In this study, TiO$_2$ is used to substitute the Bi$_2$O$_3$ and Ta$_2$O$_5$ sites of the SrBi$_2$Ta$_2$O$_9$ ceramics to form Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ composition. From the X-ray patterns, the 2θ values shift to higher values as the sintering temperatures increase. At lower sintering temperatures of 1200 to 1250°C, the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics reveal a two-phase structure, bar-typed grains and disk-typed grains coexist; When 1300°C is used as the sintering temperature, only the bar-typed grains are revealed. The sintering temperatures also have large influences on the maximum dielectric constants and the Curie temperatures of Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics.

Keywords: Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$, disk-typed grains, bar-typed grains, Curie temperatures

1. Introduction

The layered ferroelectrics have the general formula: A$_{n-1}$Bi$_2$B$_n$O$_{3n+3}$, where A is usually a divalent ion, such as Sr, Ba, or Pb, and B is Ti$^{+4}$, Nb$^{+5}$, or Ta$^{+5}$. The layer structured bismuth compounds, such as SrBi$_2$Ta$_2$O$_9$ [1,2] and SrBi$_2$Nb$_2$O$_9$ [3,4] ceramics, offer several advantages like fatigue-free, low operation voltage, and independent of ferroelectric properties with film thickness in comparison with perovskite ferroelectrics, typically Pb(Zr,Ti)O$_3$. In order to improve the dielectric characteristics, many electric properties of ceramics may be varied significantly with a change of chemical composition through doping or substituting of desired impurities. For example, in the SrBi$_2$Ta$_2$O$_9$ composition, BaO was used to substitute for SrO to form (Ba$_0.6$Sr$_0.4$)Bi$_2$Ta$_2$O$_9$ [5]. The (Ba$_{0.6}$Sr$_{0.4}$)Bi$_2$Ta$_2$O$_9$ ceramics presented ferroelectric properties and had a higher Curie temperature than SrBi$_2$Ta$_2$O$_9$ ceramics did. Except the ABi$_2$M$_2$O$_9$ (A=Ca, Sr, Ba, B=Nb, Ta, V) layer structured bismuth compounds, Bi$_4$Ti$_3$O$_{12}$ and SrBi$_4$Ti$_4$O$_{15}$ were the two system layer structured bismuth compounds with Ti$^{+4}$ ion [6-7]. In this study, SrBi$_2$Ta$_2$O$_9$ was used as the main composition, Ti$^{+4}$ ion was used to substitute Bi$^{+3}$ and Ta$^{+5}$ ion sites to format the composition of Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$. The Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics were sintered at different temperatures and their microstructures and dielectric properties, especially the temperature dependent dielectric constants and loss tangents, were studied.

2. Experimental procedure

Reagent-grade raw materials of SrCO$_3$, Bi$_2$O$_3$, Ta$_2$O$_5$, and TiO$_2$ with higher than 99.5% purity were used as starting materials, mixed according to the composition Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ and ball-milled for 5h with deionized water. After grinding, the powder was calcined at 800°C for 2h.
After calcination and grinding, the calcined powders were ground and mixed with about 8wt% polyvinylalcohol (PVA) as a binder and uniaxially pressed into pellets in a steel die. After debinding, sintering of these pellets was carried out from 1100°C to 1300°C for 4h. The crystalline structures of the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics were investigated using XRD patterns. The morphologies of the sintered specimens were observed by using scanning electronic micrograph (SEM). The Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics were polished to flat and parallel surfaces and about 1.5 mm in thickness, then electroded with Ag-Pd paste on both sides. Temperature-dependent dielectric characteristics were measured at the frequency of 1MHz with an oscillating amplitude (50mV) by an HP4194 impedance analyzer, putting the sintered ceramics in a temperature-programable testing chamber.

3. Results and Discussion

Typical X-ray diffraction patterns of Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics are shown in Fig.1. X-ray diffraction analyses indicates that Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics have similar crystalline structure to the stoichiometric SrBi$_2$Ta$_2$O$_9$ ceramics except the shift of 2θ to higher values. Sintered at the 1150°C and 1200°C, only the single-phase layered perovskite SrBi$_2$Ta$_2$O$_9$ phase (or Sr(Bi,Ta)$_{2.3}$Ti$_{1.7}$O$_9$) is revealed and no secondary phase is detectable. Sintered at 1250°C, the sintered ceramics also reveal a single phase layered perovskite SrBi$_2$Ta$_2$O$_9$ phase, accompanying the existence of some unknown secondary phases. Compared the patterns of 1250°C- and 1300°C-sintered Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics, the crystalline intensities of unknown secondary phases increase with the increase of sintering temperatures. The X-ray patterns also index that the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics reveal a pseudotetragonal (actually orthorhombic) unit cell. In all samples, the orthorhombic splitting of (2,0,0) and (0,2,0) reflections are not detected because it is too small.

