

# Effect of the $\text{Nb}_2\text{O}_5$ content on electrical properties of lead-free $\text{BaTiO}_3\text{--Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ceramics

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## Abstract

$(1-x)\text{BaTiO}_3\text{--}x\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  (BT–BNT) ceramics were prepared by the solid-state reaction method. With an increase of BNT content, both the Curie temperature and the room temperature resistivity increased. At 1 mol% BNT addition, the sample was not semiconducting, due to  $\text{Bi}_2\text{O}_3$  volatilization resulting from the decomposition of pre-calcined BNT during sintering. Appropriate extra  $\text{Nb}_2\text{O}_5$  doping in the raw materials could offset  $\text{Bi}_2\text{O}_3$  volatilization and neutralize the redundant acceptor  $\text{Na}^+$  ions. When the extra  $\text{Nb}_2\text{O}_5$  content was 0.6 mg, the sample room-temperature resistivity was  $6.3 \times 10^3 \Omega \text{ cm}$ , with the Curie point about  $135^\circ\text{C}$  and a high PTC effect of  $\sim 3$  orders of magnitude.  
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**Keywords:** Electrical properties; PTC devices; Lead-free ceramics; BT–BNT;  $\text{BaTiO}_3$

## 1. Introduction

It is well known that the donor and acceptor doped semiconducting barium titanate ( $\text{BaTiO}_3$ , BT) ceramics exhibit excellent positive temperature coefficient of resistivity (PTCR) effect above the Curie temperature ( $T_C$ ) [1,2]. Trivalent ions ( $\text{Sb}^{3+}$ ,  $\text{Y}^{3+}$ , and  $\text{La}^{3+}$ ) or pentavalent ions ( $\text{Nb}^{5+}$  and  $\text{Ta}^{5+}$ ) substitutionally incorporate at the  $\text{Ba}^{2+}$  or  $\text{Ti}^{4+}$  site, respectively, which could increase the room-temperature conductivity [3–6]. Meanwhile, acceptors such as  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  ions segregate at the grain boundaries to enhance the resistance jump at the Curie temperature ( $T_C$ ) [7,8]. The resistivity increases several orders of magnitude near the phase transition temperature. This property has been widely used in current control elements, self-controlled heaters, temperature sensors and over-current protection devices, etc.

$\text{PbTiO}_3$  is usually added into the BT to shift the  $T_C$  to a higher temperature [9]. However, Pb, which is toxic and prone to volatilize, restricts the use of lead contained PTCR ceramics. Therefore, it is necessary to develop high  $T_C$  lead-free PTCR ceramics to substitute the lead-containing ones. Recently, the BT–BNT system has been widely studied as a promising candidate

for lead-free PTCR materials [7,10–12]. BNT is a kind of perovskite structure material with relatively high  $T_C$  ( $320^\circ\text{C}$ ) and can form finite solid solution with BT. With an increase in the BNT content, the  $T_C$  of the BT-based PTCR ceramics shifts to high temperature. However, the pre-synthesized BNT can easily decompose into  $\text{Bi}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  during the sintering process. The volatilizations of  $\text{Bi}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  give rise to an increase of porosity, which is conducive to oxygen diffusion or adsorption at grain boundaries, which led to the increase of the potential barriers, thus leading to an increase of the resistivity [13,14]. Moreover,  $\text{Bi}_2\text{O}_3$  is more volatile than  $\text{Na}_2\text{O}$  because the melting temperature of  $\text{Bi}_2\text{O}_3$  ( $817^\circ\text{C}$ ) is much lower than that of  $\text{Na}_2\text{O}$  ( $1132^\circ\text{C}$ ) [12]. Therefore, the residual  $\text{Na}^+$  ions would act as acceptors, which also led to an increase of the grain resistivity. To fabricate low resistivity PTC thermistors, proper composition design is needed. From this point of view, appropriate excess donor-dopants in the starting materials could compensate the  $\text{Bi}_2\text{O}_3$  volatilization and neutralize the redundant acceptor  $\text{Na}^+$  ions.

In this paper, in order to develop lead-free BT-based PTC materials with higher Curie point, the effect of BNT content on the electrical performance and microstructure of PTCR ceramics was investigated, and the effect of  $\text{Nb}_2\text{O}_5$  doping content on the PTC behavior of the BT–BNT ceramics was also discussed.

