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A comparative study on positive temperature coefficient effect of $BaTiO_3$–$K_{0.5}Bi_{0.5}TiO_3$ ceramics by conventional and microwave sintering

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Abstract

As a promising material for lead-free positive temperature coefficient of resistivity (PTCR) ceramics, $(1-x)BaTiO_3$–$xK_{0.5}Bi_{0.5}TiO_3$ ($x=0.002$–0.008) samples were prepared by conventional sintering (CS) and microwave sintering (MS) techniques. The effects of different sintering method on the phase composition, microstructure and PTCR characteristics of the ceramics were investigated. The sintering cycle of ceramics was 2.5 h by MS, whereas it took 14 h by CS. Using the microwave heating, the sintering temperature to get high dense material is lowered by 40 °C compared to CS samples. The XRD results showed that all samples were pure tetragonal phases by both sintering process. Meanwhile, the MS samples had smaller grain size and uniform grain distribution. For PTC ceramics, MS was superior to CS due to rapid processing and uniform temperature distribution throughout the specimen. Thus, it exhibited improved PTC properties with lower room temperature resistivity (ρ_{RT}), higher Curie temperature (T_c) and steep resistance jump ($\lg(\rho_{max}/\rho_{min})$).

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1. Introduction

Barium titanate based thermistor ceramics are widely used as materials with a positive temperature coefficient of resistivity (PTCR) [1]. Donor doped $BaTiO_3$ (BT) is of high technological importance owing to its widespread application in positive temperature coefficient resistors, such as self-regulating heating elements, temperature sensors and so on [2,3]. Recently, many researchers put their attention on the lead-free materials due to the viewpoint of environmental protection [4,5]. Especially, some bismuth compounds, such as $Na_{0.5}Bi_{0.5}TiO_3$, $BiFeO_3$, $Bi_4Ti_3O_{12}$ and so on, have been studied by some researchers so as to substitute Pb and shift the Curie point [6–8].

As we know, $K_{0.5}Bi_{0.5}TiO_3$ (KBT) is a kind of perovskite structure with relatively high T_c (380 °C) and can form finite solid solution with BT [9]. The BT–KBT ceramics demonstrated excellent PTCR behaviors. There were many articles reported on PTC properties of the BT–KBT ceramics prepared by the conventional solid-state reaction. However, the pre-synthesized KBT could easily decompose into Bi_2O_3 and K_2O at high sintering temperature (above 1300 °C). Meanwhile, Bi_2O_3 is more volatile than K_2O because the melting temperature of Bi_2O_3 is much lower than that of K_2O, which lead to the more residual acceptor K^+ ions and the increase of grain resistivity. However, MS has emerged as a successful alternative to CS [10–12]. This is due to the fact that MS has significant advantages over CS, such as rapid and volumetric heating leading to enhanced microstructure, controlled grain growth, higher densification at comparatively lower sintering temperature and shorter soaking durations, substantial energy saving, etc [13]. All those characteristics are associated with the positive temperature coefficient effect.

Nowadays, most researchers focused on improving PTC effect by KBT dopant. There was no comparative study on semiconducting behavior and PTC effect of BT–KBT ceramics by CS and MS until now. In this study, lead-free BT–KBT ceramics were prepared by CS and MS technique, and effects

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of different sintering process on phase, microstructure and PTC effect of BT–KBT ceramics were investigated.

