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Effect of $SrTiO_3$ concentration and sintering temperature on microstructure and dielectric constant of $Ba_{1-x}Sr_xTiO_3$

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Abstract

The $Ba_{1-x}Sr_xTiO_3$ materials have received increased attention as one of the most important materials for electroceramic components, such as high dielectric ceramic capacitors, tunable phase shifters and PTCR. In this paper, the effect of $SrTiO_3$ concentration and sintering temperature on the microstructure and dielectric constant of $Ba_{1-x}Sr_xTiO_3$ materials at the Curie temperature have been investigated. When $Ba_{1-x}Sr_xTiO_3$ materials were sintered at 1350 °C, the peak value of the dielectric constant, ϵ_{max}, monotonically decreased with increasing $SrTiO_3$ concentration. At the sintering temperature of 1400 °C the dielectric constant maximum at the T_C increased with an increase in the x value, reaching the highest value at around $x=0.4$ and then decreased. As sintering temperature increased to 1450 °C, ϵ_{max} increased with increasing $SrTiO_3$ concentration up to $x=0.6$. The dielectric properties of $Ba_{1-x}Sr_xTiO_3$ materials were discussed in terms of $SrTiO_3$ concentration and microstructure.

Keywords: $Ba_{1-x}Sr_xTiO_3$; Curie temperature; Dielectric constant; Grain size

1. Introduction

Barium titanate has been investigated extensively because of scientific interest as well as industrial applications such as high dielectric ceramic capacitors,[1,2] tunable phase shifters,[3] and PTCR.[4,5] Pure $BaTiO_3$ shows a paraelectric to ferroelectric phase transition at 120 °C, which is accompanied by a sharp peak in the dielectric permittivity. Partial substitution of either Ba ions or Ti ions is often employed to modify the nature and temperature of the paraelectric–ferroelectric transition for particular applications. $SrTiO_3$ is usually added as a shifter in order to move the T_c to lower temperatures because it is well established that the Curie point of $BaTiO_3$ decreases linearly with a solid solution of Sr^{+2} in place of Ba^{+2}.

It is not fully understood yet, however, how the $SrTiO_3$ concentration effects on the peak value of dielectric constant at the Curie temperature of $Ba_{1-x}Sr_xTiO_3$ solid solutions. Smolenskii[6] and Zhou[7] reported that the maximum permittivity of $Ba_{1-x}Sr_xTiO_3$ ceramics at T_C increased with an increase in the x value, reaching highest value at around $x=0.6$ and then decreased. Lemanov[8] insisted that the maximum value of the dielectric constant increased with x up to $x=0.8$, and Wang[9] showed the highest value at $x=0.2$. Twari[10] reported another result that the peak value of dielectric constant increased with x up to $x=0.08$ and then exhibited a monotonic decrease for $x>0.08$. Twari explained that the maximum dielectric constant came from the maximum tetragonality of $Ba_{1-x}Sr_xTiO_3$ at $x=0.08$. On the other hand, Ota[11] suggested that the maximum dielectric permittivity decreased with increasing x value.

Since Kniekamp and Heyang[12] revealed a rather significant dependence of the dielectric permittivity of $BaTiO_3$ ceramics on their grain size, the effect of grain size on the dielectric properties of $BaTiO_3$ has been an active area of research. Nowadays, it is generally accepted that the maximum dielectric permittivity at the Curie temperature decreases with the decrease of the average grain size of $BaTiO_3$. Therefore, when the effects of $SrTiO_3$ concentration on the dielectric properties is investigated, the grain size effect should be considered. This is the reason why such disagreements occurred because the grain size effect with the change of $SrTiO_3$ concentration and sintering conditions was not taken into account.

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This paper reports the variation of the dielectric constant of $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions at the Curie temperature in the range of $x=0\sim0.6$. Different sintering temperatures were used in order to investigate the influence of the microstructure on the dielectric properties of the materials.

