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Effect of Bi_2O_3 doping methods on the positive temperature coefficient property of $Ba_{0.999}(Bi_{0.5}Na_{0.5})_{0.001}TiO_3$ ceramics

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ABSTRACT

Lead-free positive temperature coefficient of resistivity ceramics based on $0.999BaTiO_3$–$0.001(Bi_{0.5}Na_{0.5})TiO_3$ solid solution were fabricated by the conventional ceramic technique, while Bi_2O_3 was doped directly or after pre-calcining, in the molar ratio of Bi_2O_3:Na_2CO_3:TiO_2 (G) = 1:1:4, 1.005:1:4, 1.01:1:4, and 1.015:1:4, respectively. There are two synthesizing route, i.e. the materials with G = 1.005:1:4 were pre-calcined at 780 °C firstly and then doped into the basic materials and the materials were directly doped by G = 1.01:1:4 into the starting materials with another holding process at 850 °C for 30 min during co-calcining with $BaTiO_3$, both of which could obtain samples with the maximum Curie temperature about 144 °C. The latter also possessed comparatively lower room temperature resistance about 22.0 Ω. A further study was deserved to carry out in an attempt to obtain ceramics with higher Curie temperature via more Bi_2O_3-doping.

1. Introduction

$(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) is a perovskite-type ferroelectric material with a relatively higher Curie temperature (T_c, 320 °C) [1], which can form finite solid solution with $BaTiO_3$ (BT) and thus improve the Curie temperature of BT-based positive temperature coefficient of resistivity (PTCR). Among the perovskite-type compounds, BT-BNT ceramics shows the best PTC effect, i.e. lower room temperature resistance, higher Curie point and an abrupt resistivity change near Curie point [2–6].

The mechanism of BNT on improving the Curie point of BT-based ceramics is considered to be that Bi^{3+} ions can substitute Ba^{2+} ions at BT lattice. Owing to its bigger radii with a broad oxygen octahedron vacancy and the weakness of Bi–O bonds, Ti^{4+} ions could not resume its seat unless the tetragonal ferroelectric is wrecked at higher temperature [7]. But Bi_2O_3 is ready to volatilize during calcining and/or sintering because of its low melting point, so it is easily for $(1-x)$BT – xBNT ceramics to deviate its stoichiometric proportion. From this point of view, different Bi_2O_3-excess contents in the starting materials seem to have a great influence on the PTC property and Curie temperature of samples. Unfortunately, there are no systematic studies on this aspect until now.

In this study, we considered four kinds of Bi_2O_3-excess contents in the molar ratio of Bi_2O_3:Na_2CO_3:TiO_2 (G) = 1:1:4, 1.005:1:4, 1.01:1:4, and 1.015:1:4 (abbreviated as BNTB0, BNTB1, BNTB2, BNTB3, respectively in this paper), which was doped directly (called directly doping method) or after pre-calcining into the starting materials. We also investigated the influence of different pre-calcining temperature or extra holding process on the PTC property and Curie temperature.

2. Experimental procedure

$0.999BaTiO_3$–$0.001(Bi_{0.5}Na_{0.5})TiO_3$ ceramics with different Bi_2O_3-excess contents and doping methods as mentioned above were prepared by the conventional solid-state reaction. Reagent grade Bi_2O_3, Na_2CO_3 and TiO_2 were weighed with proper amounts and mixed by ball milling for 4 h. The dried powders were then synthesized at 850 °C and 780 °C, respectively for 2 h to pre-calcine BNT. The samples using high purity basic starting materials of $BaCO_3$, TiO_2 powders with the proper amounts of pre-calcined BNT or Bi_2O_3, Na_2CO_3 and TiO_2 were mixed by ball milling for 4 h, dried at 120 °C in an oven and then co-calcined to BT-BNT solid solution at 1050 °C for 2 h. After calcination, 11 wt% MnO_2 were added to the starting materials to improve the PTC property and re-milling for 6 h and dried. Then followed by granulation with PVA, the powders were pressed into discs with 15 mm in diameter and about 2 mm in thickness at a pressure of 190 MPa. The green discs were sintered at 1300 °C for 20 min in air atmosphere. The ohmic electrodes were constructed on the two grinded surfaces and treated at 680 °C for 20 min.