2. Experimental procedures

Stoichiometric amount of $BaCO_3$, K_2CO_3, Bi_2O_3 and TiO_2 powder were ball-milled for 4 h and calcined at 1150 °C and 950 °C for 3 h to obtain pure BT and KBT phase. Stoichiometric amount of synthesized powders were weighed according to the following chemical formula of $(1-x)$BT–xKBT ($x=0.002$, 0.004, 0.006, 0.008, abbreviate as BTBKT0.2, BTBKT0.4, BTBKT0.6, BTBKT0.8). The mixtures were ball-milled with zirconia media in distilled water for 4 h with a ball-to-powder weight ratio of 2:1. After drying and granulating with polyvinyl alcohol (PVA, 5 wt %), the well mixed powders were pressed into disks ($\varnothing 14 \times 2\ \mathrm{mm}^2$) under 10 MPa pressure. Then the disks were divided into two groups. One group was sintered by the CS method using a simple silicon carbide muffle furnace (KSL1700, Hefei Kjmt, China) at 1340 °C for 3 h with a heating and cooling rate of 3 °C/min. The other group was heated in air at 600 °C for 30 min in order to remove absorbed water and organic compounds and then sintered by the MS furnace at 1300 °C for 30 min and the total cycle time was 2.5 h. The microwave furnace in this study consisted of 2.45 GHz magnetrons with maximum power of 3 kW (Raptor, Shanghai PreeKem, China).

The phase composition of BT–KBT ceramics were characterized by X-ray diffraction (XRD, D/max-2200PC, RIGAKU, Japan). The microstructure of the sintered samples was studied on polished and then on thermally etched surfaces using a scanning electron microscope (SEM, Model: JSM-6700, JEOL Ltd., Tokyo, Japan). The resistivity–temperature dependence can be obtained from room temperature to 200 °C at the rate of 1 °C/ min by using the resistance–temperature characteristic test system (ZWX-B, Huazhong University of Science and Technology Wuhan, China).

3. Results and discussion

Fig. 1 shows the comparison of the time–temperature profiles for $(1-x)$BT–xKBT ($x=0.002$, 0.004, 0.006, and 0.008) ceramics by CS and MS at the best craft conditions. The total sintering cycle of MS was just about 2.5 h. Furthermore, the soaking time was just 30 min and the process of cooling was shorter. For CS, it had taken at least 10 h to heat the samples and its cooling rate was much slower, which lead to the sintering cycle was more than 14 h.

Fig. 2 shows the relative density of $(1-x)$BT–xKBT ceramics sintered at 1340 °C by CS and 1300 °C by MS as a function of KBT content. Different sintering temperatures on BT–KBT ceramics depends on the different heating mode. For the MS samples, the relative density is much higher than those sintered by CS. The BT–KBT ceramics produced by MS can reach over 90% of the theoretical density at 1300 °C. However, the CS samples sintered at 1340 °C only obtain beyond 88% of the theoretical density. In other words, the MS can achieve a higher density ceramic at a lower heating temperature (1300 °C) than the CS samples. The MS temperature is 40 °C lower than the CS, and this clearly indicates that MS substantially lower the sintering temperature. During the microwave sintering, the green compacts can absorb the microwave energy and convert it into their own internal heat to realize the rapid sintering. Moreover, under the function of microwave electromagnetic energy, the kinetic energy of the molecules or ions of the materials increases, the sintering activation energy decreases and the diffusion coefficient increases, which can totally reduce the sintering temperature. Besides, heat was produced by the sample itself during MS process; hence, there is an inverse heating profile, i.e. ‘inside-out’ profile unlike the ‘outside-in’ profile in the CS process [14,15]. This results in rapid and volumetric heating of the sample resulting into better densification at comparatively lower sintering temperature.

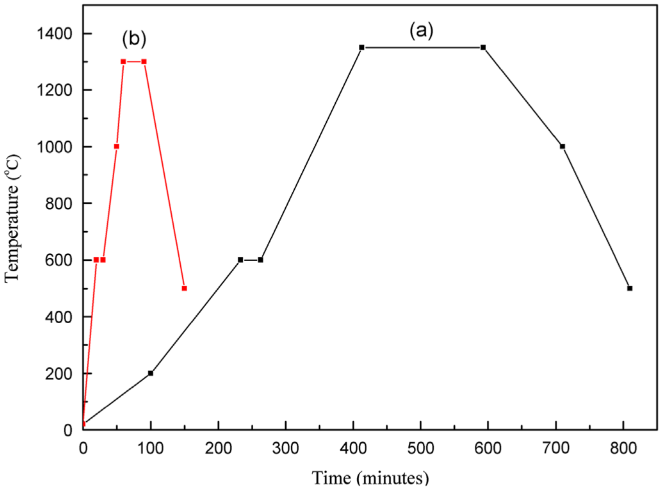

Fig. 1. Comparison of the time–temperature profiles for (a) CS and (b) MS of BT–KBT ceramics.

