FULL PAPER

Excellent sintering ability of Bi(Mn$_{2/3}$Sb$_{1/3}$)O$_3$-added (Bi$_{1/2}$K$_{1/2}$)TiO$_3$ lead-free piezoceramics with high density and low dielectric loss

Zhihua GUO$^1$, Mankang ZHU$^{1,7}$, Mupeng ZHENG$^1$ and Yudong HOU$^1$

$^1$College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China

By adding 1.5 mol.% Bi(Mn$_{2/3}$Sb$_{1/3}$)O$_3$ (BMS), (Bi$_{1/2}$K$_{1/2}$)TiO$_3$ (BKT) ceramics show an excellent sintering ability in conventional oxide sintering process. In a wide temperature range from 1020–1050°C, the 0.985BKT–0.015BMS (BKMS) ceramics demonstrate a super-high relative density of 98% and low dielectric loss tan δ of 0.017. Even though the temperature reaches to 1060°C, BKMS ceramics maintain high relative density over 95% other than being collapsed as the pure BKT did. Besides, the BKMS ceramics sintered at 1020 to 1050°C present adequately high electrical properties. The enhanced sintering ability of BKMS ceramics is attributed to the increased viscosity of liquid induced by Sb$^{5+}$ solving in the liquid phase during sintering. The work provides a way to realize the densification of BKT ceramics.

Key-words: Piezoelectric ceramic, Ferroelectric and piezoelectric properties, Phase structure

1. Introduction

Potassium bismuth titanate, (Bi$_{1/2}$K$_{1/2}$)TiO$_3$ (BKT), possesses a tetragonal perovskite structure at room temperature and a relatively high Curie temperature ($T_C$ = 410°C). By forming morphotropic phase boundary with Bi-based Bi(Mn$^{2+}$)O$_3$ complex perovskites, the electrical properties of BKT could be adequately improved, making it be one of the promising lead-free piezoceramics. Nevertheless, the volatilization of potassium and bismuth during the sintering process is a very serious issue for BKT, which results in the extremely poor sintering ability and the undesirable impurity phases. In order to improve the densification of BKT ceramic, researchers tried several methods, such as chemical synthesis and hot pressing. Nevertheless, these methods could not meet the requirements of cost-effective and large-scale industrial production. Recently, a modified sintering process of BKT by buried powders route is suggested, which reduces the volatilization of Bi and K in certain extent. But the narrow sintering temperature window less than 10°C still causes the deterioration of electrical properties of BKT ceramics due to sintering temperature fluctuation, and restricts their potential in the future industrial application. It is reported that addition of Mn$^{2+}$/ and Sb$^{5+}$ oxides could lower the sintering temperature of Pb(Mn$_{1/3}$Nb$_{2/3}$)$_3$O$_3$–Pb(Zr$_{1/2}$Ti$_{1/2}$)O$_3$ and widen the sintering temperature window of (K$_{1/2}$Na$_{1/2}$)NbO$_3$. Our previous work also demonstrated that suitable amount of Bi(Mn$_{2/3}$Sb$_{1/3}$)O$_3$ (BMS) addition can significantly improve the electrical performance of BKT ceramics. In this work, we focus on the origin of the improved sintering ability of 1.5 mol.% BMS-added BKT. It is found that the addition of 1.5 mol.% BMS could enhance the densification and widen the sintering temperature window due to the increased viscosity of liquid phase and lowered temperature that the liquid phase emerges. Besides, the BMS-added BKT ceramics with high density and low dielectric loss tan δ as well as good electric properties could be obtained in the widened sintering temperature window.

2. Experimental procedure

Pure BKT and 0.985BKT–0.015BMS (BKMS) samples were prepared by a conventional solid-state method. Chemical reagents were commercially available from Beijing Chemicals Co. Ltd., including Bi$_2$O$_3$ (99%), K$_2$CO$_3$ (99%), TiO$_2$ (99%), MnCO$_3$ (99%), and Sb$_2$O$_3$ (99.99%). The weighed powders were ball-milled in ethanol and zirconia media for 12 h. The dried powders were calcined at 800°C for 3 h, and then re-milled for 12 h. The calcined powders were pressed into green disks with a diameter of 11.5 mm under a pressure of 300 MPa, and sintered at 1000–1070°C for 10 h in a covered alumina crucible. To reduce the volatilization of Bi and K during sintering, the green compacts were embedded in the calcined powders with the corresponding compositions.