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## 2. Experiment procedure

$(1-x)\text{BT}-x\text{BNT}+a\text{Sb}_2\text{O}_3+b\text{Nb}_2\text{O}_5+c\text{AST}+d\text{MnO}_2$  ( $x=0, 0.1, 0.2, 0.4$ , and  $1 \text{ mol\%}$ ) ceramics were prepared by the conventional solid-state reaction technique. Firstly, powders of  $\text{Na}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{TiO}_2$  were mixed by ball milling in ethanol for 6 h. The dried powders were then calcined at  $780^\circ\text{C}$  for 2 h to obtain BNT. Secondly, powders of  $\text{BaCO}_3$ ,  $\text{TiO}_2$ ,  $\text{Sb}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  were mixed by ball milling for 4 h and then calcined at  $1050^\circ\text{C}$  for 2 h to obtain BT. Thirdly, proper amounts of the BT, BNT ( $\sim 0\text{--}1 \text{ mol\%}$ ), AST,  $\text{MnO}_2$  were mixed by ball milling for 6 h. At  $1 \text{ mol\%}$  BNT addition, appropriate extra  $\text{Nb}_2\text{O}_5$  was added into the start materials. Finally, the powders were granulated with  $5 \text{ wt\%}$  PVA (polyvinyl alcohol) and pressed into disks at a pressure of  $120 \text{ MPa}$ . The disks were sintered at  $1280^\circ\text{C}$  for 20 min and then cooled with the furnace in air atmosphere. After that, the aluminum paste was coated on both surfaces of the samples and treated at  $580^\circ\text{C}$  to obtain good Ohmic contacts.

The phase composition of the samples was characterized by using X-ray Diffractometer (XRD, Cu K $\alpha$  radiation, D/Max-2500 Rigaku, Japan). Microstructure of the powders and the surface of the sintered samples was observed by using scanning electron microscope (SEM, S-4800, Hitachi Ltd., Tokyo, Japan). The resistance was determined by using a temperature-programmable furnace controlled by a digital multimeter from room temperature to  $300^\circ\text{C}$ . The resistivity ( $\rho$  ( $\Omega \text{ cm}$ )) can be calculated by the formula:  $\rho = R\pi d^2/4h$ , where  $R$  ( $\Omega$ ) is the measured resistance,  $d$  (cm) is the electrode diameter and  $h$  (cm) is the thickness of samples.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the sintered ceramic samples with different BNT contents. All the diffraction peaks of the sintered samples were successfully indexed based on the published data of the host BT (JCPDS #75–0462). This

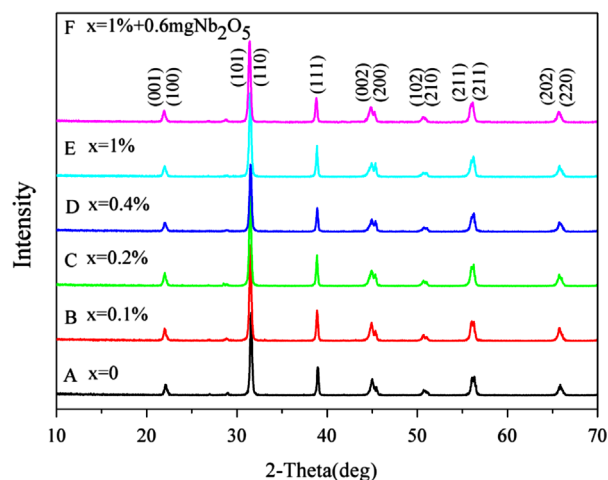


Fig. 1. X-ray diffraction patterns of the  $(1-x)\text{BT}-x\text{BNT}$  ceramics with different doping contents.

indicated that the  $\text{Bi}^{3+}$  and  $\text{Na}^{+}$  ions have occupied the  $\text{Ba}^{2+}$  site to form a homologous solid solution.

Fig. 2 illustrates the resistivity–temperature dependence of the BT–BNT ceramics. It can be seen that the Curie temperature increased with an increase of BNT content. The reason was that the  $\text{Na}^{+}$  and  $\text{Bi}^{3+}$  ions in BT–BNT solid solution strengthened the Ti–O bond and enhanced the tetragonality of the ceramic crystal lattice [7,15]. However,  $T_C$  did not rise linearly with the increase in the BNT content, which was generally in agreement with previous results [16]. Moreover, when the content of BNT was lower than  $0.4 \text{ mol\%}$ , the increase of the Curie temperature was not obvious. This was mainly due to the small content of the BNT addition and the relatively large amount of the  $\text{Bi}_2\text{O}_3$  volatilization during the high temperature sintering.