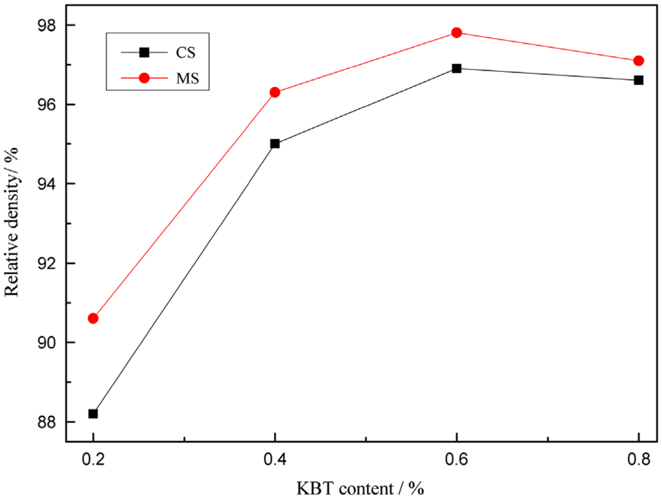

Fig. 2. Relative density of $(1-x)$BT–xKBT ceramics by CS and MS as a function of KBT content.

Fig. 3 illustrates the XRD patterns of $(1-x)$BT–xKBT ceramics sintered by CS and MS. As can be seen from Fig. 3, all samples were pure perovskite phase (ABO_3) indicating that Bi^{3+} and K^+ occupied the Ba^{2+} site to form a

