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Effects of $K_{0.5}Bi_{0.5}TiO_3$ addition on dielectric properties of $BaTiO_3$ ceramics

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Abstract

$(1-x)BaTiO_3$–$xK_{0.5}Bi_{0.5}TiO_3$ (abbreviated as BT–KBT, $0.10 \leqq x \leqq 0.15$) dielectric ceramics were prepared by a conventional oxide mixing method. The effects of KBT content on the densification, microstructure and dielectric properties of BT ceramics were investigated. The density characterization results show that the addition of KBT significantly lowered the sintering temperature of BT ceramics to about 1280 °C. The XRD results showed that the phase compositions of all samples were pure tetragonal phases. The dielectric constant and dielectric loss firstly increased and then decreased with the increase of KBT. In addition, dielectric constant and dielectric loss versus frequency were characterized in the frequency range from 100 Hz to 2 MHz. It is found that the dielectric constant and the dielectric loss changed with the increase of KBT contents regularly.

Keywords: C. Dielectric properties; D. $BaTiO_3$ and titanates; D. Perovskites

1. Introduction

Barium titanate-based ceramics are widely applied in high dielectric constant ceramic capacitors, positive temperature coefficient of resistivity (PTCR) thermistors and lead-free ceramic piezoelectric devices. However, the application and preparation of lead-based ceramics have not only caused serious lead pollution and environmental problems, but also led to instability of the composition because of its high volatility during sintering [1]. KBT is a complex perovskite type ferroelectric, and has a relatively high Curie temperature (380 °C). $(1-x)$KBT–xBT system has attracted considerable attention, and was studied by many researchers [2]. However, most researches focused on the introduction of KBT which may have effects on PTCR behaviors of BT ceramics; there are a few related reports that study effects of KBT on dielectric properties of BT ceramics with high concentrations of KBT.

In this paper, KBT as addition was discussed, aiming at obtaining high density dielectrics by low temperature sintering. The phase compositions of $(1-x)$BT–xKBT ceramics were studied by X-ray diffraction. The microstructures and dielectric properties of $BaTiO_3$ ceramics were also investigated.

2. Experimental

Stoichiometric amounts of $BaCO_3$ and TiO_2 powders were ball-milled for 4 h and calcined at 1150 °C for 4 h to obtain a pure BT phase. Then stoichiometric amounts of K_2CO_3, Bi_2O_3 and TiO_2 powders at a molar ratio of Bi:K:Ti = 1:1:4 were weighed and ball-milled for 4 h, the mixture was calcined at 950 °C for 4 h to obtain a pure KBT phase. The synthesized KBT powder and the synthesized BT powder according to the nominal composition $(1-x)$BT–xKBT ($0.05 \leqq x \leqq 0.15$) were weighed and ball-milled with zirconia media in distilled water for 4 h. After drying and granulating with polyvinyl alcohol (PVA, 5 wt%), the well mixed powders were pressed into a disk (Φ 12 × 2 mm) and then sintered at 1280–1320 °C in air for 3 h.

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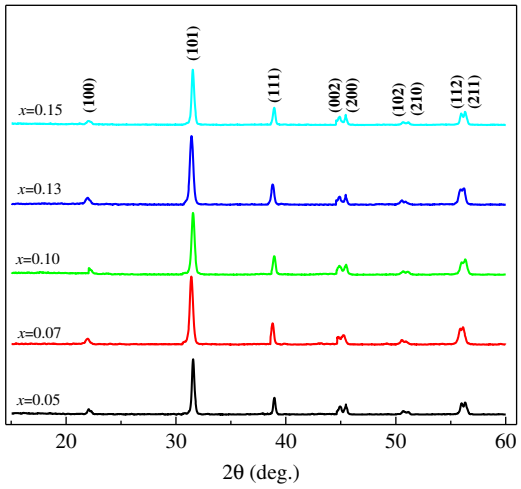

Fig. 1. XRD patterns of $(1-x)$BT–xKBT ($0.05 \leqq x \leqq 0.15$).

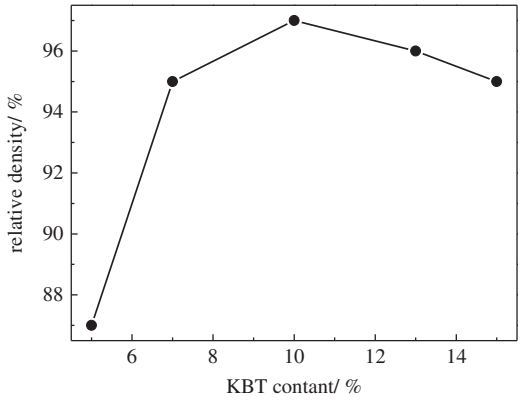

Fig. 2. Relative density of $(1-x)$BT–xKBT ($x=0.05$, 0.07, 0.10, 0.13, 0.15) ceramics as a function of KBT content.

