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Effects of $Bi_{1/2}Na_{1/2}TiO_3$ on the Curie temperature and the PTC effects of $BaTiO_3$-based positive temperature coefficient ceramics

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Abstract

In order to prepare lead-free $BaTiO_3$-based PTC with middle Curie point, the incorporation of $Bi_{1/2}Na_{1/2}TiO_3$ (abbreviated to NBT) into $BaTiO_3$-based ceramics was investigated on samples containing 0.1, 0.5, 1, 1.5, 1.6, 1.8, 2 mol% of NBT. It was found that for all samples containing up to 1.5 mol%, the Curie temperature was obviously improved with the increasing of NBT content, and the T_C raised to 150 °C from 97 °C just only 1.5 mol% NBT added. Because A–O bonds were weakened, which induced that Ti–O bonds were strengthened correspondingly, and the actions between Ti^{4+} (a departure of center) and its near O^{2-} were so strong that Ti^{4+} could not resume its seat except that it was under the higher temperature, hence the Curie temperature was improved. At the same time, the PTC effects were also meliorated which attributed to vast electron capture centers formed by Bi_2O_3 acting with MnO. However, when the amount of NBT exceeded 1.5 mol%, the samples were dielectric material and had no PTC effects, but it was worth noting that the ρ–T curve of the samples sintered in reducing atmosphere was linear.

Keywords: $BaTiO_3$-based; NBT; T_C; PTC effects

1. Introduction

Donor-doped $BaTiO_3$ ceramics has an anomalous increase in resistance near the Curie temperature (T_C) [1–4]. This behavior is commonly referred to as the positive temperature coefficient of resistivity (PTCR) effect and is a grain-boundary related phenomenon. Trivalent ions, such as Sb^{3+}, Y^{3+}, and La^{3+}, or pentavalent ion, such as Nb^{5+}, are substitutionally incorporated at Ba or Ti sites in the $BaTiO_3$ lattice, respectively, as donor dopants [5–10]. Dopant ions must be a similar size to the ion being replaced, with a higher valency for n-type semiconduction. The PTC thermistors can be used in such various kinds of electronic circuitry as a switching device and a constant temperature heater, as well as a measurement, detection, and control of temperature or parameters related to temperature [11].

As we all know, the power density of the material is in direct proportion to Curie temperature T_C when it is used as heater, and the formula can be simplified as [12]:

$$W = D(T_C - T) \quad (1)$$

W is the amount of heat power (W), D the thermal dissipation constant (W/°C), T_C the Curie temperature, and T is the ambient temperature.

From the above formula, we can learn that improving the Curie temperature of the PTC materials is an effective method in order to get the heater with ample power. With the further increasing of T_C, there was some difficulty in preparation of PTC ceramic materials, which included that it demands high quality raw materials, it is not easy to turn the specimens into semiconductors, and the PTC effect was depressed greatly, and so on.

As yet, whether the PTC materials of middle Curie point (between 120 and 200 °C) were produced or that of high Curie point (above 200 °C), it was determined that compositional modifications of Pb^{2+} for Ba^{2+} produce changes in the Curie point to higher temperatures. PTC ceramic materials with the Curie point above 120 °C were prepared by adding $PbTiO_3$, PbO or Pb_3O_4 into $BaTiO_3$.Thereby, adding Pb^{2+} into $BaTiO_3$-based PTC material to improve T_C was studied broadly, however, we all know that PbO was poisonous and prone to volatilize, then to pollute the circumstance and hurt to people, so we should dope other innocuous additives instead of lead to increase T_C of composite PTC materials.