The apparent density was measured by Archimedean method using a precision balance (Mettler Toledo XS104, Zurich, Switzerland) with a density kit. An X-ray diffractometer (XRD, Bruker D8 Advance, Karlsruhe, Germany) was used to characterize the crystal structure.

 DOI http://doi.org/10.2109/jcersj2.18155

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Corresponding author: M. Zhu; E-mail: zhumk@bjut.edu.cn
For the XRD characterization, the samples were crashed into powders and annealed at 300°C. The morphology of the fracture surface was observed using a scanning electron microscope (SEM, Hitachi S4800, Tokyo, Japan). The average grain size was estimated on about 100 grains by a freeware SmileView based on SEM observation.

For electrical measurements, the sintered plates with a thickness of 0.7 mm were electrodeposited with silver paste, and then fired at 700°C for 30 min. The dielectric loops of polarization and electric field (\(P-E\)) were measured by ferroelectric tester (Premier II, Radiant Technologies, Albuquerque, NM) at 1 Hz equipped with a temperature unit (M10, Sigma Systems, Centennial, CO). The dielectric constant and loss were measured by an LCR meter (Agilent E4980A, Santa Clara, CA) equipped with an auto temperature controller at a heating rate of 2.5 °C/min. Electrical impedance analysis was conducted by an impedance analyzer (Concept 400, Novocontrol Technologies, Montabaur, Germany) in the frequency range from 0.01 Hz to 1 MHz and at temperatures between 300 and 500°C under alternate current electric level of 0.5 V. For piezoelectric measurements, the samples stayed at 7 kV/mm for 30 min at 40°C, and cooled to room temperature under the poling field. After aging, a quasi-static \(d_{33}\) meter (ZJ-2, Institute of Acoustics, Chinese Academy of Science, Beijing, China) is used to measure the piezoelectric coefficient \(d_{33}\) value.

3. Results and discussion

It is well known that a wide sintering temperature window is an important requisite for industrial application of a ceramic composition. Figure 1 compares the apparent density and the dielectric loss tan \(\delta\) of BKT and BKMS samples at different sintering temperatures.

For BKT sample, an apparent density of around 5.50 g/cm\(^3\) arrived at the sintering temperatures lower than 1040°C, only 93% of theoretical density of BKT (5.93 g/cm\(^3\)). The apparent density (5.73 g/cm\(^3\)) and relative density (96%) reached the highest when sintering temperature increased to 1040 and 1050°C. Further increasing the sintering temperature to 1060°C, the ceramic compacts collapsed that no ceramic sample could be obtained. The collapsing of the compacts could be ascribed to the amount increase and viscosity decrease of liquid phase at overdue high temperature.\(^{14}\) Obviously, the suitable sintering temperature for BKT is limited in a narrow window with a span of 10°C. The low density and narrow sintering window show the poor sintering ability of BKT sample.

However, it is worthy noting that the BMS addition not only enhances the apparent density but also widens the sintering temperature window. For BKMS sample, the apparent density is significantly improved compared to that of BKT without BMS addition in whole sintering range. Especially, in the temperature range of 1020–1050°C, the apparent density is more than 5.88 g/cm\(^3\), which is close to the high relative density of 98%. Even at 1060°C, the sample holds on an apparent density over 5.60 g/cm\(^3\) instead of being collapsed. The reduced sintering temperature could be ascribed to that the BMS addition helps the formation of liquid phase at lower temperatures among the grain boundaries, which is beneficial to the densification of the ceramics. As to the widened sintering temperature range, it could be ascertained to the Sb\(^{5+}\) solving in the liquid phase. Sb\(^{5+}\) is a cation with high valence, its oxides is believed to be a glass former, which means that the solving of Sb\(^{5+}\) into the liquid phase could increase the viscosity of liquid phase due to the formation of \([\text{SbO}_4]_{\text{n}}\),\(^{15}\) thus avoiding the collapse of the green body during the sintering. In brief, the temperature lowering and the viscosity increasing of the liquid phase due to the BMS addition enhance the sintering activity of BKT greatly.