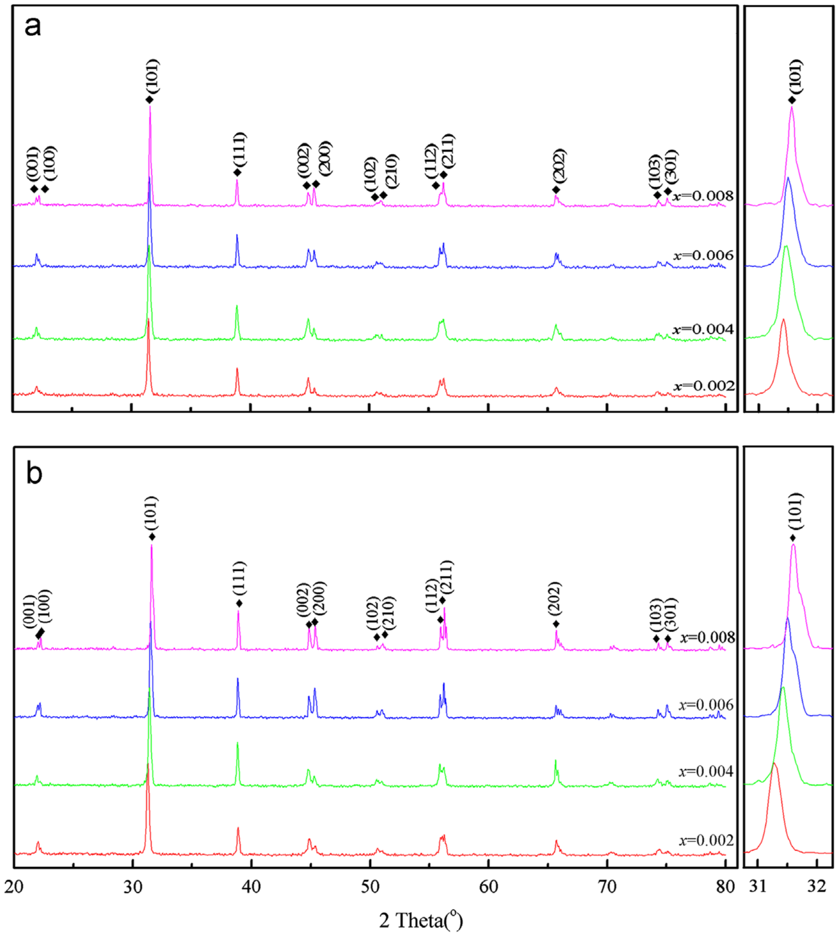

Fig. 3. XRD patterns of $(1-x)$BT–xKBT ceramics sintered by (a) CS and (b) MS.

homologous solid solution during two sintering technique. Meanwhile, it was found that the BT–KBT ceramics sintered by both sintering technique showed a tetragonal perovskite structure in which the reflections (002) and (200) can be split into two peaks [16]. As the KBT content increased, it can be found that the (101) peaks of MS samples shifted obviously toward higher angle (Fig. 3(b)) and those of CS samples only shifted slightly (Fig. 3(a)). This was because the ionic radii of Bi^{3+} (0.096 nm) and K^{+} (0.0135 nm) were smaller than that of Ba^{2+} (0.161 nm), and the volatilization of Bi_2O_3 and K_2O came from the decomposition of KBT in MS samples was lower than that in CS samples. In addition, the axial ration (c/a) increased (Table 2) with the increase of KBT and it closely related to the spontaneous polarization (P_s) and Curie temperature (T_c). The incorporation of KBT strengthened Ti–O bond and enhanced the tetragonality of the ceramic crystal lattice. As can be seen from Table 2, the samples sintered by MS exhibit higher c/a value as compared to the CS samples when they had the same x value.

Fig. 4 shows the surface microstructure of the CS and MS samples and the average grain sizes (AGS) are listed in Table 1. As a whole, inhomogeneous grain sizes were clearly observed for CS samples; however, MS samples showed smaller grain size, uniform grain distribution and denser microstructure. The rapidity and uniformity of MS avoided undesirable grain growth and provided a fine and more uniform microstructure. It can be seen that the AGS increased and then decreased with the increasing x by two sintering technique, which could be explained as the concentration of oxygen vacancies. According to the research of Singh [17], the formation of oxygen vacancies favored the mass and energy transport via grain boundaries. Therefore, the abnormal growth of grains was inhibited when the formation of oxygen vacancies was restrained. Besides, the other reason was that the residual acceptor K_2O would segregate on crystal boundaries and hinder the movement of grain boundaries, which would restrain the growth of crystal grain indirectly. It is worth noting that the maximum AGS could be obtained in $x=0.004$ by CS and $x=0.006$ by MS. It can be explained that MS heating could effectively inhibit the

Table 1
The AGS of the CS and MS samples.

Ceramic samples	AGS-CS (μm)	AGS-MS (μm)
BTBKT0.2	5.2	4.5
BTBKT0.4	8.3	7.2
BTBKT0.6	7.8	7.6
BTBKT0.8	4.8	4.2

Table 2
Positive temperature coefficient property and lattice parameters of BT–KBT ceramics sintered by CS and MS technique.

