The Preparation of Bi-Layered SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ Ceramics ($0.1 \leq x \leq 0.4$)

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Abstract. V$_2$O$_5$ is used to substitute Ta$_2$O$_5$ site of the SrBi$_2$Ta$_{2}$O$_9$ ceramics to form SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ composition, where $0.1 \leq x \leq 0.4$. The sintering and the dielectric properties of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics have been developed. For all SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ composition, the crystal intensities of the (0,0,1) planes increase with the increase of sintering temperature and saturate at 1050°C-sintered ceramics, and the increase in the crystal intensities of the (0,0,8) and (0,0,10) planes are more obvious. For the same sintering temperature, the crystal intensities of the (0,0,l) planes increase with the increase of V$_2$O$_5$ content and saturate at SrBi$_2$Ta$_{1.7}$V$_{0.3}$O$_9$ ceramics. This study will show that the sintering temperature and V$_2$O$_5$ content have large influences on the maximum dielectric constants ($\varepsilon_T c$) and the Curie temperatures of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics.

Introduction

The layer structured bismuth compound ferroelectric has 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$^{5+}$ [1-3]. Within the bismuth family, SrBi$_2$Ta$_{2}$O$_9$ ceramics had attracted the most attention in the past years [4-7]. Although the polarization of SrBi$_2$Ta$_{2}$O$_9$ ceramics is less than the competing Pb(Ti,Zr)O$_3$-based materials, the bismuth-layer compounds are much stable to polarization fatigue free property, i.e. almost no charge loss will happen when polarization is reversed many cycles.

In the SrBi$_2$Nb$_{2}$O$_9$ composition, the substitution of Nb$_2$O$_5$ by V$_2$O$_5$ will lower the sintering temperature and produce materials with enhanced dielectric properties that are useful in many applications [8]. In this study, we are interested to investigate ceramic materials based on SrBi$_2$Ta$_{2}$O$_9$ composition, V$_2$O$_5$ is used to substitute for Ta$_2$O$_5$ to form the SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ compositions. Bulk SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ materials are sintered at different temperature and their morphologies and crystal phases are examined. The temperature-dependent dielectric characteristics are also investigated as a function of sintering temperature and V$_2$O$_5$ content.

Experimental Procedures

Reagent-grade raw materials of SrCO$_3$, Bi$_2$O$_3$, Ta$_2$O$_5$, and V$_2$O$_5$ with higher than 99.5% purity were used as starting materials, mixed according to the composition SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ($x=0.1$, 0.2, 0.3, and 0.4, respectively) and ball-milled for 5h with deionized water. After dried and ground, the powder was calcined at 850°C for 3h. After calcination and ground again, then polyvinylalcohol (PVA) was added as a binder. The calcining powder was uniaxially pressed into pellets in a steel die. After debinding, sintering of these pellets was proceeded from 900°C to 1100°C for 4h. The crystal structures of the SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics were investigated using XRD patterns, and the
morphologies were observed by using scanning electronic micrograph (SEM). The sintered ceramics were painted with Ag-Pd paste and sintered at 700°C for 15min. Temperature-dependent dielectric characteristics were measured at 1MHz with an oscillating amplitude (50mV) by an HP4194 impedance analyzer, putting the sintered ceramics in a temperature-programmable testing chamber.

Results and Discussion

The changes in density and grain size can be seen in the SEM photographs of selected SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics and the results are shown in Fig.1. For 950°C-sintered SrBi$_2$Ta$_{1.9}$V$_{0.1}$O$_9$ ceramics, as Fig.1(a) shows, the pores are still observed and the grain growth is not obvious. Further increasing the sintering temperature to 1000°C, homogeneously fine microstructures with less pores are observed, as shown in Fig.1(b). The temperature for SrBi$_2$Ta$_2$O$_9$ ceramics to reveal homogeneous grain growth is 1200°C (not shown here), this result suggests that the sinterability of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics has improved due to the V$_2$O$_5$ substitution. The pores of all SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics decrease and the grain sizes increase with the increase of sintering temperature independent of V$_2$O$_5$ content. Sintered at 1050°C, as Figs.1(c), 1(d), and 1(e) are compared, the grain sizes apparently increase as x changes from 0.1 to 0.2 and the grain sizes slightly increase as x change from 0.2 to 0.4.

![SEM micrographs of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics](image)

Fig.1 The micrographs of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics. For x=0.1 and sintered at (a) 950°C and (b) 1000°C, sintered at 1050°C for (c) x=0.1, (d) x=0.2, and (d) x=0.4.