Figure 1(b) compares the dielectric loss tan \(\delta\) of BKT and BKMS samples sintered at different sintering temperatures. Commonly, the BKT-based solid solutions present a high value of tan \(\delta\) over 0.06.\(^{2),3),16,17}\) As shown in Fig. 1(b), for pure BKT, even though that the tan \(\delta\) decreases as the sintering temperature increases, the minimum tan \(\delta\) of 0.050 achieved at the temperature close to 1060°C at where BKT ceramics collapses, comparable to those reported previously.\(^{18}\) It is worth noting that the BKMS samples present a significantly reduced tan \(\delta\) compared to pure BKT samples. The tan \(\delta\) of BKMS samples sintered in the...
temperature of 1020–1050°C stabilizes around 0.017, much smaller than most of BKT-based systems. Generally, tanδ is closely related to density, crystallinity and grain size, etc. As mentioned above, the increased density is beneficial to the reduction of tanδ in the sintering temperature of 1020–1050°C. However, the addition of BMS will affect the grain size due to the lowered temperature at that liquid phase emerges. Figure 2 shows SEM micrographs of pure BKT sintered at 1040°C and BKMS ceramics sintered at 1020, 1040 and 1060°C. The corresponding insets give the size distribution counting on about 100 grains fitting to the logarithm normal function. Figure 3 demonstrates the sintering temperature dependence of average grain size. The grain size of BKMS is much larger than that of BKT sample sintered at 1040°C, and increases with the sintering temperature increasing from 1000 to 1060°C. The increased grain size will lead to the increase of tanδ due to the contribution from motion of domain walls. In order to probe the intrinsic cause for the reduced loss, the electric impedance analysis was carried out to explore the crystallization of BKT and BKMS sample. Figure 4 shows the temperature variable M′′(f) spectra for BKT sample sintered at 1040°C (a) and BKMS samples sintered at 1020°C (b), 1040°C (c), 1060°C (d), respectively.
assigned to the bulk response, and believed to be closely correlated to the oxygen vacancies. In addition to bulk response, a shoulder response emerges in higher frequency at about 5 kHz, which could be regarded as the response from the nanoclusters existing the BKT matrix. Figure 5 shows the logarithm of $f_{\text{max,MM}}$ in bulk response versus the reciprocal temperature for samples BKT and BKMS. Obviously, all the data align in linear arrangement, implying that the bulk response obey the Arrhenius law:

$$f_{\text{max,MM}} = f_0 \exp\left(-\frac{E_a}{kT}\right).$$

The activation energy $E_a$ for the dielectric relaxation is also shown in Fig. 5. As seen from Fig. 5, for the samples sintered at 1040°C, the activation energy for BKMS is much larger than that of pure BKT. Besides, the activation energy for BKMS sample increases with the increase of sintering temperature. As is well known, the doubly ionized oxygen vacancies is an important origin of conductivity in ABO$_3$ perovskite materials. The $E_a$ varies with the change of oxygen vacancy concentration, from 0.5 to $2.0\, \text{eV}$. According to Steinvik et al., the higher activation energy corresponds to the lower oxygen vacancy concentration at high temperature range, implying the well-developed crystallinity. In brief, the reduction of tan $\delta$ is mainly due to the enhanced densification and the improved crystallinity.

It is well known that the sintering temperature play an important effect on the phase structure of BKT ceramic. In order to explore the effect of sintering temperature on phase structure, XRD patterns of BKMS ceramics was given in Fig. 6(a). No impurity phase was found in the ceramics sintered from 1000 to 1060°C. To observe the effect of sintering temperature on phase evolution, the fine patterns of 200 diffraction around 46° were recorded, as shown in Fig. 6(b). It could be observed that the 200 diffraction of BKMS ceramics almost keep unchanged in the temperature range of 1020–1050°C, illustrating the stability of phase structure. When the sintering temperature rises to 1060°C, the 200 diffraction splits and shifts toward higher ones, which may be attributed to the decomposition of BKT at high temperature. Besides, it is found that the cell volume is affected by the sintering temperature. As shown in Fig. 6(c), compared with the cell volume of pure BKT prepared by us, the cell volume of BKMS is closer to the theoretical value of pure BKT (61.48 Å). And the cell volume of BKMS presents an obvious shrinkage at low and high sintering temperature regions. It is suggested that the cell shrinkage may be the result of the sintering ability of the BKMS ceramics. At low temperature as 1000°C, the ceramic is not completely fired, as mentioned...
above. The increasing of the sintering temperature will bring in the dense microstructure, which will bring in the internal stress and result in cell shrinkage. However, the cell shrinkage occurred at high sintering temperature may be ascribed to the volatilization of K$^+$ and Bi$^{3+}$ and the decomposition of BKT.