2. Experimental

Specimens were prepared from commercial $BaTiO_3$ and $SrTiO_3$ (Ferro Corp., Penn Yan, NY, USA) powders. According to the data provided by the producers, the purity and average size of $BaTiO_3$ were 99.8% and 1.5 μm, respectively, and those of $SrTiO_3$ were 99.8% and 1.3 μm. Powder slurries were made by mixing $(BaTiO_3)_{1-x}(SrTiO_3)_x$ (in unit of mol%) powder mixtures (where $x=0.1$, 0.2, 0.3, 0.4, 0.5, 0.6) for 24 h in a polyethylene bottle with ethyl alcohol and zirconia balls. The dried slurry was crushed in an agate bowl and sieved to 125 μm. The pure $BaTiO_3$ and mixed powders were slightly pressed into disks 10 mm in diameter and 2 mm in thickness and then isostatically pressed again under 150 MPa. The compacts were sintered at 1350, 1400 and 1450 °C, respectively, for 1 h in air.

The microstructures of the sintered specimens were observed using an optical microscope after etching polished sections in a 50 H_2O–45 HNO_3–5 HF (vol%) solution for 10–30 s. X-Ray diffraction was performed to identify the phases and their tetragonality. The dielectric properties of the specimens with silver electrodes were measured by an impedance/gain-phase analyzer (HP 4194A) at 1 kHz from −150 to 150 °C.

3. Results and discussion

Fig. 1 shows the dielectric constant versus temperature of $Ba_{1-x}Sr_xTiO_3$ specimens sintered 1350 °C for 1 h. The Curie temperature and the peak value of the dielectric constant decreased with increasing $SrTiO_3$ concentration. This result is a similar to the result of Ota.[11] When the sintering temperature was increased to 1400 °C, however, the dielectric constant maximum increased with an increase in the x value, reaching highest value at around $x=0.4$ and then decreased. This result is similar to the result of Smolenski,[6] Zhou,[7] Lemanov,[8] Wang,[9] and Twari.[10] Fig. 3 represents the variation of dielectric constant of $Ba_{1-x}Sr_xTiO_3$ ceramics sintered at 1450 °C for 1 h. The dielectric constant maximum monotonically increased with increasing $SrTiO_3$ concentration up to $x=0.6$. As the sintering temperature increases from 1350 to 1450 °C, the dielectric constant maximum of $Ba_{1-x}Sr_xTiO_3$ ceramics increases in all range of x value except $x=0$.

In order to investigate the tetragonality of $Ba_{1-x}Sr_xTiO_3$ ceramics with the change of $SrTiO_3$ concentration and sintering temperature, $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions sintered at each temperature were examined by an X-ray diffractometer. Fig. 4 shows X-ray diffraction profiles of the sintered samples between $43° < 2\theta$

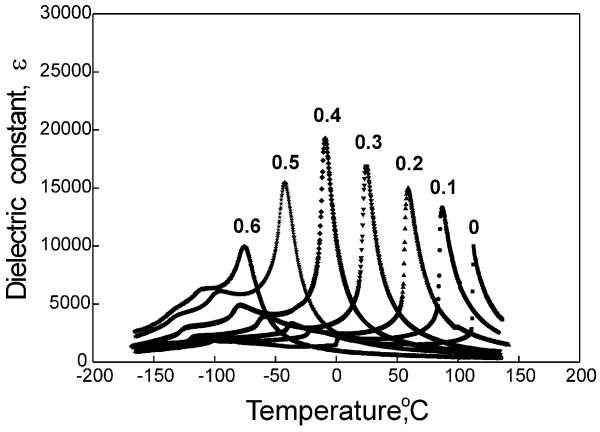

Fig. 2. Dielectric property of $Ba_{1-x}Sr_xTiO_3$ ceramics sintered at 1400 °C for 1 h.

