The Influences of Excess Bi$_2$O$_3$ Content on the Characteristics of 0.8 (Bi$_{0.5}$K$_{0.5}$)TiO$_3$-0.2 BaTiO$_3$ Ceramics

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The Bi-layer structure bismuth 0.8 Bi$_{0.5}$K$_{0.5}$TiO$_3$-0.2 BaTiO$_3$ + x wt% (0.8 BKT-0.2 BT$_3$-x, x = 0, 1, 2, and 3) Bi$_2$O$_3$ ceramic was sintered in air for 2 h from 1000$^\circ$C to 1100$^\circ$C. The excess content of Bi$_2$O$_3$ was used as the sintering aid and to compensate the vaporization of Bi$_2$O$_3$ during the sintering process. A narrow range of sintering temperature could be used to densify the 0.8 BKT-0.2 BT$_3$-x ceramics. The addition of excess Bi$_2$O$_3$ would lower down the sintering temperature and extend the temperature range to sinter the 0.8 BKT-0.2 BT$_3$-x ceramics. The Curie temperatures of 0.8 BKT-0.2 BT$_3$-x ceramics would be shifted to lower temperatures as the sintering temperatures and the content of excess Bi$_2$O$_3$ increase.

Keywords Ceramics; electronic materials; electrical properties

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1. Introduction

Due to the high environmental pollution problem of PbO during the fabricating process, the major tendency of recently reports were to form lead-free piezoelectric materials with the characteristics similar to Pb(Zr,Ti)O$_3$ (abbreviated as PZT) ceramics. Many researches hoped to find materials that the Curie Temperatures (Tc) were near those of PZT ceramics and the contaminations were lower than PZT. Bi$_{0.5}$K$_{0.5}$TiO$_3$ (abbreviated as BKT) and Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT), which were a typical of Bi-layer perovskite structure bismuth oxides, were the most popular lead-free ferroelectric perovskite materials. BKT ceramic had a high Curie temperature (Tc) of 380–385$^\circ$C [1–4], which was higher than that of BNT.
ceramic ($T_c = 300^\circ C$) [2–4]. BKT ceramics had the advantage for the applications in piezoelectric filters, resonators and micro-electric-mechanical systems (MEMS). Compared to the reports of BNT-BKT-BT3 (BaTiO$_3$) ceramics and BNT-BT3 systems, the discussions of mixed different ratio of BKT-BT3 system were only fewer than those of the BNT-BT3 ceramics.

However, the influences of different additives, such as Bi$_2$O$_3$ and B$_2$O$_3$, on the sintering and dielectric characteristics of BKT-BT3 ceramics also had not been developed. Though excess amount of Bi$_2$O$_3$ in Bi-layer structure bismuth oxides was known to affect the ferroelectric properties as well as the crystal structure [5, 6]. In the past, we had found that the addition of excess content of Bi$_2$O$_3$ had large influence on the crystal and dielectric characteristics of SrBi$_2$Ta$_2$O$_9$ ceramic [7]. For that, the excess content of Bi$_2$O$_3$ was added into 0.8(Bi$_{0.5}$K$_{0.5}$)TiO$_3$-0.2BaTiO$_3$ (0.8 BKT-0.2 BT3) ceramic for two functions. The first was that the excess Bi$_2$O$_3$ was used as sintering aid, and the excess Bi$_2$O$_3$ was hoped to improve the sintering characteristics of 0.8 BKT-0.2 BT3 ceramics. The second was that the excess Bi$_2$O$_3$ addition was used to compensate the vaporization of Bi$_2$O$_3$ during the fabrication process and was hoped to improve the dielectric characteristics of 0.8 BKT-0.2 BT3 ceramics. In the past, the BKT-based ceramics were formed using the sol-gel method [1–3]. In this paper, the solid-state reaction method was used to fabricate the 0.8 BKT-0.2 BT3 $+x$ wt% Bi$_2$O$_3$ ceramics. The influences of sintering temperatures and excess content of Bi$_2$O$_3$ on the sintering and dielectric characteristics of 0.8 BKT-0.2 BT3 ferroelectric ceramics were developed with the aid of SEM observation, X-ray diffraction patterns and dielectric-temperature curves.