It can also be observed from the Fig. 2 that all the samples possessed remarkable resistivity jump ( $\rho_{\text{max}}/\rho_{\text{min}} > 10^3$ ) near the Curie temperature. The height of potential barriers and the density of surface acceptor states of the BT-based ceramics were two indispensable requirements for PTC effect, which attributed to chemisorbed oxygen at the grain boundaries. Mn possessed three oxidation states ( $\text{Mn}^{4+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Mn}^{2+}$ ) in BT, and the valence state of Mn would change from  $\text{Mn}^{3+}$  in tetragonal phase to  $\text{Mn}^{2+}$  in the cubic phase near the Curie temperature, which led to the increase of the number of electron traps at the Curie temperature. Therefore, it could be concluded that the Mn ions acted as the acceptors and improved the acceptor state density ( $N_s$ ). The variable valence Mn ions segregated on grain boundaries and played a leading role in improving the PTC effect by joining with the existing acceptors such as the cation vacancies or the adsorbed oxygen [17]. As the adsorbed oxygen formed and the acceptor segregated at grain boundaries, both the surface charge density ( $N_s$ ) and the potential barriers height increased, which resulted in the excellent PTC effect of ceramic samples.

Table 1 shows that the room temperature resistivity increased with an increase of the BNT content. There were two major factors contributing to this phenomenon. The

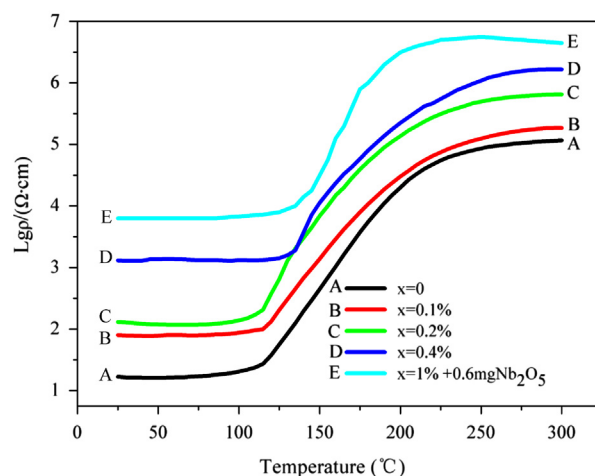


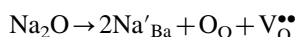
Fig. 2. Temperature dependence of resistivity of the  $(1-x)\text{BT}-x\text{BNT}$  samples with different contents of BNT sintered at  $1280^\circ\text{C}$  in air.

Table 1  
Variations of the room resistivity for the BT–BNT ceramics.

BNT content (mol%)	Color	Room resistivity ( $\Omega$ cm)
0	Dark blue	9.4
0.1	Dark blue	79.7
0.2	Dark blue	130.4
0.4	Dark blue	1307
1	Yellow	$> 10^7$

remnant acceptor  $\text{Na}^+$  ions generated from the decomposition of the pre-calcined BNT could increase the resistivity of the samples.

The residual  $\text{Na}^+$  ions would act as the acceptors and the reaction of  $\text{Na}_2\text{O}$  was shown as follows:



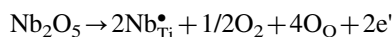
The residual  $\text{Na}^+$  ions tended to segregate on grain boundaries, which led to the increase of the potential barrier height. Therefore, the resistivity increased because it was difficult for the electron to jump over the higher potential barriers.

In addition, the volatilization of BNT would result in many cation vacancies at A site, which would compensate for the donor dopants or the oxygen vacancy [11]. Then the electric charge would become negative because the cation vacancies hindered the change from  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ . Hence, the charge carrier density would decrease while the resistivity would increase. In a word, the Curie temperature of the BT–BNT ceramics improved at the cost of the room temperature resistivity. However, at 1 mol% BNT addition, the color of the ceramic sample was yellow, and the resistivity was greater than  $10^7 \Omega \cdot \text{cm}$ . Therefore, in order to decrease the room temperature resistivity, appropriate amount of donor dopants was required to offset the volatilization of  $\text{Bi}_2\text{O}_3$ .

