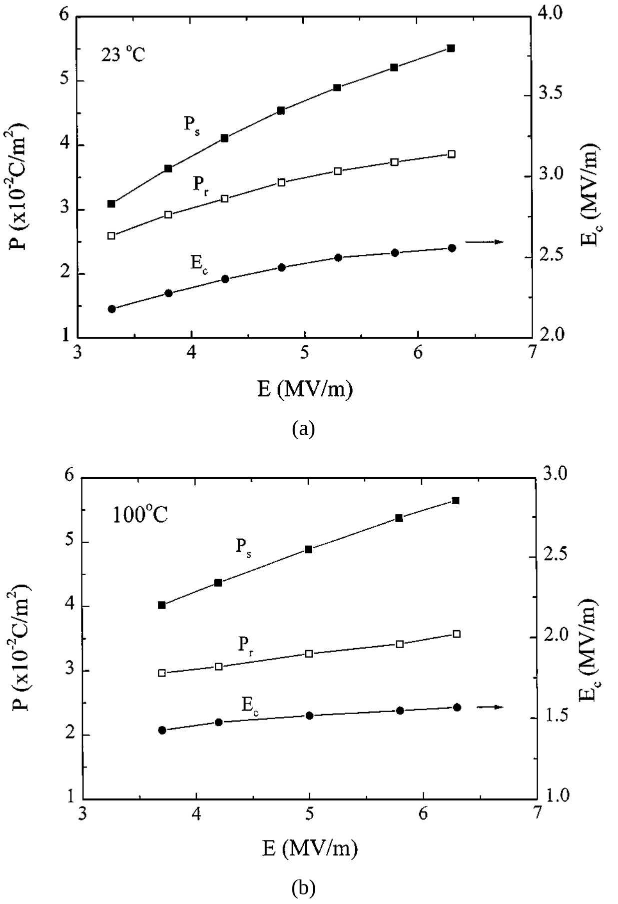
	Applied field (MV/m)	SBT (1185°C sintered) at 23°C	SBT (1185°C sintered) at 100°C	SBT (1230°C sintered) at 23°C	SBT (1230°C sintered) at 100°C
P_s ($\times 10^{-2}$ C/m^2)	3.8	3.64	4.02	3.04	3.70
P_r ($\times 10^{-2}$ C/m^2)	3.8	2.92	2.97	2.42	2.59
E_c (MV/m)	3.8	2.27	1.47	2.46	1.54
P_s ($\times 10^{-2}$ C/m^2)	6.0	5.50	5.64	4.50	4.89
P_r ($\times 10^{-2}$ C/m^2)	6.0	3.86	3.55	3.25	3.20
E_c (MV/m)	6.0	2.56	1.57	2.96	1.95



(a)

(b)

Figure 2 Hyteresis (P-E) loops of (a) SBT (1185°C sintered) and (b) SBT (1230°C sintered).



(a)

(b)

Figure 3 P_s, P_r and E_c of SBT (1185°C) as functions of applied electric field at (a) 23°C and (b) 100°C.

than that of SBT (1185°C sintered) at low frequency. This may be related to the crystallite orientation (hence dipole orientation) in the 1230°C sintered sample. However, the ε values for the two samples become closer with increasing frequency, which may indicate that the effect of dipole orientation is less important at higher frequency.

The effect of poling is shown in Fig. 6. There is a marked decrease in ε at low frequency after poling. However, poling at 180°C and at applied fields of 3–6 MV/m gives only a very slight decrease in ε, thus indicating that similar degrees of domain switching are achieved in this range of electric fields. The most "well-poled" sample (poled at 180°C with 6 MV/m for 10 min.) has the lowest ε and the highest piezoelectric coefficient (as will be discussed).