The crystalline phases of the pre-calcined BNT at different temperatures were identified by X-ray powder diffraction (XRD) method. The microstructure of the samples was investigated by using a scanning electron microscope (SEM). The resistance as a function of temperature was measured using a temperature-programmable furnace controlled by a computer and a digital multimeter from 25 °C to 380 °C at a heating rate of 3 °C min^{-1}. The accuracy of the furnace temperature is ±0.5 °C. The resistivity (ρ (Ω cm) was calculated on the basis of the measured resistance (R (Ω)), electrode diameter (d (cm)) and sample thickness (h (cm)) from the formula below:

$$\rho = \frac{R\pi d^2}{4h} \qquad (1)$$

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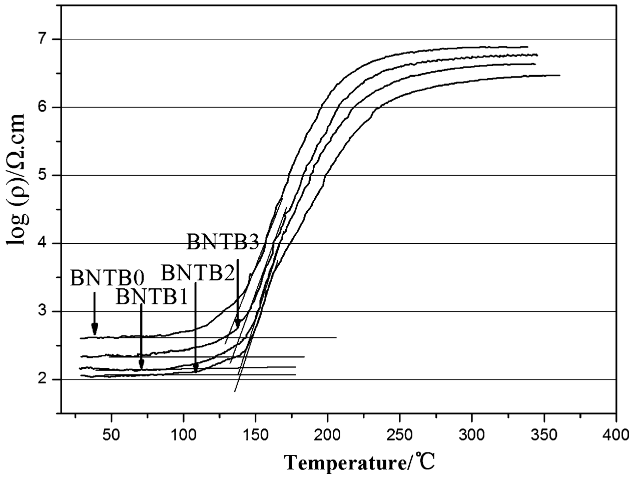

Fig. 1. ρ–T curves of samples doped with pre-calcined BNT at 850 °C.

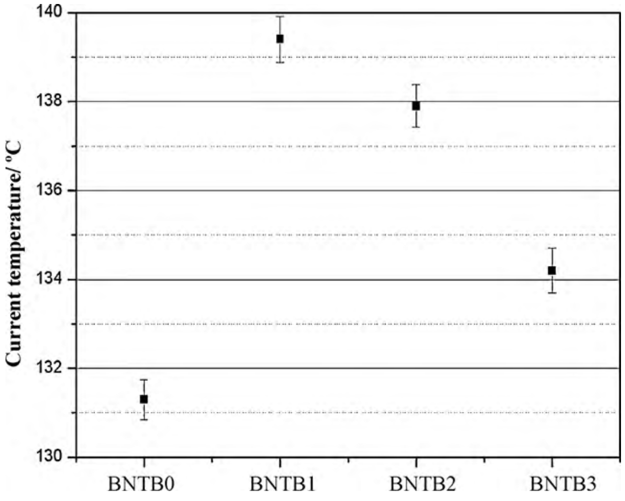

Fig. 2. The Curie temperature of samples doped with pre-calcined BNT at 850 °C.

3. Results and discussion

Fig. 1 represents the resistivity-temperature (ρ–T) curves of samples with different Bi_2O_3-excess contents in 850 °C pre-calcined BNT doping method. A little Bi_2O_3-excess contents (~0.5 mol%) could evidently lower the room temperature resistivity. It would vary unapparent when keeping increasing Bi_2O_3-excess contents and be increased when Bi_2O_3-excess contents bigger than 1 mol%. Fig. 2 shows the Curie temperature (T_c) of the samples obtained at this experiment. The T_c was increased more than 8 °C when doping 0.5 mol%-excess Bi_2O_3 in BNT compounds, compared with BNTB0. A little excess of Bi^{3+} ions could offset the volatilization of Bi_2O_3 when BNT was pre-calcined at 850 °C, so more excellent BNT precursors could be obtained. It was only when Bi^{3+} ions entering BT main lattice to substitute Ba^{2+} ions as donor that could improve the Curie temperature and decrease room temperature resistivity. But when more extra Bi_2O_3 doped into the samples, the chance of Bi^{3+} ions getting into the grain boundary would be increased, which caused the increasing of the room temperature resistivity.