2. Experimental Procedure

In this paper, the solid-state reaction method was adopted to form the 0.8(Bi$_{0.5}$K$_{0.5}$)TiO$_3$-0.2 BaTiO$_3 + x$ wt% Bi$_2$O$_3$ ceramics. At first, reagent-grade raw materials of Na$_2$CO$_3$, Bi$_2$O$_3$, BaCO$_3$ and TiO$_2$ with purity higher than 99.5% were mixed according to the compositions of 0.8(Bi$_{0.5}$K$_{0.5}$)TiO$_3$-0.2BaTiO$_3 + x$ wt% Bi$_2$O$_3$ (abbreviated as 0.8 BKT-0.2 BT3-$x$, $x = 0, 1, 2$ and $3$). After drying and grinding, the 0.8 BKT-0.2 BT3-x powders were calcined at 800$^\circ C$ for 2 h. After grinding again, polyvinylalcohol (PVA) was added into the 0.8 BKT-0.2 BT3-$x$ powders as a binder. The mixing powders were pressed into pellets in a steel die, and the sizes of pellets were 1mm thick and 12mm in diameter. After debindering, the sintering of 0.8 BKT-0.2 BT3-$x$ ceramics was carried out from 1000$^\circ C$ to 1100$^\circ C$ for 2 h. The morphologies of sintered 0.8 BKT-0.2 BT3-$x$ ceramics were investigated using scanning electronic microscope (SEM), and the crystalline structures of 0.8 BKT-0.2 BT3-$x$ ceramics were investigated using X-ray diffraction (XRD) patterns. The sintered ceramics were painted with Ag-Pd paste, fired at 700$^\circ C$ for 15 min. The temperature-dielectric characteristics were measured with an oscillating amplitude (50 mV) from 30$^\circ C$ to 500$^\circ C$ at 1 MHz by an HP4294 impedance analyzer, putting the sintered ceramics in a temperature-programmable testing chamber. The dielectric constants of 0.8 BKT-0.2 BT3-$x$ ceramics were calculated as followed:

$$
\varepsilon_r = (C \ast d)/(\varepsilon_o \ast A)
$$

where $C$ was the measured capacitance, $d$ the thickness ($\sim 1$ mm), $A$ the electrode area (6 mm in diameter), $\varepsilon_o$ the permittivity of free space and $\varepsilon_r$ the measured dielectric constant.
Figure 1. The micrographs of 0.8 BKT-0.2 BT3 ceramics, as a function of sintering temperatures and excess Bi$_2$O$_3$ content ((a) 1050 °C, 0wt%, (b) 1050 °C, 3wt%, (c) 1075 °C, 0wt%, (d) 1075 °C, 1wt%, (e) 1075 °C, 3wt%, and (f) 1100 °C, 0wt%).

3. Results and Discussion

Figure 1 shows the SEM micrographics of 0.8 BKT-0.2 BT3-x ceramics as a function of sintering temperatures and the content of excess Bi$_2$O$_3$. It is found that different content of excess Bi$_2$O$_3$ will lead to different results in the morphologies of 0.8 BKT-0.2 BT3 ceramics. Sintered at 1000 °C and 1025 °C, the 0.8 BKT-0.2 BT3-x ceramics show a porous structure, and grain growth is only observed in the 1025 °C-sintered 0.8 BKT-0.2 BT3-3 ceramic (not shown here). For 1050 °C-sintered 0.8 BKT-0.2 BT3-x ceramics, grain growth is apparently observed, as shown in Figs. 1(a) and 1(b). Pores are apparently observed in the 0.8 BKT-0.2 BT3-0 (Fig. 1(a)) and 0.8 BKT-0.2 BT3-1 ceramics. But for 0.8 BKT-0.2 BT3-2 and 0.8 BKT-0.2 BT3-3 (Fig. 1(b)) ceramics almost no pores are observed and the morphologies show the densified surfaces. This result proves that the excess content of Bi$_2$O$_3$ can be used as sintering aid and will improve the sintering of 0.8 BKT-0.2 BT3 ceramics.

Comparing the SEM micrographics of 1075 °C-sintered ceramics revealed in Figs. 1(c), 1(d) and 1(e), the grain size apparently increases with the increase of excess Bi$_2$O$_3$ content. This result proves again that excess Bi$_2$O$_3$ is helpful for the ceramic densification and grains growth of 0.8 BKT-0.2 BT3-x ceramics. Further increasing in the sintering temperature to 1100 °C, as shown in Fig. 1(f) for 0.8 BKT-0.2 BT3-0 ceramic, even the grain size increases but the pores are apparently observed on the 0.8 BKT-0.2 BT3-x ceramics. Using the solid-state reaction method to fabricating 0.8 BKT-0.2 BT3-x ceramics, only a narrow sintering temperature range can be used to densify the 0.8 BKT-0.2 BT3 ceramic. SEM micrographs shown in Fig. 1 suggest that the addition of excess Bi$_2$O$_3$ will broaden the range of sintering temperature to densify the 0.8 BKT-0.2 BT3 ceramic. The results shown
Figure 2. X-ray diffraction patterns for 0.8 BKT-0.2 BT3 ceramics, sintered at 1050°C as a function of excess Bi$_2$O$_3$ content.

in Fig. 1 also suggest that using the solid-state reaction method as the fabrication method, the sintering temperature and the content of excess Bi$_2$O$_3$ have large influences on the sintering characteristics of 0.8 BKT-0.2 BT3 ceramics. And furthermore, the sintering temperature and the content of excess Bi$_2$O$_3$ will have large influence on the dielectric characteristics of 0.8 BKT-0.2 BT3 ceramics.