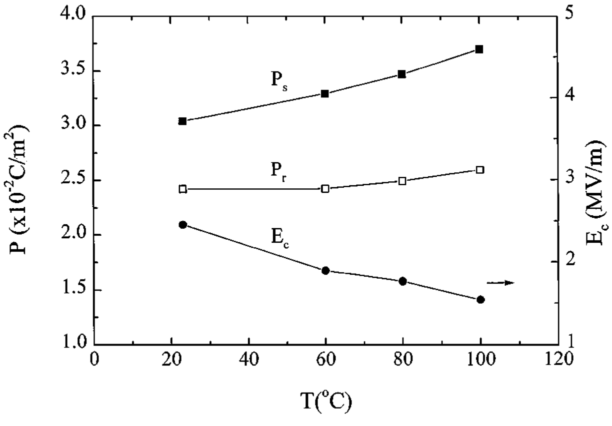


Figure 4 P_s, P_r and E_c of SBT (1230°C) as functions of temperature. The applied electric field was 3.8 MV/m in the P-E loop measurement.

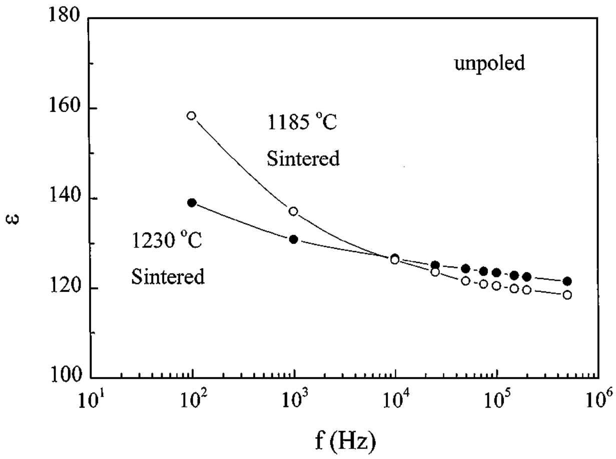


Figure 5 Permittivities of unpoled SBT sintered at 1185°C and 1230°C as functions of frequency.

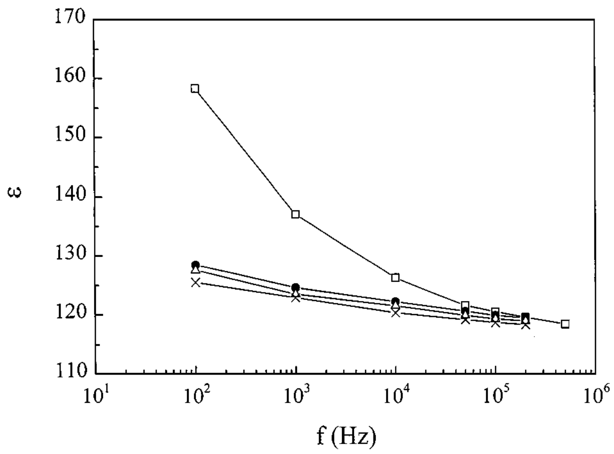


Figure 6 Permittivities of SBT (1185°C sintered) as functions of frequency. □: unpoled; •: poled at 3 MV/m and 180°C for 10 min; △: poled at 4.5 MV/m and 180°C for 10 min; ×: poled at 6 MV/m and 180°C for 10 min.

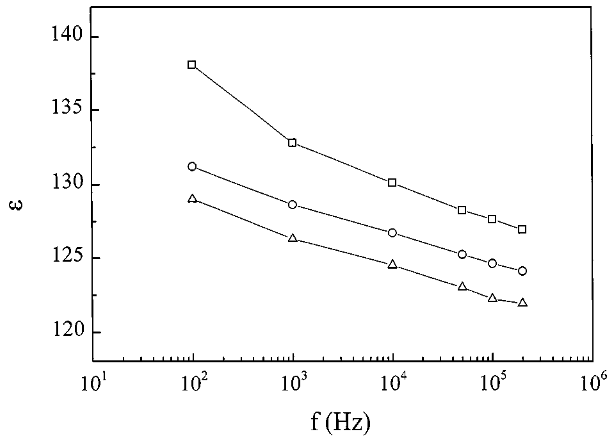


Figure 7 Permittivity of SBT (1230°C sintered) as functions of frequency. □: unpoled; ○: after P-E loop measurement at 3.5 MV/m and 85°C; △: poled at 6 MV/m and 85°C for 10 min.