Sintering method	Sample	T_c (°C)	$\lg(\rho_{max}/\rho_{min})$	ρ_{RT} (Ω cm)	c/a
CS	BT (pure)	120	–	1×10^9	1.00021
	BTKBT0.2	127.8	1.59	7.18×10^4	1.00321
	BTKBT0.4	131.0	3.01	1.69×10^2	1.00420
	BTKBT0.6	132.6	2.54	6.38×10^3	1.00509
	BTKBT0.8	135.0	1.58	1.72×10^4	1.00598
MS	BTKBT0.2	129.6	1.46	5.77×10^4	1.00396
	BTKBT0.4	132.1	2.78	1.63×10^2	1.00522
	BTKBT0.6	133.1	2.53	8.21×10^1	1.00575
	BTKBT0.8	137.2	1.39	7.12×10^3	1.00628

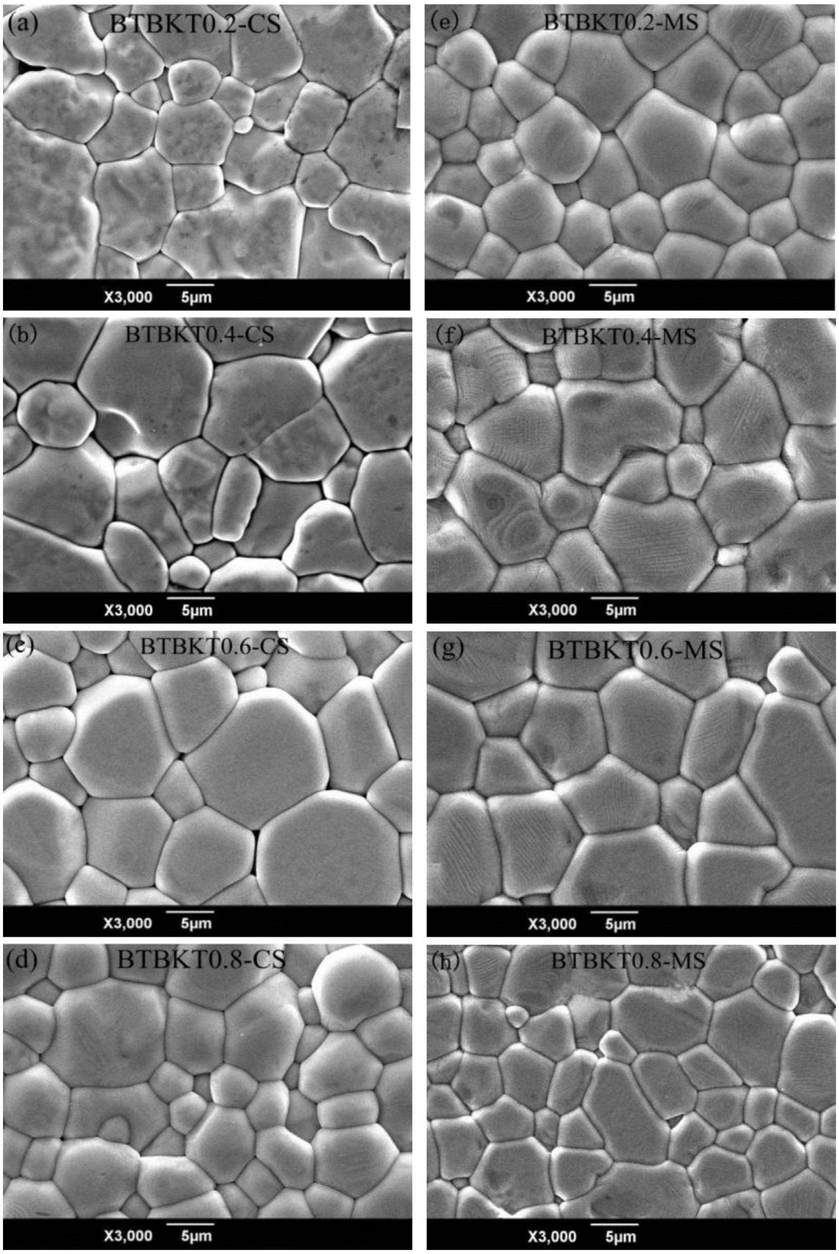

Fig. 4. SEM micrographs of CS samples (a–d) and MS samples (e–h).