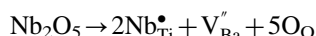
As we all know, compared with the single donor doping ceramics, the double donor doping BT ceramics have lower resistivity. In this paper, in order to decrease the resistivity, the samples were prepared by doping  $\text{Sb}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  which were used as donors to replace the  $\text{Ba}^{2+}$  ions and the  $\text{Ti}^{4+}$  ions respectively. However, as the size of the  $\text{Sb}^{3+}$  ion (0.076 nm) was quite different from that of the  $\text{Ba}^{2+}$  ion (0.161 nm), the addition of the  $\text{Sb}_2\text{O}_3$  would lead to the lattice distortion. In addition, the substitution of the  $\text{Bi}^{3+}$ ,  $\text{Na}^+$  and  $\text{Sb}^{3+}$  ions for the  $\text{Ba}^{2+}$  ions could give rise to the A-site complex. On the contrary, the size of the  $\text{Nb}^{5+}$  ion (0.064 nm) is almost the same as that of the  $\text{Ti}^{4+}$  (0.061 nm) ion. Therefore, extra  $\text{Nb}_2\text{O}_5$  content was added to 50 g of raw materials in our work. Table 2 shows the effect of the  $\text{Nb}_2\text{O}_5$  content on the semiconductivity of the samples at 1 mol% BNT addition. It can be clearly seen that the ceramic was a semiconductor when the extra  $\text{Nb}_2\text{O}_5$  content was 0.6 mg, while the other ceramic samples displayed dielectric property. When the content of  $\text{Nb}_2\text{O}_5$  was lower than 0.5 mg, the quantity of  $\text{Nb}_2\text{O}_5$  could not compensate the loss of  $\text{Bi}_2\text{O}_3$  caused by the volatilization of BNT. The action formula of  $\text{Nb}_2\text{O}_5$  was shown as follows [3]:

Table 2  
Effect of  $\text{Nb}_2\text{O}_5$  content on the semiconductivity of the 0.99BT–0.01BNT samples.

$\text{Nb}_2\text{O}_5$ content (mg)	Color	Room resistivity ( $\Omega$ cm)
0.4	Yellow	$> 10^7$
0.5	Yellow	$> 10^7$
0.6	Dark blue	$6.3 \times 10^3$
0.7	Yellow	$> 10^7$
0.8	Yellow	$> 10^7$



When the content of  $\text{Nb}_2\text{O}_5$  was over 0.7 mg, the resistivity of ceramic materials was greater than  $10^7 \Omega \text{ cm}$ , which could be explained by the defects compensating mechanisms from electronic compensation to cation vacancies compensation. The action formula of  $\text{Nb}_2\text{O}_5$  was shown as follows:



The resistivity would be increased because the Ba vacancies formed and then diffused from the grain boundary to the interior.

Neutrality would be maintained as long as the donor and the acceptor could compensate completely. A trace of donor concentration remaining from the compensation would in fact act as active donors which contributed to the semiconductivity in BT-based lead-free PTCR materials [18]. Under this circumstance,  $\text{Ti}^{4+}$  ions would change to  $\text{Ti}^{3+}$  ions for the electric charge compensation. Therefore, the BT-based semiconducting ceramics showed an n-type conductivity and PTC behavior. It could be observed that the optimum donor content of  $\text{Nb}_2\text{O}_5$  for realizing semiconducting of the samples with 1 mol% BNT addition was 0.6 mg.

Fig. 3 shows the microstructures of the natural surface of the BT–BNT ceramics. The distribution of the grain size was nonuniform, and the average size of the grains monotonously decreased as the content of BNT increased. It is well known that the oxygen vacancies could enhance the transfer of mass and energy between the reactants during sintering. However, the residual  $\text{Na}^+$  ions tended to segregate on grain boundaries and formed a thin Na-rich shell outside the BT–BNT grains. This resulted in the decrease of the concentration of oxygen vacancies, thus inhibiting the grain growth indirectly [19,20]. The grain size of the 0.99BT–0.01BNT sample contained extra 0.6 mg  $\text{Nb}_2\text{O}_5$  (Fig. 3f) was larger than that of the sample without extra  $\text{Nb}_2\text{O}_5$  (Fig. 3e), which indicated that appropriate  $\text{Nb}_2\text{O}_5$  could facilitate grain growth. These phenomena were in agreement with the variation of resistivity. It is generally accepted that the decrease of the resistivity is associated with the increase of grain size because the decrease of grain boundary volume is beneficial to conductivity.