The permittivities of selected 1230°C sintered SBT samples (unpoled, poled and after P-E loop measurement) were measured as a function of frequency, giving the results shown in Fig. 7. The permittivity decreases after P-E loop measurement because there is some domain switching and the sample has become "partially poled". The sample poled at 85°C and 6 MV/m has the lowest ε. Apparently, the degree of the domain switching in the DC poled sample is higher than that in the sample poled by cycling through a P-E loop since the poling field is higher and the poling duration is longer.

3.4. Piezoelectric and pyroelectric properties

The piezoelectric (d_{33}) and pyroelectric (p) coefficients were measured for the poled samples. The value of d_{33} increases with the poling field. For example, when SBT (1230°C sintered) is poled at 180°C, d_{33} increases from 10.8 pC/N to 11.4 pC/N as the poling field increases from 3 MV/m to 6 MV/m. On the other hand, at a fixed poling field, d_{33} increases as the poling temperature increases. When this sample is poled at 6 MV/m, d_{33} increases from 9.7 pC/N to 11.4 pC/N as the poling temperature increases from 80°C to 180°C. This is because E_c decreases as the temperature rises, so the ratio of the poling field E to the coercive field (E/E_c) becomes larger at higher temperature. In fact, a high d_{33} value of 11.4 pC/N can be achieved for both 1185°C and 1230°C sintered SBT by poling at room temperature if the poling field is sufficiently high e.g. 11 MV/m. We have found that "well poled" samples can be produced by DC poling if E/E_c exceeds about 4. A d_{33} value of 8.3 pC/N was obtained for the SBT(1230°C sintered) sample after P-E loop measurement at 85°C and 3.5 MV/m which indicates that the sample is partially poled.

Fig. 8 shows the pyroelectric coefficient (p) as a function of temperature for the most well-poled SBT sample (1230°C sintered). The value of p at room temperature is 55 μ C/m^{2}K and it increases about 20% as the measurement temperature increases from 10°C to 60°C. For SBT (1185°C sintered) poled under the same condition, p is 57 pC/m^{2}K at room temperature and has a similar temperature dependence.

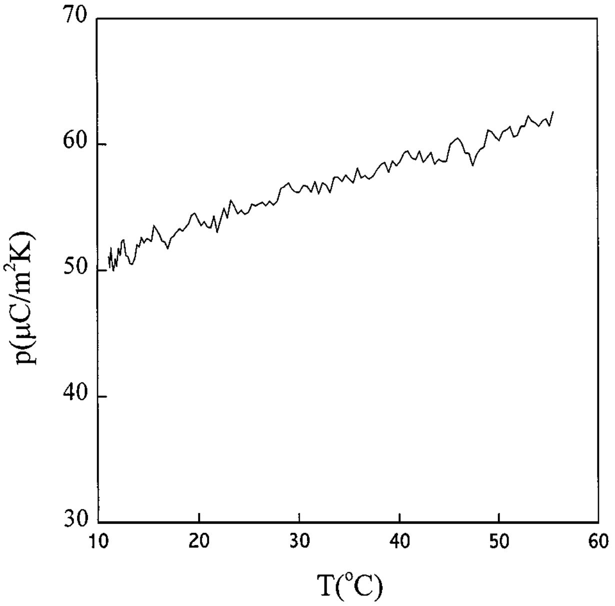


Figure 8 Pyroelectric coefficient (p) of SBT (1230°C sintered) poled at 6 MV/m and 180°C for 10 min. as a function of temperature.

4. Conclusions

$SrBi_2Ta_2O_9$ ceramic materials were prepared by the conventional mixed-oxide method using different sintering temperatures. Anisometric plate-like crystalline grains were observed in the microstructure, thus revealing the layered structure of the material. The saturation polarization (P_s), remanent polarization (P_r) and coercive field (E_c) of samples sintered at different temperatures were measured at various temperatures and applied fields. E_c decreases with increasing temperature, indicating that poling is more effective at higher temperature. Before poling, the 1230°C sintered sample has a lower permittivity than that sintered at 1185°C at low frequency, but both samples have roughly the same permittivity at all frequencies after poling. The SBT ceramic has lower piezoelectric and pyroelectric coefficients than those of lead zirconate titanate (PZT).

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