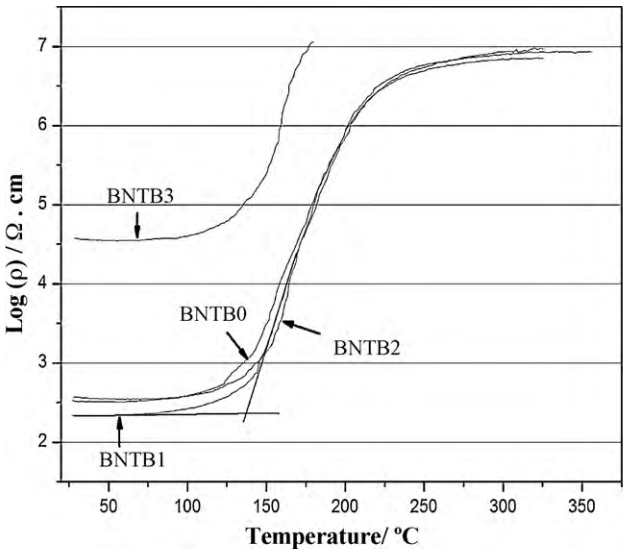

Fig. 3. ρ–T cures of samples doped with oxide state Bi_2O_3.

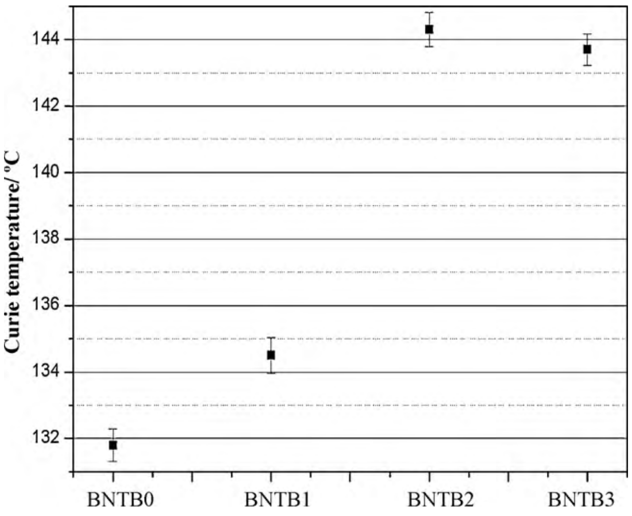

Fig. 4. The Curie temperature of samples doped with oxide state Bi_2O_3.

Figs. 3 and 4 demonstrate the influence of Bi_2O_3-excess contents on the PTC property of samples with directly doping method. The samples doped with BNTB0 here possessed higher T_c than that with pre-calcining. It indicated that the substitution of Bi^{3+} to Ba^{2+} ions was easier to occur when BT and BNT form perovskite-type solid solutions at the same time. Owing to the acute volatility of Bi_2O_3 at BT co-calcining temperature of 1050 °C, more excess amount of Bi_2O_3 (~1 mol%) needed in order to furthest offset its volatilization and improve the T_c distinctly. But as mentioned above, superfluous Bi_2O_3-doping would make them enter BT grain boundary easily and induce the increase of room temperature resistivity. As shown in Fig. 3, the room temperature resistivity deteriorated when doping with 1.5 mol%-excess Bi_2O_3.

Fig. 5 shows the XRD patterns of pre-calcined BNTB0 at different temperatures, which indicates that, the pre-calcined BNT at 850 °C and 780 °C both possess excellent perovskite structure. Compared with Fig. 1, Fig. 6 gives the PTC property of samples doped with BNTB0 and BNTB1, which were pre-calcined at 780 °C. Table 1 list the PTC property of samples doped with pre-calcined BNTB0 and BNTB1 at 850 °C and 780 °C, respectively. The Curie temperature was increased more than 3 °C when reducing the pre-calcined temperature below the melting point of Bismuth oxide, which meant that the volatilization of Bi_2O_3 was decreased to some extent and more BNT contents could be formed at the same Bi_2O_3-doping amounts when pre-calcined at lower temperature. Its concluded that 780 °C pre-calcined BNT with 0.5 mol% Bi_2O_3-excess doped BT-