Figure 2 shows the changes in lattice constant for the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics as a function of sintering temperatures. As Fig.2 shows, the lattice constants a and c decrease gradually with the increase of sintering temperatures. The ions size of Ti$^{4+}$ (0.64 Å) have a much smaller size as compared with the ions of Ta$^{5+}$ (0.68Å) and Bi$^{3+}$ (0.96Å). As the sintering temperatures increase, it is believed that more Ti$^{4+}$ ions to substitute the ions of Ta$^{5+}$ and Bi$^{3+}$ and that will lead to the decrease of the lattice constants a and c.

SEM micrographs of the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics are investigated under the sintering temperatures of 1100°C~1300°C, and the results are shown in Fig.3. Sintered at 1100°C, the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics show a porous structure and the isolated Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ particles are easily observed (not shown here). Sintered at 1150°C, the pores decrease apparently but still exist in the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics (Fig.3(a)). For 1200°C-sintered Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics, the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics reveal a densified structures and the homogeneously fine grains with almost no pores are obtained (Fig.3(b)). Sintered at 1250°C, the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics illustrate a texture of two-phase components, where bar-typed grains and disk-typed grains coexist (Fig.3(c)). When 1300°C is used as the sintering temperature, the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics illustrate the bar-typed grains (Fig.3(d)), the disk-typed grains are not revealed in the sintered surfaces. As the micrographs of the 1250°C- and 1300°C-sintered
Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics are compared, the sizes of the bar-typed grains also increase with the increase of the sintering temperatures.

Figure 4 shows the dielectric constants and loss tangents of the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics at the frequency range of 1kHz to 10MHz at room temperature. For the 1100°C-sintered Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics, the dielectric constants and the loss tangents critically decrease with the increase of frequency, the porous structure may cause this result. As 1150°C is used as the sintering temperature, the dielectric constants of the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics slightly decrease with the increase of frequency. The loss tangents decrease from 6% at 1 kHz to less than 2% at 10kHz~5MHz, and then slightly increase to 2.5% as the frequency is higher than 5MHz. As the sintering temperature is higher than 1150°C, the dielectric constants of the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics slightly decrease with the increase of frequency, reach a minimum at 1MHz, than slightly increase with the increase of frequency. The loss tangents are lower than 2.5% at 1 kHz and less than 1.5% at 10kHz~10MHz.

Figure 5 shows the temperature dependence of dielectric constants of the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics at the frequency of 1MHz. The ferroelectric Curie temperature for SrBi$_2$Ta$_2$O$_9$ ceramics is about 300°C [8]. As Fig.5 shows, at a temperature of 25°C, the dielectric constants slightly increase with the increase of sintering temperatures. As the measured temperatures increase, the peak dielectric constants at their respective Curie temperatures also increase approximately. The 1100°C-sintered ceramics reveal the lower dielectric constants, the porous structure will cause this result. The Curie temperature (the temperatures to reveal the maximum dielectric constants) is 375°C for 1100°C-sintered Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics. As 1150°C-1300°C are used as the sintering temperatures, the Curie temperatures of Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics increase from 325°C, reach a maximum of 450°C for 1250°C-sintered ceramics, and then drops to 375°C for 1300°C-sintered ceramics. As Fig.5 shows, as the sintering temperatures are higher than 1200°C, the dielectric constants revealed at Curie temperatures are larger than the reported SrBi$_2$Ta$_2$O$_9$ ceramics did.

4. Conclusions

As Ti$^{4+}$ is used to substitute the Bi$^{3+}$ and Ta$^{5+}$, the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics reveal a single phase layered perovskite structure (sintered at 1150°C and 1200°C) or a single phase layered perovskite structure accompanied some unknown phases (sintered at 1250°C and 1300°C). As sintering temperature is higher than 1150°C, the dielectric characteristics are stable with frequency. The incorporation of Ti$^{4+}$ into the SrBi$_2$Ta$_2$O$_9$ composition results in the decrease of lattice constant and a shift of the Curie temperature to a higher temperature, but the Curie temperature is not sintering temperature dependence.

References

Fig.1 The X-ray patterns for Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics as a function of sintering temperatures. (x : Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ phase, o : unknown phase)

Fig.2 Lattice constant of the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics.
Fig. 3 Micrographs of the Sr(Bi$_{2}$Ta$_{2}$)$_{0.95}$Ti$_{0.2}$O$_{9}$ ceramics, sintered at: (a) 1150°C, (b) 1200°C, (c) 1250°C, and (d) 1300°C.
Fig. 4 The frequency-dependent (a) dielectric constants (b) loss tangents of the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics as a function of sintering temperature.

Fig. 4 The temperature-dependent dielectric constants of the Sr(Bi$_2$Ta$_2$)$_{0.95}$Ti$_{0.2}$O$_9$ ceramics as a function of sintering temperature.