Figure 2 shows the XRD patterns of 0.8 BKT-0.2 BT3-\(x\) ceramics, the sintering temperature is 1050°C. As the results show in Fig. 2, the perovskite ABO$_3$ phase is revealed as the main peaks, some unknown or satellite phases are also observed. From the JCPD standard, the tetragonal (Bi$_{0.5}$K$_{0.5}$)TiO$_3$ ceramic has a peak of (110) plane around the \(2\theta = 32.3^\circ\), and this is not revealed in Fig. 2. For that, the 0.8 BKT-0.2 BT3 ceramics seems to be cubic (or pseudo-cubic) phase rather than a tetragonal phase. However, as the XRD patterns showed in Fig. 2, there are some differences between the different excess-Bi$_2$O$_3$-doped 0.8 BKT-0.2 BT3 ceramics. As the content of excess Bi$_2$O$_3$ increases from 0 wt% to 3wt%, the \(2\theta\) values of main crystal peak are shifted from 32.18\(^{\circ}\) to lower value of 31.96\(^{\circ}\). The full width of half maximum (FWHM) values of (110) peak of 0.8 BKT-0.2 BT3-0, 0.8 BKT-0.2 BT3-1, 0.8 BKT-0.2 BT3-2 and 0.8 BKT-0.2 BT3-3 ceramics are 0.22\(^{\circ}\), 0.23\(^{\circ}\), 0.25\(^{\circ}\) and 0.27\(^{\circ}\), respectively. These results suggest that the FWHM values slightly increase as the content of excess Bi$_2$O$_3$ increases from 0 to 3wt%. These results prove again that the excess Bi$_2$O$_3$ content will influence the lattice constants and the crystalline characteristics and then will influence the dielectric characteristics of 0.8 BKT-0.2 BT3 ceramics.

The \(2\theta\) values of crystalline peaks of 0.8 BKT-0.2 BT3-\(x\) ceramics will be changed as the sintering temperatures and the content of excess Bi$_2$O$_3$ are changed. This result suggests that the lattice constants of 0.8 BKT-0.2 BT3-\(x\) ceramics will also be changed, and the results are shown in Fig. 3. Because the 0.8 BKT-0.2 BT3-\(x\) ceramics are the cubic phase, only the lattice constant \(a\) is needed to be calculated. The lattice constant \(a\) is calculated using the (001) (or (100)) plane for \(2\theta\) value at around 22.450\(^{\circ}\). As Fig. 3 shows, the lattice constant \(a\) apparently increases as the sintering temperatures and the content of excess Bi$_2$O$_3$ increase. The result shown in Fig. 3 suggests again that the content of
excess Bi$_2$O$_3$ has apparent influence on the lattice constants of 0.8 BKT-0.2 BT3 ceramics and that will have apparent influence on the dielectric characteristics of 0.8 BKT-0.2 BT3 ceramics.

Figure 4 (a) shows the maximum dielectric constants ($\varepsilon_{\text{max}}$, revealed at Curie temperatures) of 0.8 BKT-0.2 BT3-x ceramics as a function of sintering temperatures and the content of excess Bi$_2$O$_3$, the measuring frequency is 1 MHz. For all 0.8 BKT-0.2 BT3-x ceramics, as the sintering temperature increases from 1000°C to 1075°C, the $\varepsilon_{\text{max}}$ values linearly increase. Sintered at 1075°C, the $\varepsilon_{\text{max}}$ values of 0.8 BKT-0.2 BT3-1 and 0.8 BKT-0.2 BT3-2 ceramics are larger than those of 0.8 BKT-0.2 BT3-0 and 0.8 BKT-0.2 BT3-3 ceramics. The decrease in pores and the increase in grain size are the reasons to cause this result. After reaching the maximum values after sintering at 1075°C, the $\varepsilon_{\text{max}}$ values of all 0.8 BKT-0.2 BT3-x ceramics decrease apparently as 1100°C is used as sintering temperature. From the SEM micrographs shown in Fig. 1, the pores revealed in the 1100°C-sintered ceramics will decrease the dielectric constants. As the sintering temperatures are higher than 1050°C, the $\varepsilon_{\text{max}}$ values of 0.8 BKT-0.2 BT3-3 ceramic are smaller than those of 0.8 BKT-0.2 BT3-1 and 0.8 BKT-0.2 BT3-2 ceramics. From the XRD patterns shown in Fig. 2, the unknown secondary phases are apparently observed, and that is another reason to cause the decrease of dielectric constant in the 0.8 BKT-0.2 BT3-3 ceramics. And this also suggests that too much Bi$_2$O$_3$ addition is not necessary, because the Bi$_2$O$_3$ is low dielectric constant material that will low down the $\varepsilon_{\text{max}}$ values of 0.8 BKT-0.2 BT3-x ceramics.