#### 4. Conclusions

In this study, the BT–BNT lead-free PTCR ceramics were prepared by the conventional solid-state reaction method and



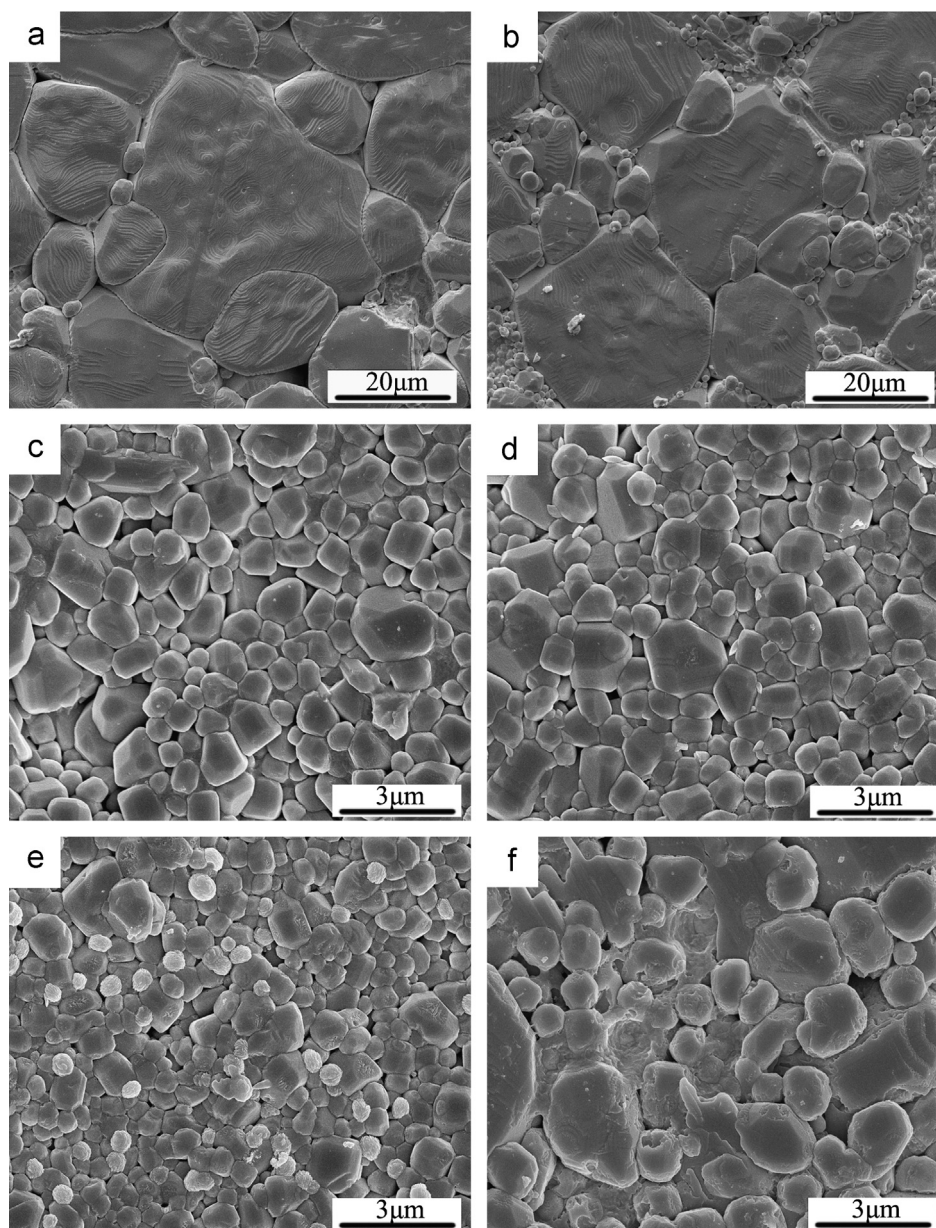


Fig. 3. Microstructure of the  $(1-x)\text{BT}-x\text{BNT}$  ceramics with different doping content: (a)  $x=0$ , (b)  $x=0.1\%$ , (c)  $x=0.2\%$ , (d)  $x=0.4\%$ , (e)  $x=1\%$ , and (f)  $x=1\% + 0.6 \text{ mgNb}_2\text{O}_5$ .

these samples showed excellent PTC properties. With an increase of BNT, both the Curie temperature and the room temperature resistivity increased, but the average size of the grains decreased obviously. At 1 mol% BNT addition, the sample displayed dielectric property, which was mainly due to the volatilization of  $\text{Bi}_2\text{O}_3$ . When the addition of extra  $\text{Nb}_2\text{O}_5$  content was 0.6 mg, the sample possessed a relatively low room temperature resistivity about  $6.3 \times 10^3 \Omega \text{ cm}$ , a relatively high Curie point about  $135^\circ\text{C}$ , and a high PTC effect of  $\sim 3$  orders of magnitude.

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