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Sintering and dielectric properties of $Sr(Bi_2Ta_2)_{1-x}Ti_{4x}O_9$ ceramics

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Abstract

The influence of Ti^{4+} substitution on the dielectric properties of $Sr(Bi_2Ta_2)_{1-x}Ti_{4x}O_9$ (SBTT) ceramics (x up to 0.2) has been studied. The sintering temperature of SBTT slightly decreases as the TiO_2 content increases with the partial substitution of Bi_2O_3 and Ta_2O_5 by TiO_2. X-ray diffraction analysis on SBTT ceramics with low TiO_2 content and sintered at lower temperature indicate that single-phase layered perovskite ferroelectrics are obtained and no TiO_2 phase is found, while the TiO_2 crystal phase increases with the TiO_2 content and sintering temperature. The incorporation of Ti^{4+} into $SrBi_2Ta_2O_9$ results in a shift of the Curie temperature to higher values than for $SrBi_2Ta_2O_9$. Nevertheless, the Curie temperature is not a function of sintering temperature and TiO_2 content.

Keywords: C. Ferroelectric properties; C. Dielectric properties; Curie temperature

1. Introduction

In order to improve the dielectric characteristics, many electrical properties of ceramics may be varied significantly by changing chemical composition. For example, as Bi_2O_3 was substituted by Sm_2O_3 to form $(Bi_{1-x}Sm_x)NbO_4$ [1] or Nb_2O_5 by Ta_2O_5 to form $Bi(Nb_{1-x}Ta_x)O_4$ [2], both $(Bi_{1-x}Sm_x)NbO_4$ and $Bi(Nb_{1-x}Ta_x)O_4$ possessed high quality (Qxf) values and lower temperature coefficients of resonant frequency. Another example is the solid solution of $PbZrO_3$ and $PbTiO_3$ [3]; with titanium to zirconium ratio near unity, both the dielectric constants and piezoelectric coupling coefficients reached maximum values due to an abrupt structural change at the morphotropic phase boundary.

Single-phase layered ferroelectric ceramics, such as $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ [4–7], offer several advantages like fatigue-free, low operation voltage, and ferroelectric properties independent of film thickness. Zhang et al. [6] used BaO to substitute for SrO of $SrBi_2Ta_2O_9$ composition ($(Ba_{0.6}Sr_{0.4})Bi_2Ta_2O_9$, BSBT) and Shimakawa et al. [4] used V_2O_5 to substitute for Nb_2O_5 of $SrBi_2Nb_2O_9$ composition ($SrBi_2(Nb_{1-x}V_x)_2O_9$, SBNV). Both BSBT and SBNV compositions also possessed single-phase layered perovskite structures and ferroelectric characteristics. In this study, $SrBi_2Ta_2O_9$ was used as the host material and TiO_2 was used to substitute for Bi_2O_3 and Ta_2O_5 to form $Sr(Bi_2Ta_2)_{1-x}Ti_{4x}O_9$. The influence of sintering temperature and TiO_2 content on the crystalline phase evolution and the microstructures of SBTT ceramics are presented, as well as the influence of sintering temperature and TiO_2 content on the temperature dependent dielectric constant.

2. Experimental procedure

$Sr(Bi_2Ta_2)_{1-x}Ti_{4x}O_9$ compositions with $x=0.05$ (SBTT1), 0.1 (SBTT2), 0.15 (SBTT3), and 0.2 (SBTT4) were prepared by solid state reaction sintering. Reagent-grade 99.5% purity $SrCO_3$, Bi_2O_3, Ta_2O_5, and TiO_2 raw materials used as starting materials were ball-milled for 5 h in deionized water. After drying and grinding, the powder was calcined at 850 °C for 3 h. After calcination and grinding, the SBTT powders were mixed with about

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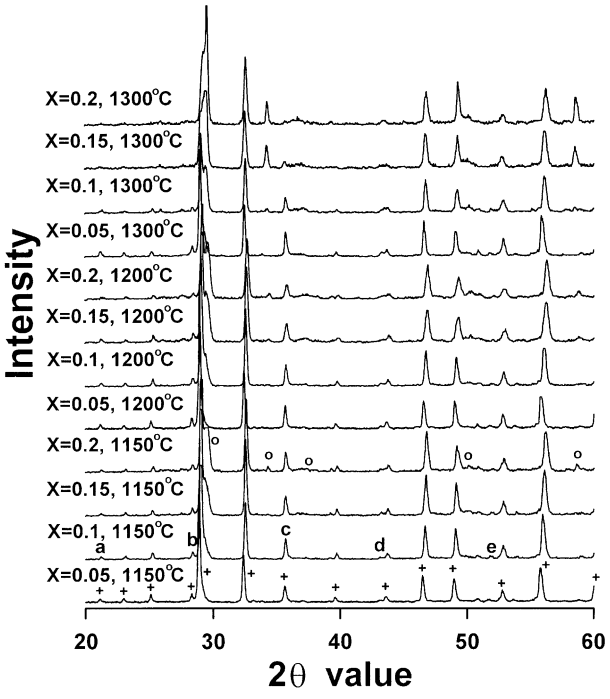