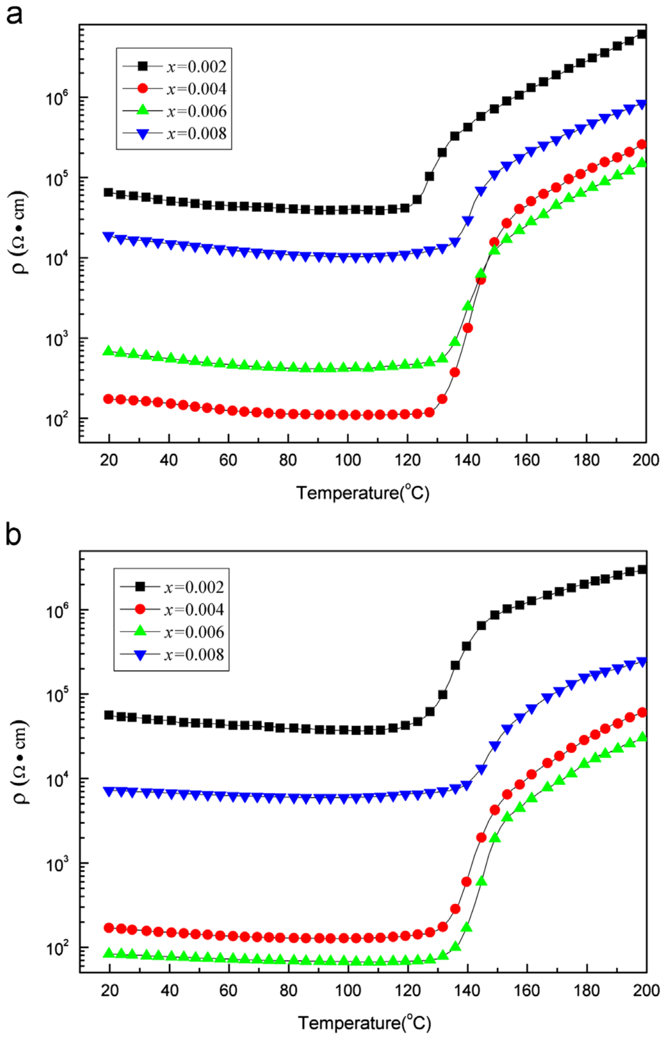

Fig. 5. Temperature dependence of resistivity of the sintered (1−x)BT–xKBT ceramics: (a) CS samples and (b) MS samples.

volatilization of Bi_2O_3 and K_2O, thus it declined the residual acceptor K_2O on grain boundaries and made the crystal grains continue to growth in $x=0.6$. According to SEM micrographs, the MS process was observed to densify effectively the $BaTiO_3$ materials without inducing the growth of grains at a very rapid rate and at a substantially lower temperature, and it had a good agreement with density analysis.

Fig. 5 illustrates the temperature dependence of resistivity of semiconducting (1−x)BT–xKBT ceramics sintered at 1340 °C for 3 h by CS and sintered at 1300 °C for 30 min by MS, respectively. Also, Table 2 lists the PTC property and lattice parameters for both sintering samples. As can be seen from Fig. 5, all samples exhibited lower room-temperature resistivity and a moderate PTC effect with resistivity change of 1–3 orders of magnitude. It is well known that the potential barriers height on grain boundaries and the density of the grain surface acceptor state of BT-based ceramics are the two critical factors in the PTCR characteristic [18]. The T_c of all samples was shifted to higher temperature with the increase in x by the two sintering technique (as shown in Table 2). It was found that the ρ_{RT} declined firstly and then increased with the increase in x. This was because the KBT was unstable and it could easily decompose into Bi_2O_3 and K_2O at high sintering temperature [19–21]. When the concentration of Bi^{3+} was low, the semiconducting behavior could be explained by Eq. (1). As the concentration of Bi^{3+} increased, the introduction of donor impurity Bi^{3+} was more likely to produce V''_{Ba} (Eq.(2)), which led to a rapid increase of ρ_{RT}. It is generally accepted that the increase of the resistivity is associated with an increase of the grain boundary volume caused by the decrease of the grain size [22], and can be clarified by the defects compensating mechanisms from electronic compensation to cation vacancies compensation [23].

