The Influence of Excess Bi$_2$O$_3$ on the Characteristics of (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$-BaTiO$_3$ Ceramics

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Abstract. In this study, piezoelectric materials 0.95 (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$-0.05 BaTiO$_3$ (NBT-BT) composition with excess x wt% Bi$_2$O$_3$ (x=0, 1, 2, and 3) are investigated as a function of sintering temperatures. The sintering characteristics and dielectric characteristics of excess Bi$_2$O$_3$-doped 0.95 (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$-0.05 BaTiO$_3$ ceramics are developed with the aid of SEM, X-ray diffraction patterns, and dielectric-temperature curves. The sintering process is carried out in air for 2h from 1120°C to 1200°C. Dielectric-temperature properties are investigated in the temperature range of 30°C~350°C at the frequencies of 10KHz~1MHz. The maximum dielectric constants of NBT-BT ceramics first increase with the increase of Bi$_2$O$_3$ content, reach the maximum at 1wt%-Bi$_2$O$_3$-added NBT-BT ceramics, and then decrease with the further increase of Bi$_2$O$_3$ content. The maximum dielectric constants of NBT-BT ceramics are almost unchanged as the measured frequency increases. The Curie temperatures of NBT-BT ceramics are also developed in this study.

Introduction

(Na$_{0.5}$Bi$_{0.5}$)TiO$_3$ (NBT) was a kind of perovskite ABO$_3$-type ferroelectric discovered by Smolenskii et al. in 1960 [1]. To improve its properties, some modifications on NBT composition had been performed. It had been reported that NBT-based compositions modified with K$_{0.5}$Bi$_{0.5}$TiO$_3$ (KBT) and NaNbO$_3$ (NN) showed improved piezoelectric properties and ease of poling compared with pure NBT ceramics [2-4]. In the past, the (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$-BaTiO$_3$ compositions (NBT-BT) [5] were developed as the piezoelectric materials and their dielectric characteristics were well developed. However, the influences of different additives, such as Bi$_2$O$_3$ and B$_2$O$_3$, on the sintering and dielectric characteristics of (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$-BaTiO$_3$ compositions 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 [6,7]. In this study, we were interesting to investigate materials based on 0.95 (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$-0.05 BaTiO$_3$ ceramics, excess Bi$_2$O$_3$ addition was hoped to improve the sintering and dielectric characteristics of 0.95 (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$-0.05 BaTiO$_3$ ceramics. The x (x=0, 1, 2, and 3) wt% Bi$_2$O$_3$-doped 0.95 (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$-0.05 BaTiO$_3$ ceramics were sintered at different temperatures and their crystal structures and grain growth were examined by X-ray diffraction patterns and scanning electronic microscope (SEM). The relative dielectric characteristics were investigated as a function of sintering temperature, Bi$_2$O$_3$ content, measured temperature, and measured frequencies.

Experimental Procedure

The ceramic materials 0.95 (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$-0.05 BaTiO$_3$ (NBT-BT) were prepared by the
mixed oxide method. Reagent-grade raw materials of Na\textsubscript{2}CO\textsubscript{3}, Bi\textsubscript{2}O\textsubscript{3}, BaCO\textsubscript{3}, and TiO\textsubscript{2} with higher than 99.5% purity were used as starting materials, mixed according to the composition 0.95 (Na\textsubscript{0.5}Bi\textsubscript{0.5})TiO\textsubscript{3}-0.05 BaTiO\textsubscript{3} + xwt% Bi\textsubscript{2}O\textsubscript{3}, x=0, 1, 2, and 3, and ball-milled for 5h with deionized water. After drying and ground, then the 0.95 (Na\textsubscript{0.5}Bi\textsubscript{0.5})TiO\textsubscript{3}-0.05 BaTiO\textsubscript{3} + xwt% Bi\textsubscript{2}O\textsubscript{3} (NBT-BT) powders were calcined at 850\textdegree C for 2h. After calcinations, the powders were ground again and the polyvinylalcohol (PVA) was added as a binder. The mixing powders were uniaxially pressed into pellets in a steel die with the size of 1mm in thick and 12mm in diameter. After debinding, the sintering of NBT-BT ceramics was carried out from 1120\textdegree C to 1200\textdegree C for 4h. The morphologies of sintered NBT-BT ceramics were observed by using SEM. The crystal structures of x wt%-Bi\textsubscript{2}O\textsubscript{3}-added NBT-BT ceramics were investigated by using XRD patterns. The sintered ceramics were painted with Ag-Pd paste and sintered at 700\textdegree C for 15min. Temperature-dependent dielectric characteristics were measured with an oscillating amplitude (50mV) at 1MHz by an HP4194 impedance analyzer, putting the sintered ceramics in a temperature-programmable testing chamber.