The BKMS sample not only presents an improved sintering ability, but also demonstrates good electric properties in the sintering temperature range of 1020–1050°C. Figure 7 shows the temperature dependences of the dielectric constant ($\varepsilon_r$) and loss (tan $\delta$) of poled BKMS samples on the different sintering temperatures. It can be seen that there exists a hump of dielectric constant, which corresponds to the transition from normal ferroelectric to spontaneous relaxor, and is defined as the depolarization temperature $T_d$. The value of $\varepsilon_r$ value reaches maximum ($\varepsilon_m$), corresponding to the transition from spontaneous relaxor to paraelectric state, and is expressed as $T_m$.

For all ceramics, the depolarization temperature $T_d$ and $T_m$ are insensitive to the sintering temperature, $T_d$ holds on a narrow range from 205–225°C and $T_m$ hold on 380°C.

Figure 8 depicts the $P$–$E$ loops and $J$–$E$ curves at 1 Hz for BKMS samples sintered from 1020 to 1050°C. As shown in Fig. 8(a), the increase of sintering temperature makes the $P$–$E$ loops being saturated and the remnant polarization ($P_r$) being increased gradually. The measured $J$–$E$ curves are in accordance with the $P$–$E$ loops. As shown in Fig. 8(b), the current peak caused by domain switching is intensified gradually with the sintering temperature, which indicates the reversal of ferroelectric domain being enhanced.

The small-signal piezoelectric coefficient ($d_{33}$), room temperature dielectric constant ($\varepsilon_r$) and remnant polarization ($P_r$) as a function of sintering temperature are plotted in Fig. 9. It can be seen that the $\varepsilon_r$ keeps at a similar level, while the $d_{33}$ shows a similar tendency to the $P_r$. The piezoelectric constants $d_{33}$ maintains in high values of 76–104 pC/N in the temperature range 1020–1050°C. Generally, the piezoelectric coefficient $d_{33}$ relates to $P_r$ and $\varepsilon_r$ that $d_{33} = 2\varepsilon_r P_r Q_{33}$ ($Q_{33}$ is the electrostrictive coefficient). $d_{33}$ contribution of motion of domain walls due to that the domain wall motion could contribute considerably to the dielectric constant ($\varepsilon_r$) and remnant polarization ($P_r$).

4. Conclusions

Lead-free (Bi$_{1/2}$K$_{1/2}$)TiO$_3$ piezoceramics with super-high density and ultra-low dielectric loss were prepared by
a new additive Bi(Mn$_{2/3}$Sb$_{1/3}$)O$_3$ through a conventional solid-state route. The addition of Bi(Mn$_{2/3}$Sb$_{1/3}$)O$_3$ not only improves the densification and crystallinity of (Bi$_{1/2}$K$_{1/2}$)TiO$_3$-based ceramics but also widens the sintering temperature span, which is ascribed to the lowered temperature and increased viscosity of liquid phase during the sintering. In the widened sintering temperature range, the samples present a stable phase structure and the excellent electric properties. The significantly improved sintering behavior of (Bi$_{1/2}$K$_{1/2}$)TiO$_3$ ceramics though an adequate additive provides a basis to develop their electric properties.

Acknowledgement This work was supported by the National Natural Science Foundation of China (Grant No. 51602012, 51677001), the Natural Science Foundation of Beijing (Grant No. 4164078), Ri-Xin Talents Project of Beijing University of Technology (Grant No. 2017-RX(1)-15), and Jing-Hua Talents Project of Beijing University of Technology (Grant No. 2015-JH-L04).

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