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Table 1
Chemical composition of the samples designed in this study

Samples	Composition
A	$Ba_{0.92}Sr_{0.08}TiO_3 + Sb_2O_3 + Nb_2O_5 + (AST) + MnO_2$
B	$(Ba_{0.92}Sr_{0.08})_{0.999}(Bi_{0.5}Na_{0.5})_{0.001}TiO_3 + Sb_2O_3 + Nb_2O_5 + (AST) + MnO_2$
C	$(Ba_{0.92}Sr_{0.08})_{0.995}(Bi_{0.5}Na_{0.5})_{0.005}TiO_3 + Sb_2O_3 + Nb_2O_5 + (AST) + MnO_2$
D	$(Ba_{0.92}Sr_{0.08})_{0.99}(Bi_{0.5}Na_{0.5})_{0.01}TiO_3 + Sb_2O_3 + Nb_2O_5 + (AST) + MnO_2$
E	$(Ba_{0.92}Sr_{0.08})_{0.985}(Bi_{0.5}Na_{0.5})_{0.015}TiO_3 + Sb_2O_3 + Nb_2O_5 + (AST) + MnO_2$
F	$(Ba_{0.92}Sr_{0.08})_{0.984}(Bi_{0.5}Na_{0.5})_{0.016}TiO_3 + Sb_2O_3 + Nb_2O_5 + (AST) + MnO_2$
G	$(Ba_{0.92}Sr_{0.08})_{0.982}(Bi_{0.5}Na_{0.5})_{0.018}TiO_3 + Sb_2O_3 + Nb_2O_5 + (AST) + MnO_2$
H	$(Ba_{0.92}Sr_{0.08})_{0.98}(Bi_{0.5}Na_{0.5})_{0.02}TiO_3 + Sb_2O_3 + Nb_2O_5 + (AST) + MnO_2$

In this work, In order to develop lead-free $BaTiO_3$-based PTC materials with middle Curie point, NBT/$BaTiO_3$ composite PTCR ceramics were prepared by doping Nb_2O_5 and Sb_2O_3 which were used as donor to replace B site and A site, respectively, and the influence of NBT on the T_C and PTCR effect was investigated, and the main studies was focused on whether the incorporation of NBT into $BaTiO_3$-based ceramics could raise the Curie temperature or not, and why the T_C could be raised. The result showed that the NBT/$BaTiO_3$ composite material was a new system worth studying.

2. Experimental set-up

2.1. Sample preparation

At first, NBT was compounded as standby material by conventional solid-state reaction technique. The powders of Na_2CO_3, Bi_2O_3, and TiO_2 with high purity were mixed by wet ball milling for 4 h and reacted at 850 for 2 h.

The samples were prepared by solid-state reaction method too. The basic starting materials were $BaCO_3$, TiO_2, Nb_2O_5, and Sb_2O_3 powders, and the proper amounts of them were mixed by wet ball milling for 4 h, dried at 120 °C in an oven for 3 h and reacted at 1050 °C for 2 h to prepare the nominal compositions $BaTiO_3$, at the same time, Sb^{3+} replaced Ba^{2+} and Nb^{5+} replaced Ti^{4+}, hence, the $BaTiO_3$ was already semiconducting ceramics. We call it the first materials.

In succession, the proper amounts of second materials including Al_2O_3, SiO_2, TiO_2, and MnO_2 were added in the first materials. The mixtures were wet-milled for 6 h, dried, granulated with a small amount of PVA as binder, and pressed into the samples with the desired forms ($\Phi \times d = 16.0\,mm \times 2.0\,mm$). Sintering was conducted in air at maximum temperature of 1275 °C for 20 min. After cleaned by ultrasonic, the both of the surfaces were daubed with Ag electrode slurry. The Ag electrode were dried under the light and treated at 490 °C for 10 min. The samples were shown in Table 1.

The general flow chart of the experiment is as follows in Fig. 1.

2.2. Measurements

The microstructures of samples were investigated by scanning electron microscopy (SEM). The grain form, size, and distribution could be obtained. The resistance was measured at a heating rate of 3 °C min^{-1} by a digital multimeter and a temperature-programmable chamber controlled by computer. The resistivity T_{25} and T_{max} were, respectively, calculated on the basis of the measured resistance, electrode area, and sample thickness. Phase composition and lattice parameters were investigated by X-ray diffraction (XRD).