Fig. 1. X-ray patterns for $Sr(Bi_2Ta_2)_{1-x}Ti_{4x}O_9$ ceramics. [+: $SrBi_2Ta_2O_9$ phase, o: rutile TiO_2 phase, a: (0,0,6), b: (0,0,8), c: (0,0,10), d: (0,0,12), e: (0,0,14)].

8 wt.% polyvinylalcohol (PVA) as a binder and uniaxially pressed into pellets. After debindering, sintering was carried out from 1100 to 1300 °C for 4 h. The crystal structures and morphologies of SBTT were investigated by using XRD patterns and scanning electronic micrograph (SEM), respectively. After polishing to flat and about 1.5 mm in thickness, both sides of SBTT were electroded with Ag-Pd paste. Temperature-dependent dielectric characteristics were measured at 1 MHz with an oscillating amplitude (50 mV) by an HP4194 impedance analyzer.

3. Results and discussion

X-ray diffraction (XRD) patterns of SBTT are shown in Fig. 1. Sintered at 1150 °C, the intensities of (0,0,*l*) planes (*l* = 6, 8, 10, 12, and 14, and 2θ values are at around 21.4, 28.6, 35.9, 43.4, and 51.1°, respectively) do not change but the TiO_2 crystal phase slightly increases with the increase of TiO_2 content; sintered at 1200 °C, the intensities of (0,0,*l*) planes slightly decrease and the intensity of TiO_2 phase slightly increases with the increase of TiO_2 content; sintered at 1300 °C, the intensities of (0,0,*l*) planes apparently decrease and the

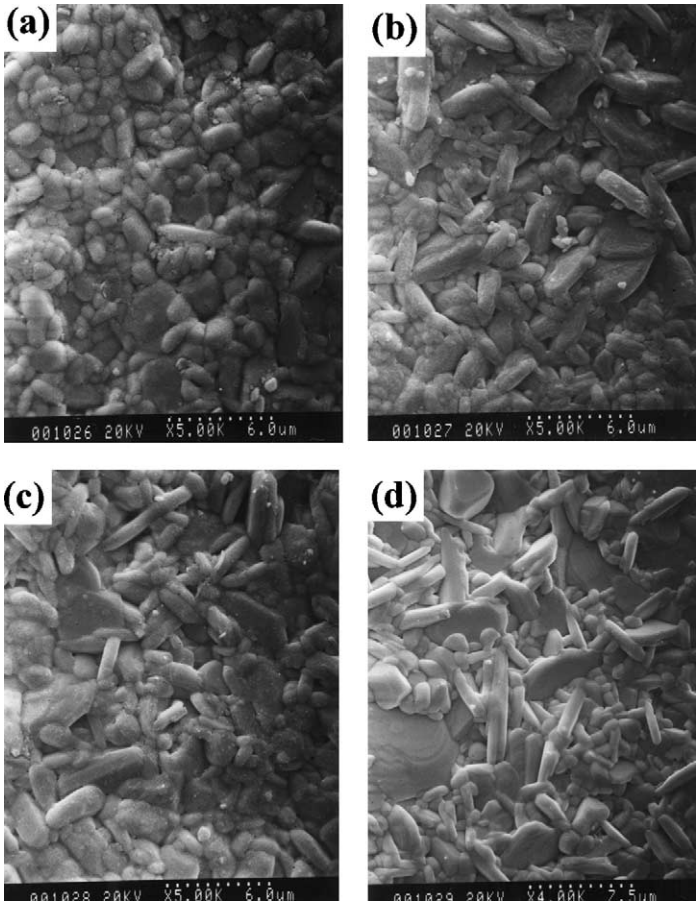

Fig. 2. Micrographs of $Sr(Bi_2Ta_2)_{1-x}Ti_{4x}O_9$ ceramics, sintered at 1200 °C for (a) $x = 0.05$, (b) $x = 0.1$, (c) $x = 0.15$, and (d) $x = 0.2$.

intensity of TiO_2 phase apparently increase with the increase of TiO_2 content. The intensities of (0,0,*l*) planes disappear at 1300 °C-sintered SBTT4. According to the X-ray patterns, most of the SBTT preserve the single-phase layered perovskite structure, and the 2θ values are shifted to the higher angles as both the sintering temperature and the TiO_2 content increase. These results suggest a structure distortion and a decrease of lattice constant as a consequence of the substitution of the smaller ionic radius of Ti^{+4} (0.61 Å for coordination number = 6) for Bi^{3+} (0.96 Å) and Ta^{5+} (0.64 Å).