Results and Discussion

The morphologies of NBT-BT ceramics + x wt% Bi\textsubscript{2}O\textsubscript{3} ceramics are investigated and the results are shown in Fig.1. Even sintered at 1120\textdegree C, the stoichiometry NBT-BT ceramic shows a porous structure and the grain growth is not observed (not shown here). For stoichiometry NBT-BT ceramic and sintered at 1160\textdegree C, as shown in Fig.1(a), the grain growth is observed and almost no pores are observed in the 1160\textdegree C-sintered stoichiometry NBT-BT ceramic and the many small sizes of grain are also revealed in the morphologies. For 1 wt%-Bi\textsubscript{2}O\textsubscript{3}-added NBT-BT ceramic and sintered at 1160\textdegree C, as shown in Fig.1(b), the grain size increases slightly as compared with that of stoichiometry NBT-BT ceramic, and also no pores are revealed and the small size grain are also observed; But further increasing the excess Bi\textsubscript{2}O\textsubscript{3} to 2wt% (not shown here) and 3wt% (Fig.1(c)), the grain size increases apparently and becomes more uniformly as compared with those of stoichiometry and 1 wt%-Bi\textsubscript{2}O\textsubscript{3}-added NBT-BT ceramics. However, the pores revealed in Fig.1(c) are also more apparent as compared with those of stoichiometry and 1 wt%-Bi\textsubscript{2}O\textsubscript{3}-added NBT-BT ceramics. For that the excess Bi\textsubscript{2}O\textsubscript{3} content has large influence on the morphologies of NBT-BT ceramics, and furthermore, the excess Bi\textsubscript{2}O\textsubscript{3} content has large influence on dielectric characteristics of NBT-BT ceramics.

![Fig.1 The micrographs of NBT-BT ceramics sintered at 1160\textdegree C as a function of Bi\textsubscript{2}O\textsubscript{3} content. (a) 0wt%, (b) 1wt%, and (c) 3wt%](image)

Typical X-ray diffraction (XRD) patterns of NBT-BT ceramics are shown in Fig.2 as a function of excess Bi\textsubscript{2}O\textsubscript{3} content and sintering temperatures. As shown in Fig.2(a), using 1120\textdegree C ~1200\textdegree C as the sintering temperatures of the undoped NBT-BT ceramics, only the ABO\textsubscript{3} phase is revealed in the XRD patterns, no unknown or satellite phases are observed. The crystal intensity of (002) plane have slightly increased but the crystal intensities of the other planes are almost unchanged as the sintering temperatures increase. Using 1160\textdegree C as the sintering temperatures of the NBT-BT + x wt% Bi\textsubscript{2}O\textsubscript{3} ceramics, similarly, only the ABO\textsubscript{3} phase is revealed in the XRD patterns, as shown in Fig.2(b). The crystal intensities of (102) plane have decreased slightly but
the other planes are almost unchanged as the Bi$_2$O$_3$ content increase. Even the known phases are observed in the morphologies of 3wt%-Bi$_2$O$_3$-added NBT-BT ceramic, but the unknown phases are not observed in the XRD patterns. Comparing the XRD patterns shown in Fig.4, the 2θ values are almost unchanged as the Bi$_2$O$_3$ content and sintering temperatures increase.

![X-ray patterns for (a) NBT-BT (x=0) ceramics and (b) NBT-BT + x wt% Bi$_2$O$_3$ ceramics as a function of sintering temperature and Bi$_2$O$_3$ content and sintered at 1160ºC.](image1)

![Fig.2 The X-ray patterns for (a) NBT-BT (x=0) ceramics and (b) NBT-BT + x wt% Bi$_2$O$_3$ ceramics as a function of sintering temperature and Bi$_2$O$_3$ content and sintered at 1160ºC.](image2)

Fig.2 The X-ray patterns for (a) NBT-BT (x=0) ceramics as a function of sintering temperature and (b) NBT-BT + x wt% Bi$_2$O$_3$ ceramics as a function of Bi$_2$O$_3$ content and sintered at 1160ºC.