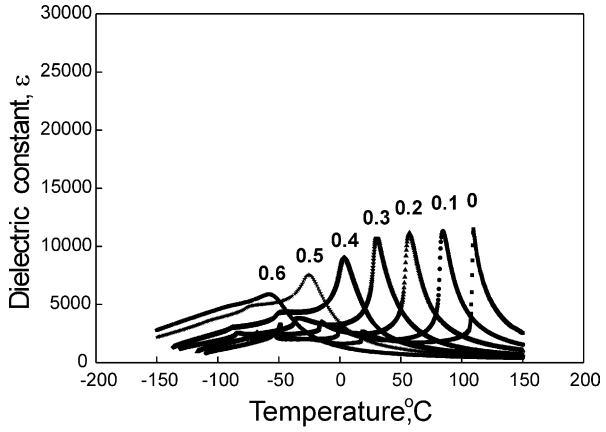

Fig. 1. Dielectric property of $Ba_{1-x}Sr_xTiO_3$ ceramics sintered at 1350 °C for 1 h.

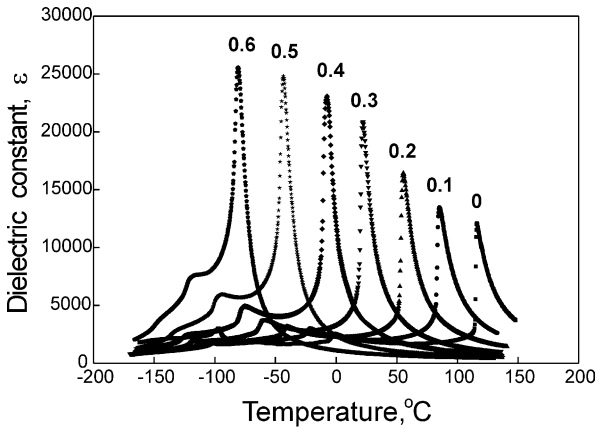

Fig. 3. Dielectric property of $Ba_{1-x}Sr_xTiO_3$ ceramics sintered at 1450 °C for 1 h.

$<48°$ which depicts the tetragonal splitting for (002)/(200) pairs of reflections. The extent of tetragonal splitting decreases with increasing strontium titanate concentration, regardless of the sintering temperature. This result reveals that the tetragonality does not depend on the sintering temperature but on the Ba/Sr ratio of $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions. Therefore, the tetragonality is not the reason for the variation of the dielectric constant maximum by the change of the sintering temperature from 1350 to 1450 °C, as shown in Figs. 1–3.

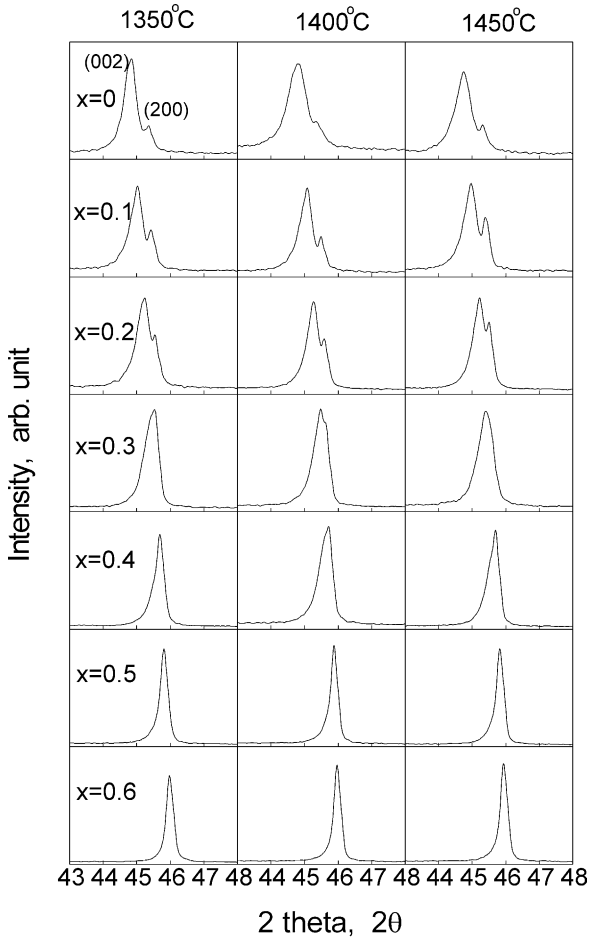

Fig. 4. X-ray diffraction profiles of $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions sintered at 1350, 1400 and 1450 °C for $x=0$–0.6 for (002)/(200) reflections.