The crystalline phases of $(1-x)$BT–xKBT ($0.05 \leqq x \leqq 0.15$) were characterized by X-ray diffraction (XRD, D/max-2200PC, RIGAKU, Japan) analysis. A scanning electron microscope (JSM-6700, JEOL Ltd., Tokyo, Japan) was used to investigate the microstructure of BT–KBT ceramics. The temperature dependence of permittivity at 100 kHz was obtained by using an Agilent E4980A from room temperature to 550 °C at the rate of 2 °C/min. In addition, dielectric constant and dielectric loss versus frequency were obtained by using Agilent 4192A from 100 Hz to 2 MHz.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $(1-x)$BT–xKBT ($x=0.05$, 0.07, 0.10, 0.13, 0.15) ceramics. It is found that all diffraction peaks of BT–KBT ceramic samples were indexed according to the BT ceramics, which indicated that the BT and KBT phases have formed a solid solution during sintering. Moreover, it can be seen from Fig. 1 that the BT–KBT ceramic samples show a tetragonal structure in which the reflections (200) and (002) can be split into two peaks.

Fig. 2 shows the relative density of BT ceramics as a function of the KBT content. The densification rate of BT is very slow, and temperatures above 1300 °C are needed for sintering. Low relative density leads to poor dielectric properties [3]. The relative density of the sintered BT with 5 mol% KBT reached 87%. However, since samples with 10–15 mol% KBT doping exhibited relative densities higher than 95%, the sintering temperature can be effectively reduced to 1280 °C due to liquid phase sintering that enhances the cation diffusion and sinterability.

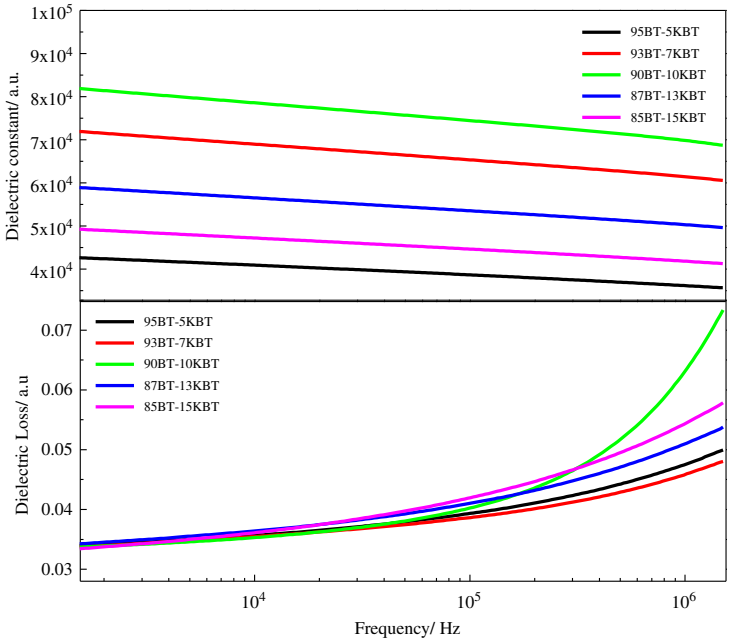

Fig. 3. Frequency spectra of dielectric constant and dielectric loss obtained for $(1-x)$BT–xKBT ($x=0.05$, 0.07, 0.10, 0.13, 0.15) ceramics.

Fig. 3 illustrates the frequency spectra of dielectric constant and dielectric loss obtained from $(1-x)$BT–xKBT ceramic samples. It can be seen that the dielectric constant firstly decreased and then increased with the increase of KBT content over the frequency range from 100 Hz to 2 MHz, especially at low frequency range ($<10^4$ Hz). As can be seen, when the KBT content is 10 mol%, the dielectric constant reached the maximum value. However, the dielectric loss had the minimum value as KBT content increased to 15 mol%. This phenomenon could be explained by the interfacial polarization. KBT would be accumulated at the grain boundaries and it impeded the transfer of free charge, which resulted in accumulation of charges or ions in intergranular areas and formation of interfacial polarization. However, the spontaneous polarization would be weakened with the further increase of KBT content because it could hamper the grain growth, and the grain size of BT ceramics had a great influence on dielectric constant. In addition, dielectric constant decreased and dielectric loss rapidly increased with the increase of frequency. Generally, a higher value of the dielectric constant at low frequency is due to the appearance of all types of polarizations (i.e., electronic, ionic, dipolar, interfacial, etc.) in the samples at room temperature [4,5]. Since only electronic polarizations are dominating at the higher frequency (i.e., other type of polarization vanished), the value of the dielectric constant decreases with the increase of frequency. At the same time, the dielectric loss is much lower at low frequency, which is similar to the dielectric constant.