Figure 4 (b) shows the Curie temperatures (the temperatures to reveal the maximum dielectric constants) of 0.8 BKT-0.2 BT3 ceramics. As shown in Fig. 4(b), the Curie temperatures are shifted to lower temperatures as the content of excess Bi$_2$O$_3$ and sintering temperatures increase. The predicted Curie temperatures of 0.8 BKT-0.2 BT3 ceramics can be calculated by Eq. (2):

$$T_c = 0.8 \times 380 + 0.2 \times 120$$  \hspace{1cm} (2)
Figure 4. (a) Maximum dielectric constant and (b) the Curie temperatures for 0.8 BKT-0.2 BT3 ceramics, as a function of excess Bi₂O₃ content and sintering temperature.

Where 380 and 120 are the Curie temperatures (Tc) of (Bi₀.₅K₀.₅)TiO₃ and BaTiO₃ ceramics, and Tc is the predicted Curie temperature. The predicted Curie temperature for 0.8 BKT-0.2 BT3 ceramics is 328°C. When compared with the results shown in Fig. 4(b), except the 0.8 BKT-0.2 BT3-3 ceramic, the most 0.8 BKT-0.2 BT3-x ceramics revealed in Fig. 4(b) have the Curie temperatures higher than the predicted values. The needed sintering temperatures of (Bi₀.₅K₀.₅)TiO₃ and BaTiO₃ ceramics are about 1050°C and 1350°C, respectively. The Bi₂O₃ has the low melting point of about 820°C and can be used as the sintering aid of BaTiO₃-based ceramics. For that, the higher sintering temperatures and more excess Bi₂O₃ addition will improve the sintering of BaTiO₃ composition, and that will cause the 0.8 BKT-0.2 BT3-x ceramics to have lower Curie temperatures.

The temperature-dependent dielectric constants (εᵣ-T) curves of 0.8 BKT-0.2 BT3-x ceramics are investigated, and the results are shown in Fig. 5. For all 0.8 BKT-0.2
BT3-\(x\) ceramics, the dielectric constants show a ferroelectric characteristic rather than a relaxor characteristic. As the measured temperatures increase, the dielectric constants first increase, reach a maximum at Curie temperature and then decrease. However, as the content of excess Bi\(_2\)O\(_3\) increases, the \(\varepsilon_r\)-T curves show the diffusion Curie temperature characteristics, because the \(\varepsilon_r\)-T curves has a broaden range of high dielectric constant than a narrow range of high dielectric constant. As the results in Fig. 5 are compared, even with a lower \(\varepsilon_{\text{max}}\) value, 0.8 BKT-0.2 BT3-3 ceramic has a broaden range of high dielectric constant than the other 0.8 BKT-0.2 BT3-\(x\) ceramics do.

4. Conclusions

In this study, we have proven that the addition of excess content of Bi\(_2\)O\(_3\) have the large influence on the sintering and dielectric characteristics of 0.8 (Bi\(_{0.5}\)K\(_{0.5}\))TiO\(_3\)-0.2 BaTiO\(_3\) (0.8 BKT-0.2 BT3) ceramics. Using the solid-state reaction method, 0.8 BKT-0.2 BT3
ceramics are hard to form a single phase because of the existence of unwanted secondary phases. The addition of 1wt% or 2wt% excess Bi$_2$O$_3$ is the optimal content to sinter 0.8 BKT-0.2 BT3 ceramics. Because the addition of 1wt% or 2wt% excess Bi$_2$O$_3$ will lower down the sintering temperatures and improve the dielectric constants of 0.8 BKT-0.2 BT3 ceramics. Another important results for the addition of excess Bi$_2$O$_3$ are that it will broaden the maximum dielectric constant and lead to 0.8 BKT-0.2 BT3 ceramics have a diffusion Curie temperature.

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