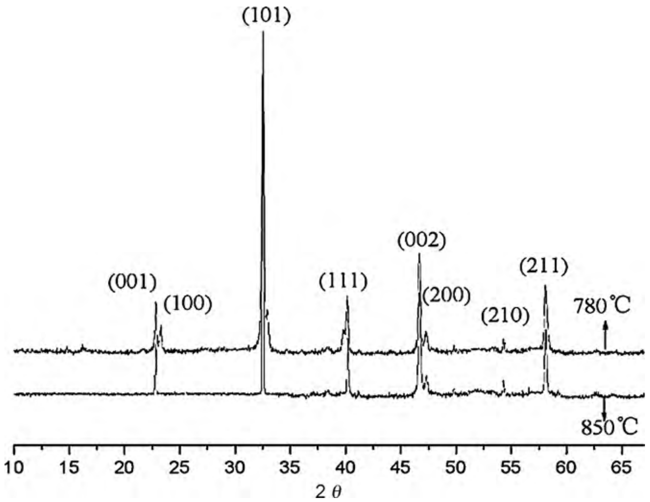

Fig. 5. XRD patterns of pre-calcined BNTB0 at 780 °C and 850 °C.

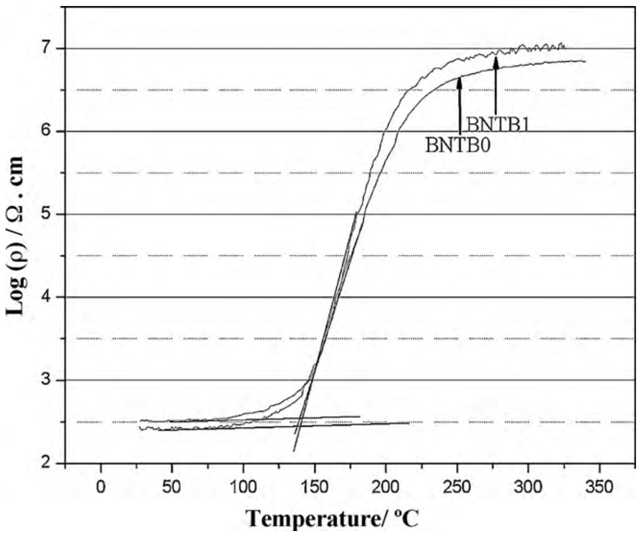

Fig. 6. ρ–T cures of samples doped with 780 °C pre-calcined BNT.

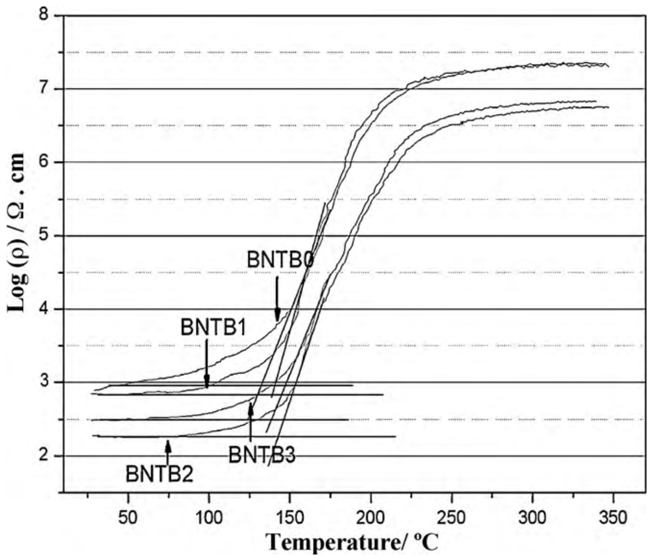

Fig. 7. ρ–T cures of samples doped with oxide state Bi_2O_3 executed heat preservation process.