Fig. 5 shows typical micrographs of the microstructure of $Ba_{1-x}Sr_xTiO_3$ ceramics sintered at 1350 °C for 1 h. $BaTiO_3$ system is well known to grow by abnormal grain growth mode during sintering. In the case of sintering pure $BaTiO_3$ and $Ba_{0.9}Sr_{0.1}TiO_3$, 1350 °C for 1 h is enough to finish abnormal grain growth. In the composition range of $x \geqslant 0.2$, abnormal grain growth is still on going and the microstructure shows a bimodal structure consisting of abnormally growing grains and fine matrix grains. The average grain size and total volume fraction of abnormally growing grains were decreased with increasing $SrTiO_3$ concentration. When sintering temperature was increased to 1400 °C, shown in Fig. 6, almost all the fine matrix grains had disappeared at up to $x=0.3$ but they are still present in the range of $x \geqslant 0.4$. Under the sintering condition of 1450 °C for 1 h, however, fine matrix grains were not observed even $x=0.6$, as shown in Fig. 7.

When the dielectric constant at the Curie point of $Ba_{1-x}Sr_xTiO_3$ ceramics were compared, the grain size effect should be taken into account. Even though Jaffe[13] reported that $Ba_{1-x}Sr_xTiO_3$ solid solutions have higher peak value of dielectric constant than pure $BaTiO_3$, it should be based on the hypothesis that the materials have the same average grain size. The $Ba_{1-x}Sr_xTiO_3$ ceramics can exhibit lower peak value of dielectric constant than pure $BaTiO_3$ if they have much smaller grain size than pure $BaTiO_3$. For example, the peak value of the dielectric constant of $Ba_{1-x}Sr_xTiO_3$ ceramics sintered at 1350 °C show smaller peak dielectric constant than pure $BaTiO_3$, as shown in Fig. 1, because the grain size of $Ba_{1-x}Sr_xTiO_3$ ceramics decreases significantly with increase of $SrTiO_3$ concentration, as shown in Fig. 5. The reason for the decrease of the peak dielectric constant above $x=0.5$ for the materials sintered at 1400 °C (shown in Fig. 2), seems to be due to the smaller grain size below a critical value as the x value increases to 0.5 and 0.6. As the sintering temperature increased from 1350 to 1450 °C, the increase of grain growth rate increased in proportion to the x value. This is the reason for the increase of the peak dielectric

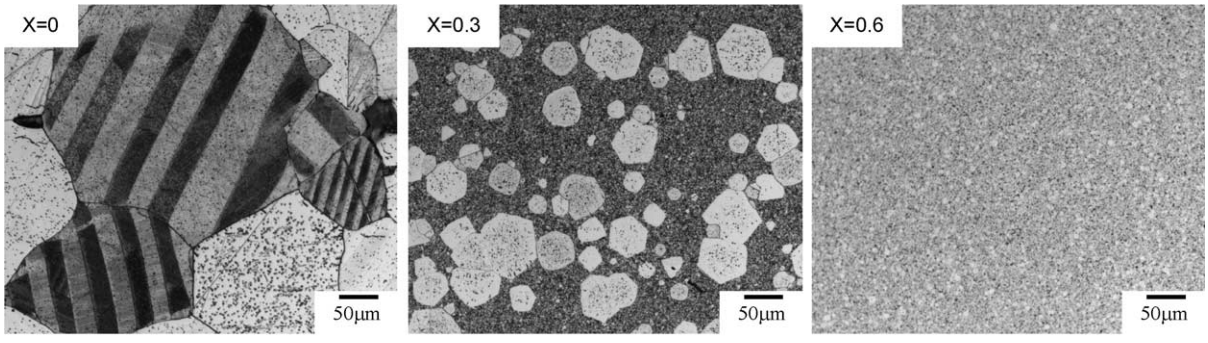

Fig. 5. Typical micrographs of $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions sintered at 1350 °C for 1 h.