The X-ray patterns of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics, for x=0.1, 0.2, and 0.3, are shown in Fig.2 as a function of sintering temperature and V$_2$O$_5$ content. X-ray diffraction analyses indicate that only the single-phase layered perovskite structure is found, no secondary or unknown phases are detectable. For that Ta$_2$O$_5$ will completely be substituted by V$_2$O$_5$ in the SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ composition. Because the peneavalence vanadium ion (V$^{5+}$, 0.58 Å) has a smaller size compared with tantalate ion (Ta$^{5+}$, 0.68Å), the 20 values are slightly shifted to higher values with the increase of V$_2$O$_5$ content. For the same composition, the 20 values have no apparent shift with the increase of sintering temperature.
The crystal intensities of the (0,0,l) planes (l = 6, 8, 10, 12, and 14, and 20 values at around 21.4°, 28.6°, 35.9°, 43.4°, and 51.1°, respectively) increase with the increase of sintering temperature and saturate at 1050°C-sintered ceramics, and the increase in the crystal intensities of the (0,0,8) and (0,0,10) planes are more obvious. For the same sintering temperature, the crystal intensities of the (0,0,l) planes increase with the increase of V_2O_5 content and saturate at SrBi_2Ta_{1.7}V_{0.3}O_9 ceramics.

Figure 3 shows the maximum dielectric constants (ε_{Tc}, revealed at Curie temperature) of the SrBi_2Ta_{2-x}V_xO_9 ceramics as a function of sintering temperature and V_2O_5 content. Even only 900°C is used as the sintering temperature, the ε_{Tc} values of SrBi_2Ta_{2-x}V_xO_9 ceramics are 443~485, which are higher than that SrBi_2Ta_2O_9 ceramic present. There are many factors will influence the ε_{Tc} values, including the addition of dopant, the pores ratio, and the increase in the polarization because of the increase in grain growth. The ε_{Tc} values critically increase from 443~485 to 682~749 as the sintering temperature increases from 900°C to 1000°C, the decrease in pores and increase in grain growth will cause the ε_{Tc} values to increase. From the results show in Fig.1 and Fig.2, the crystal intensities of (0,0,l) planes increase with the increase of sintering temperature and V_2O_5 content. This result suggests that the polarization of c-axis will increase with the increase of sintering temperature and V_2O_5 content and that will increase the ε_{Tc} values. As the sintering temperature increases from 1000°C to 1100°C the ε_{Tc} values of SrBi_2Ta_{1.9}V_{0.1}O_9 and SrBi_2Ta_{1.8}V_{0.2}O_9 ceramics decrease and the ε_{Tc} values of SrBi_2Ta_{1.7}V_{0.3}O_9 and SrBi_2Ta_{1.6}V_{0.4}O_9 ceramics are almost unchanged. The Curie temperatures of SrBi_2Ta_{2-x}V_xO_9 ceramics are also shown in Fig.3. As the sintering temperature increases from 900°C~1100°C, the Curie temperatures of SrBi_2Ta_{1.9}V_{0.1}O_9 ceramics critically decrease from around 450°C (sintered at 900°C) to 350°C (sintered at 1100°C), and the Curie temperatures of SrBi_2Ta_{1.8}V_{0.2}O_9, SrBi_2Ta_{1.7}V_{0.3}O_9, SrBi_2Ta_{1.6}V_{0.4}O_9 ceramics linearly decrease from 387°C (sintered at 900°C) to 325°C (sintered at 1100°C).

The dielectric constant-temperature (ε-T) curves of SrBi_2Ta_{2-x}V_xO_9 ceramics are investigated at 1MHz and sintered at 1000°C, the results are shown in Fig.4. According the literature on the layered perovskite ferroelectrics, the shift of the Curie temperatures to a higher temperature corresponds to a larger polarizability could well be explained by the increasing rattling space due to the incorporation of smaller V^{5+} ion [7]. In addition, an increase in dielectric constant at the Curie temperature is an indicative of the enhanced polarizability. As the Fig.4 shows, as the sintering temperature is higher than 1000°C, both the maximum dielectric constant and the Curie temperatures decrease with the increase of sintering temperature. The polarizabilities decrease with the increase of sintering temperature. It is the reason that as the sintering temperature is higher than 1000°C, the ε_{Tc} values of SrBi_2Ta_{1.9}V_{0.1}O_9 and SrBi_2Ta_{1.8}V_{0.2}O_9 ceramics decrease. In this study, sintering temperature higher than 1000°C is not necessary, because the higher sintering temperature will cause the decrease of the
maximum dielectric constants and Curie temperatures. Fig.4 also shows that the SrBi$_2$Ta$_{1.9}$V$_{0.1}$O$_9$ ceramic shows a ferroelectric characteristic because the $\varepsilon_r$-T curve first increases, reaches a maximum, then decreases with the increase of measured temperature. The other SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics reveal a relaxor characteristics because the dielectric constant decreases and then increases as the measured temperature is higher than Curie temperature.

Conclusions

The substitution of Ta$_2$O$_5$ by V$_2$O$_5$ has reduced the sintering temperature of SrBi$_2$Ta$_2$O$_9$ ceramics to around 1000°C. For $x=0.1$ and 0.2 and sintered at the same temperatures, the maximum dielectric constants of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics first increase, reach a maximum at about 1000°C, then slightly decrease; For $x=0.3$ and 0.4, the $\varepsilon_{Tc}$ values will saturate at 1000°C. The sintering temperature higher than 1000°C is not necessary, because of the decrease of the Curie temperatures and the maximum dielectric constants of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics. In this study, SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics sintered at 1000°C has the maximum dielectric constant and the higher Curie temperatures.

References