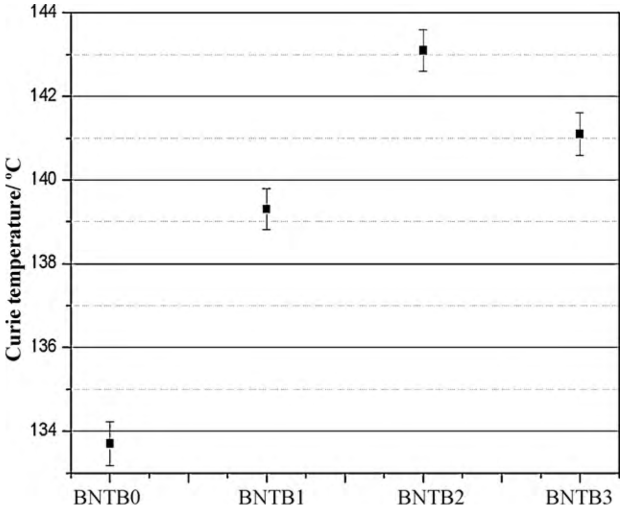

Fig. 8. The Curie temperature of samples doped with oxide state Bi_2O_3 executed heat preservation process.

based PTCR ceramics was one of the best ways to improve its Curie temperature.

In directly doping method, Bi_2O_3 would be readily to volatilize because the stable perovskite-type structure of BNT could not form without holding time until co-calcining at 1050 °C to form BT-BNT solid solution together. So during the process of co-calcining, another holding process at 850 °C for 30 min was executed. The results were shown in Figs. 7 and 8. This process further improved the Curie temperature and the highest T_c obtained here was 143.1 °C using BNTB2 doping method. The Bi_2O_3-doping methods had little influence on the other PTC property and the approximate T_c could be obtained according to the above two synthesizing path. So 1 mol% Bi_2O_3-excess in directly doping method was also one of the best ways to improve the T_c of BT-based PTCR ceramics when another holding process was adopted during co-calcining.

Due to the relatively low melting point of Bi_2O_3 (~820 °C), and sintering temperature usually higher, liquid phase is normally present during synthesizing. The densification and grain size uniformity, which are very important to the property of samples, is accelerated by its presence in the initial stages of sintering. However, if this situation is not controlled, which means that more liquid phase forming because Bi_2O_3 excess too much, the particle sizes will be increased rapidly and caused the appearance of discontinuous grains and stable pores growing at the grain boundary. In the latter stage of sintering, it therefore appears that the liquid phase inhibits the achievement of full density. Fig. 9(a–c) shows the SEM images from the surface of as-sintered samples obtained

Table 1
Effect of pre-calcined temperature on PTC properties.

Samples	T_c (°C)	Room temperature (Ω)	Resistance temperature factor (%°C^{-1})	Resistivity abrupt change
Calcined at 850 °C				
BNTB0	132.1	55.8	11.91	4.29
BNTB1	141.2	18.6	12.82	4.51
Calcined at 780 °C				
BNTB0	135.3	36.1	10.93	4.45
BNTB1	144.6	41.5	12.57	4.56