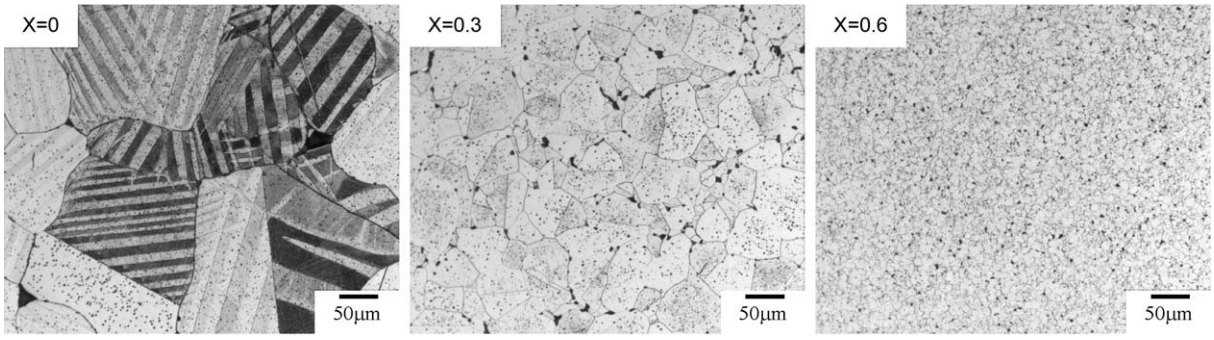

Fig. 6. Typical micrographs of $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions sintered at 1400 °C for 1 h.

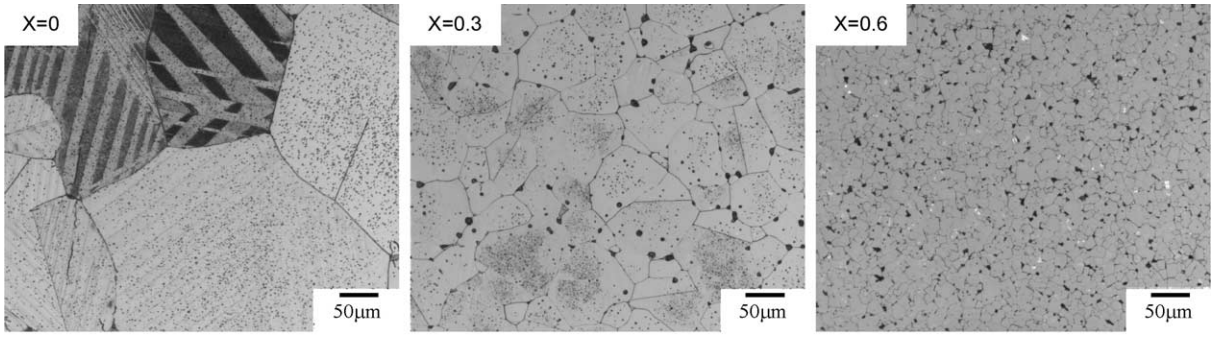

Fig. 7. Typical micrographs of $Ba_{1-x}Sr_xTiO_3$ ceramic solid solutions sintered at 1450 °C for 1 h.

constant of $Ba_{1-x}Sr_xTiO_3$ ceramics with increasing $SrTiO_3$ concentration.

4. Conclusions

From this study, the peak value of dielectric constant at the Curie temperature of $Ba_{1-x}Sr_xTiO_3$ ceramics was found to be dependent on $SrTiO_3$ concentration and their average grain size. The $SrTiO_3$ affects contrarily on the peak value of the dielectric constant when it is incorporated into $BaTiO_3$. On the one hand, the intrinsic dielectric constant maximum of $Ba_{1-x}Sr_xTiO_3$ increases with increasing $SrTiO_3$ concentration as Jaffe[11] reported. On the other hand, the addition of $SrTiO_3$ reduces the peak value of the dielectric constant of $Ba_{1-x}Sr_xTiO_3$ ceramics by decreasing their average grain size. When the sintering temperature was increased from 1350 to 1450 °C, the grain size of pure $BaTiO_3$ was not actually changed but the increase of grain growth rate of $Ba_{1-x}Sr_xTiO_3$ was increased with increasing $SrTiO_3$ concentration. This is the reason for the variation of the dielectric property with the change of $SrTiO_3$ concentration and the sintering temperature.

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