![Maximum dielectric constants (ε$_{max}$) and Curie temperatures (T$_c$) of NBT-BT ceramics sintered at 1160ºC as a function of measured frequencies and Bi$_2$O$_3$ content.](image3)

![Fig.3 The (a) maximum dielectric constants (ε$_{max}$) and (b) Curie temperatures (T$_c$) of NBT-BT ceramics sintered at 1160ºC as a function of measured frequencies and Bi$_2$O$_3$ content.](image4)

Fig.3 The (a) maximum dielectric constants (ε$_{max}$) and (b) Curie temperatures (T$_c$) of NBT-BT ceramics sintered at 1160ºC as a function of measured frequencies and Bi$_2$O$_3$ content.

Figure 3 shows the maximum dielectric constants (revealed at Curie temperatures, ε$_{max}$) of 1160ºC-sintered NBT-BT + x wt% Bi$_2$O$_3$ ceramics as a function of measured frequencies. For the same measured frequency, the ε$_{max}$ values first increase with the increase of Bi$_2$O$_3$ content, reach a maximum at 1wt%-added NBT-BT ceramics, and then decrease with the further increase the Bi$_2$O$_3$ content. The decrease in grain size and the increase in the second phases, as shown in Fig.1, are the reason to cause the decrease of dielectric constants. The all ε$_{max}$ values of NBT-BT + x wt% Bi$_2$O$_3$ ceramics first decrease as the measured frequencies increase from the 10kHz to 100kHz and then all ε$_{max}$ values increase as the measured frequencies further increase to 1MHz. Figure 3 also shows the Curie temperatures (the temperatures to reveal the maximum dielectric constants) of 1160ºC-sintered NBT-BT + x wt% Bi$_2$O$_3$ ceramics as a function of measured frequencies. As Fig.3(b) shows, the Curie temperature of undoped NBT-BT ceramic is 250ºC and those of excess
Bi$_2$O$_3$-doped NBT-BT ceramics are 260°C independent of measured frequencies; For all NBT-BT + x wt% Bi$_2$O$_3$ ceramics, the Curie temperatures are unchanged as the measured frequencies increase.

The dielectric constant-temperature ($\varepsilon_r$-T) curves of 1160°C-sintered NBT-BT + x wt% Bi$_2$O$_3$ ceramics are investigated at 10kHz, 100kHz, and 1MHz, and the results are shown in Fig.4. For all NBT-BT + x wt% Bi$_2$O$_3$ ceramics, the dielectric constant will show a ferroelectric characteristic rather than a relaxor characteristic. Because as the measured temperature increase, the dielectric constants of all NBT-BT + x wt% Bi$_2$O$_3$ ceramics first increase, reach a maximum at Curie temperature, and then decrease apparently. Even having a lower dielectric constant, the 3wt%-Bi$_2$O$_3$-added NBT-BT ceramic reveal a more broaden $\varepsilon_r$-T curve than the 0wt%- and 1wt%-Bi$_2$O$_3$-added NBT-BT ceramics do.

Fig.4 The temperature-dependent dielectric constants of NBT-BT ceramics as a function of measured temperatures, measured frequencies, and Bi$_2$O$_3$ content.

Conclusions

1. The addition of excess Bi$_2$O$_3$ have no apparent effect on lowering down the sintering temperatures of NBT-BT ceramics.

2. In the NBT-BT + x wt% Bi$_2$O$_3$ system, the 1wt%-Bi$_2$O$_3$-added NBT-BT ceramics will reveal the maximum grain size and the maximum dielectric constant.

3. The Curie temperatures of 1160°C-sintered NBT-BT + x wt% Bi$_2$O$_3$ ceramics are almost unchanged as the measured frequencies and Bi$_2$O$_3$ content increase.

4. The NBT-BT + x wt% Bi$_2$O$_3$ ceramics reveal a ferroelectric characteristic rather than a relaxor characteristic.

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