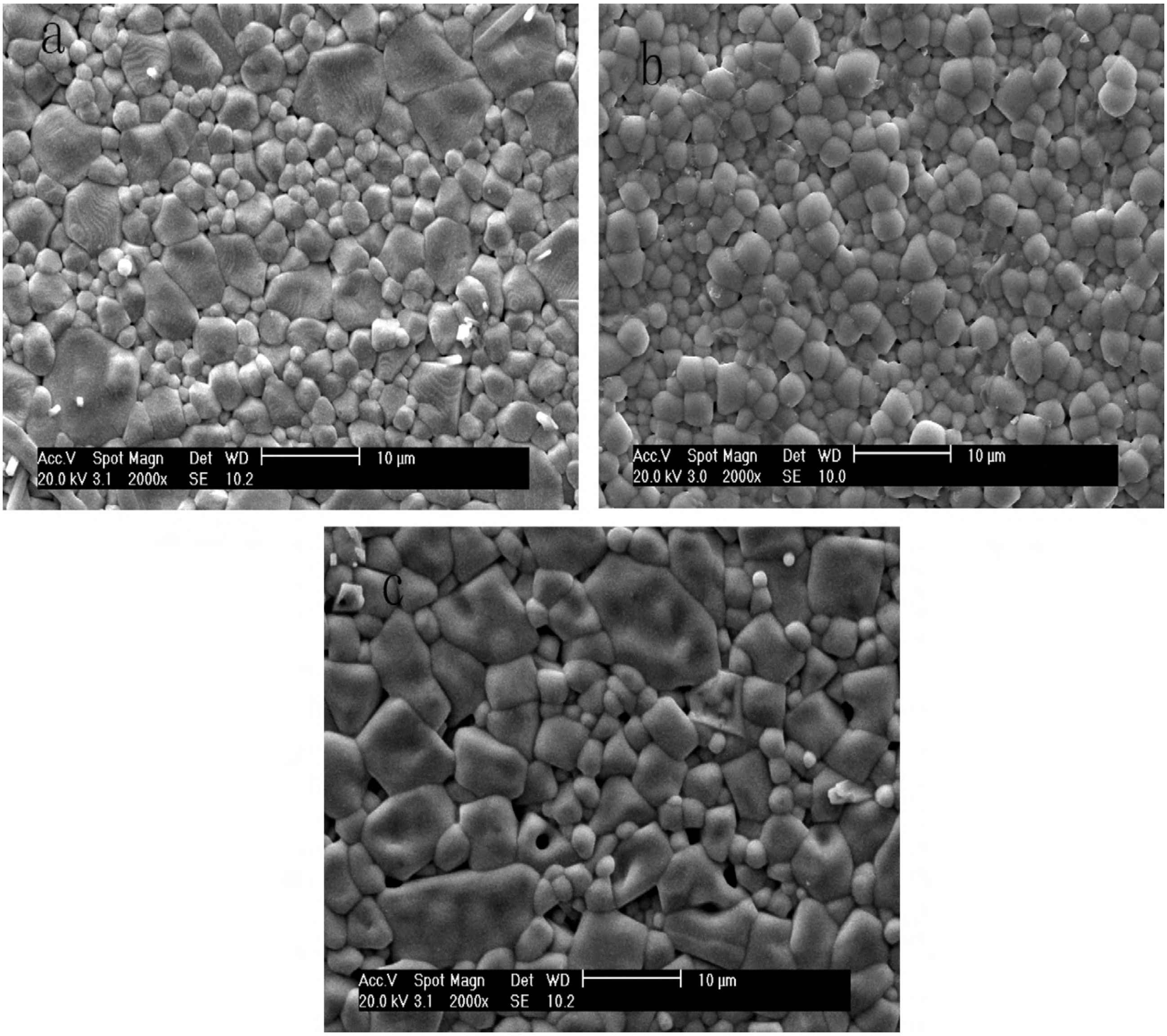

Fig. 9. (a–c) SEM images of samples obtained by directly doping method: (a) BNTB1, (b) BNTB2 and (c) BNTB3.

by directly doping method of BNTB1, BNTB2 and BNTB3, respectively. With an increase of Bi_2O_3-excess contents, the grain size became smaller and more homogeneous firstly because the donor dopant restricted the grain growth of BT-BNT at the sintering temperature and then, a strong inhibition of the grain growth in those dopant enriched region was achieved. However, when more extra Bi_2O_3 doped into the starting materials at BNTB3, large quantity of liquid phase might be generated, so in Fig. 9(c), the discontinuous grains and stable pores appeared which caused the high room temperature resistivity (found in Fig. 3).

In addition, bismuth deficiency can accelerate the final stages of sintering with Bi and O vacancy concentrations enhancing the solid-state transport mechanisms [8,9]. Therefore, a classical solid-state sintering route under constant Bi_2O_3 activity, attained by Bi_2O_3-excess, is necessary to obtain materials with high density and controlled defect levels. Sufficient Bi_2O_3 excess was added to the batch to promote liquid phase formation and enhance densification during the early stages of sintering, however as sintering progresses and Bi_2O_3 volatilizes, the system swings into Bi_2O_3 deficient, allowing solid-state mechanisms to complete the job.

4. Conclusions

Different Bi_2O_3-excess contents and doping methods had a great influence on the positive temperature coefficient property of $BaTiO_3$-based ceramics. The samples with higher Curie temperature and lower room temperature resistance were obtained by the following two doping methods, respectively, i.e. Bi_2O_3 was excess 1 mol% when directly doped into the starting materials with holding process at 850 °C for 30 min during co-calcining with $BaTiO_3$ and Bi_2O_3 was pre-calcined with Na_2CO_3 and TiO_2 in the molar ratio of 1.005:1:4 at 780 °C before doping into the basic materials. The highest Curie temperature obtained according to these two ways was both about 144 °C and the samples with the first doping method also had a comparatively lower room temperature resistance of 22.0 Ω.

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