SEM micrographs of SBTT sintered at 1200 and 1300 °C are shown in Figs. 2 and 3. Sintered at 1150 °C, the pores are still residual in SBTT1, and SBTT2, SBTT3, and SBTT4 reveal a densified structure (not shown here). For 1200 °C-sintered SBTT1, homogeneously fine grains are obtained [Fig. 2(a)]. SBTT2, SBTT3, and SBTT4 [Fig. 2(b)–(d)] show two-phase texture, where bar-typed grains and disk-typed grains coexist, the lengths of the bar-typed grains increasing with the increase of TiO_2 content. Sintered at 1250 °C, SBTT1 (not shown here) starts to reveal a texture of two-phase components. Sintered at 1300 °C, the SBTT1 only the bar-typed grains as shown in [Fig. 3(a)]. As the micrographs of the 1300 °C-sintered SBTT are compared [Fig. 3(a)–(d)], SBTT2, SBTT3, and SBTT4 still reveal a texture of two-phase components, and the grain sizes increase with the increase of TiO_2 content.

Table 1
Curie temperature of $Sr(Bi_2Ta_2)_{1-x}Ti_{4x}O_9$ ceramics as a function of TiO_2 content and sintering temperature

	1100 °C	1150 °C	1200 °C	1250 °C	1300 °C
$x=0.05$	375 °C	325 °C	350 °C	450 °C	375 °C
$x=0.1$	400 °C	400 °C	400 °C	425 °C	375 °C
$x=0.15$	400 °C	400 °C	400 °C	425 °C	425 °C
$x=0.2$	350 °C	350 °C	325 °C	325 °C	325 °C

Fig. 4 shows the maximum dielectric constants of SBTT. Sintered at 1150 °C, the SBTT reveal a lower dielectric constant, possibly causes were of the porous structure. Sintered at 1150 and 1200 °C, the maximum dielectric constants increase critically. This is caused by that the increases in density, and grain growth in turn results in the increase of polarization. At sintering temperatures higher than 1200 °C, the maximum dielectric constants slightly increase. As the same sintering temperature is used, the maximum dielectric constants decrease with the increase of TiO_2 content and will be found at SBTT1.

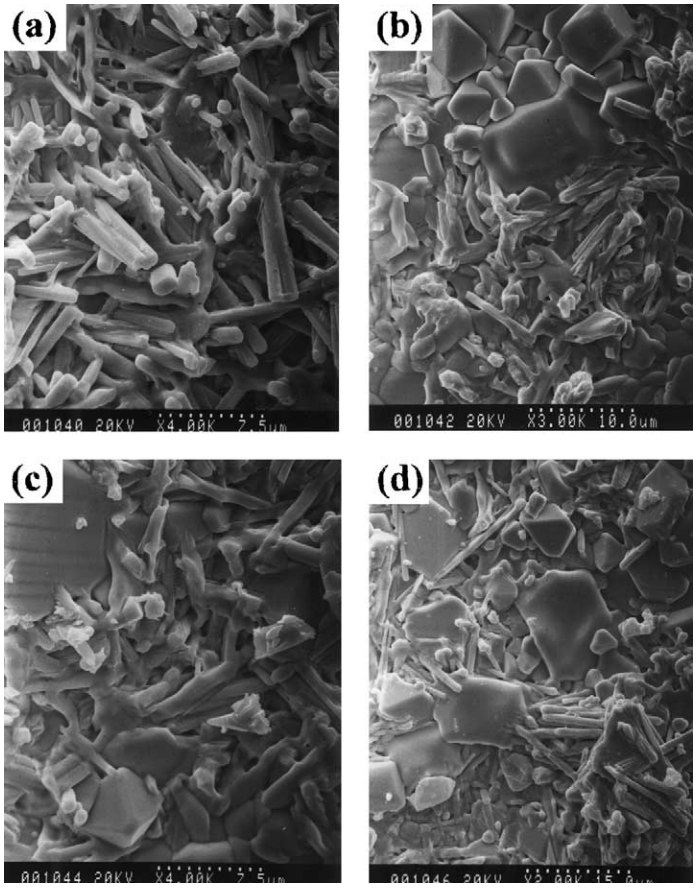

Fig. 3. Micrographs of $Sr(Bi_2Ta_2)_{1-x}Ti_{4x}O_9$ ceramics, sintered at 1300 °C for (a) $x=0.05$, (b) $x=0.1$, (c) $x=0.15$, and (d) $x=0.2$.