$$Ba^{2+}Ti^{4+}O_3^{2+} + xBi^{3+} \rightarrow Ba^{2+}_{(1-x)}Bi^{3+}_x[Ti^{4+}_{(1-x)}e]O_3^{2-} + xBa^{2+} + xe' \tag{1}$$

$$Ba^{2+}Ti^{4+}O_3^{2+} + xBi^{3+} \rightarrow Ba^{2+}_{(1-(3/2)x)}Bi^{3+}_xTi^{4+}O_3^{2-} + 3/2xBa^{2+} + 1/2xV''_{Ba} \tag{2}$$

For BT–KBT ceramics with different sintering method, they had a minimum value of ρ_{RT} when $x=0.004$ sintered by CS and $x=0.006$ sintered by MS, respectively. It was found that the ρ_{RT} of MS samples were lower than CS samples when they had the same x value. This was because the MS process inhibited the generation of V''_{Ba} to some extent due to the special heating fashion, which made the x value increase in Eq. (1), i.e. there was more Bi^{3+} in place of Ba^{2+} and more weak constraint electron existing in the form of $Ti^{4+}e$. Meanwhile, Curie temperature (T_c) had a continuous increasing tendency with the increase in x by CS and MS, which was higher than the T_c (~120 °C) of pure BT and was in accordance with the XRD analysis. Generally, the incorporation of Bi^{3+} has effect on the transition temperature (T_c), at which the crystal structure transforms from tetragonal phase to cubic phase. Moreover, it can be seen that the CS samples showed a significant resistivity rise of 1.58–3.01 orders of magnitudes (Fig. 5(a)), while the MS samples showed a significant resistivity rise of 1.39–2.58 orders of magnitudes (Fig. 5(b)). The rapid cooling rate reduced the concentration of adsorbed oxygen in grain boundary layer, which made the resistance jump of MS samples slightly lower than the CS samples. Therefore, based on the XRD, morphology and PTC effect analysis of the two sintering samples, the higher incorporation of KBT content in MS samples would be mainly due to two factors: (a) lower sintering temperature reduced the volatilization of Bi_2O_3 and K_2O; (b) special heating fashion: 'inside-out' profile in MS process avoided the direct decomposition KBT in the solid-state reaction method.

4. Conclusion

As a promising material for lead-free positive temperature coefficient of resistivity ceramics, (1−x)BT–xKBT ($x=0.002$–0.008) ceramics were prepared by CS and MS techniques respectively. The effects of different sintering method on the phase composition, microstructure and PTCR characteristics of

BT–KBT ceramics were investigated. The total sintering cycle of MS was just 2.5 h, whereas it took 14 h by the CS method. Compared with CS, the MS samples achieved a high relative density and its sintering temperature (1300 °C) was lower than the CS samples (1340 °C). Meanwhile, the MS samples show smaller grain size and more uniform grain growth than CS samples. Curie temperature (T_c) had a continuous increasing tendency in each group by CS and MS with the increase in x. The minimum ρ_{RT} (169 Ω cm) of CS samples could be obtained when $x=0.004$; however, the minimum ρ_{RT} (82 Ω cm) of MS samples could be got when $x=0.006$. Moreover, the CS samples showed a steeper resistance jump with 1.58–3.01 orders of magnitude than that of MS samples with 1.39–2.58. BTBKT0.6 ceramics sintered at 1300 °C for 30 min by MS can obtained an optimal comprehensive properties: $\rho_{RT}=82\ \Omega$ cm, $\lg(\rho_{max}/\rho_{min})=2.53$ and $T_c=133.1$ °C.

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