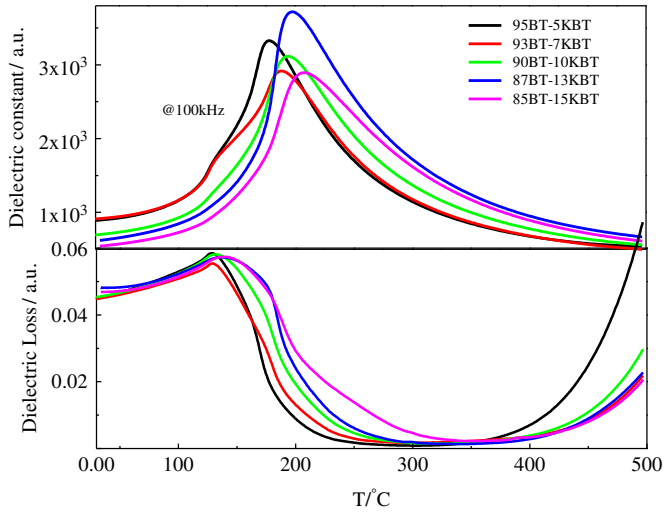

Fig. 4. Temperature dependence of dielectric constant and dielectric loss of $(1-x)$BT–xKBT ($x=0.05$, 0.07, 0.10, 0.13, 0.15) ceramics.

Fig. 4 shows the temperature dependence of dielectric constants and dielectric loss of the BT–KBT system for various amounts of KBT content. It can be observed that when the amount of KBT increased from 5 to 15 mol%, the dielectric constant gradually decreased but the dielectric loss increased over the temperature range of 30–500 °C. Obviously, the sample with 15 mol% KBT had the lowest dielectric constant.

From Fig. 4, it is found that T_c progressively moved toward higher temperature as the amount of KBT was increased from 5 to 15 mol%. The T_c of the samples with 5, 7, 10, 13 and 15 mol% KBT were 178.2, 188.8, 194.6, 198.3 and 208.4 °C respectively, this is because Bi^{3+} enters Ba-site, and T_c increased with Bi^{3+} incorporation.

Fig. 5 shows the SEM micrographs of polished and thermal etched surfaces of the sintered samples doped with different amounts of KBT content. It can be seen from Fig. 5(a)–(d) that the average grain size became smaller and more homogeneous with increasing of the KBT content, and a small grain size may yield higher dielectric constants [6]. No continued reduction in the grain size was observed with further addition of KBT ($x=0.15$). This was because the sintering temperature can be effectively reduced with the high concentrations of KBT and lower temperatures which lead to grain due to the lack of sufficient energy to further grow up.

4. Conclusions

$BaTiO_3$ ceramics with different KBT additions were prepared through the conventional solid-state method.

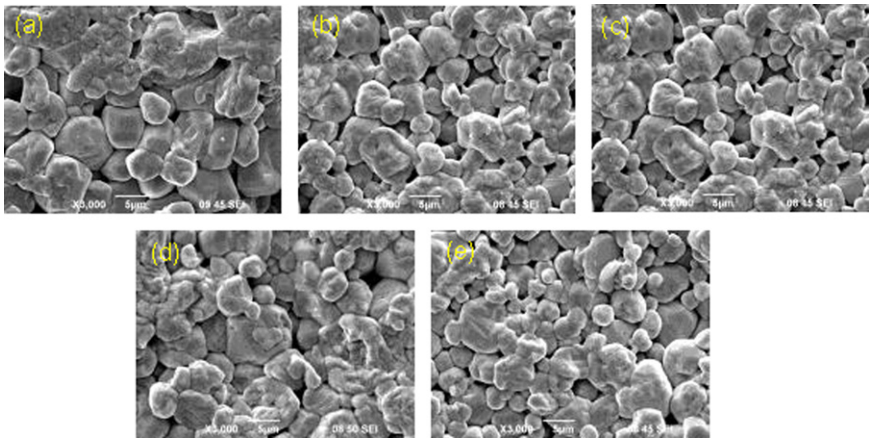

Fig. 5. SEM images of $(1-x)$BT–xKBT ceramics sintered in air: (a) $x=0.05$; (b) $x=0.07$; (c) $x=0.10$; (d) $x=0.13$; and (e) $x=0.15$.

KBT had a strong influence on the densification, microstructure and dielectric properties of $BaTiO_3$ ceramics. The density characterization results show that the addition of KBT significantly lowered the sintering temperature of $BaTiO_3$ ceramics to about 1280 °C. There was such a trend of dielectric properties of the samples that dielectric constant and dielectric loss firstly increased and then decreased with the increase of KBT. The dielectric constant reached the maximum value when the KBT content is 10 mol% and the dielectric loss had the minimum value as KBT content increased to 15 mol%. The average grain size became smaller and more homogeneous with increasing of the KBT content; no continued reduction in the grain size was observed with further addition of KBT ($x=0.13$–0.15).

Acknowledgments

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