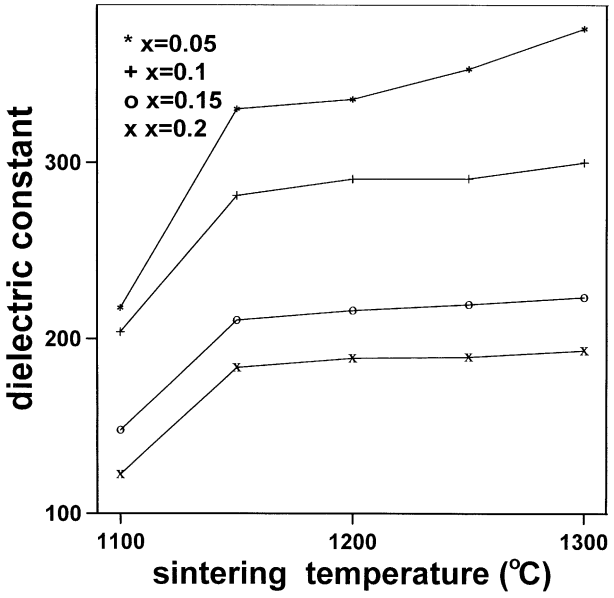

Fig. 4. Maximum dielectric constant of $Sr(Bi_2Ta_2)_{1-x}Ti_{4x}O_9$ ceramics as a function of TiO_2 content and sintering temperature.

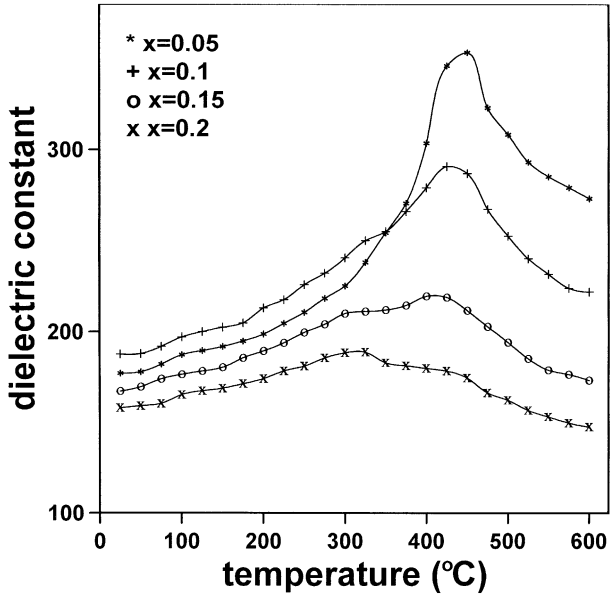

Fig. 5. Temperature dependence of $Sr(Bi_2Ta_2)_{1-x}Ti_{4x}O_9$ ceramics. The sintering temperature is 1250 °C.

Table 1 shows the Curie temperature of SBTT. The Curie temperatures of SBTT1, SBTT2, SBTT3, and SBTT4 are in the range of 325–450, 375–425, 400–425, and 400–425 °C, respectively. The temperature dependence of dielectric constants of 1250 °C-sintered SBTT is shown in Fig. 5. For SBTT1 and SBTT2, the dielectric constant curves reveal both a high value and high temperature coefficient of dielectric constant. Such a result also suggests that SBTT1 and SBTT2 retain the characteristics of perovskite ferroelectric ceramics. SBTT3 and SBTT4 reveal a broad and faint peak (or a diffusion Curie temperature peak). The distortion of crystalline structure and the increase of TiO_2 phase may lead to this result.

4. Conclusions

With partial substitution of Bi^{3+} and Ta^{5+} by Ti^{4+} (x up to 0.2), the $Sr(Bi_2Ta_2)_{1-x}Ti_{4x}O_9$ ceramics preserve the single-phase layered perovskite structure ($x=0.05$) or preserve the single-phase layered perovskite structure with some distortion and TiO_2 phases. The maximum dielectric constant increases with the increase of sintering temperature but decreases with the increase of TiO_2 content. SBTT1 and SBTT2 have lower sintering temperatures and higher dielectric constant than $SrBi_2Ta_2O_9$ ceramic and my be used as ferroelectric ceramics. On the contrary, SBTT3 and SBTT4 composition, because the poor dielectric constant appear unsuitable for ferroelectric application.

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