3. Results and discussion

3.1. Characteristic of NBT

Bismuth sodium titanate, NBT [13–17], is an attractive lead-free A-site complex-perovskite with high T_C ferroelectric relaxor material. It is considered to be an excellent candidate as a key material of lead-free piezoelectric ceramics. The NBT shows strong ferroelectric properties of a large remanent polarization, $P_r = 38\,\mu C/cm^2$, and has a Curie temperature, $T_C = 320$ °C, and a phase transition point from ferroelectric to anti-ferroelectric, $T_P = 200$ °C. In addition, NBT can form solid solutions with $BaTiO_3$. Fig. 2 shows XRD patterns of NBT powders obtained by state reaction technique at 850 °C for 2 h, and the structure of NBT crystal belongs to pure perovskite type, and no other intermediate phase is found.

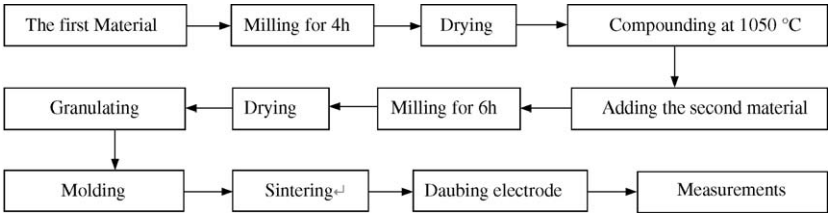

Fig. 1. The flow chart of the experiment.

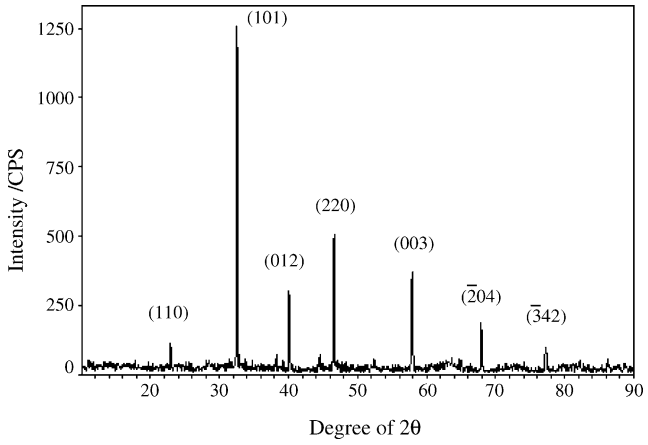

Fig. 2. XRD pattern of NBT powder obtained by solid-state reaction.

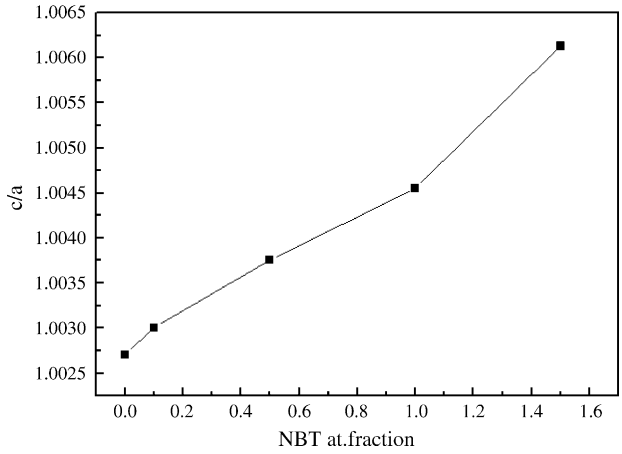

Fig. 3. Tetragonality (*c*/*a* ratio) of $BaTiO_3$-based ceramics sintered at 1275 °C as a function of NBT molar fraction.

3.2. Effects of NBT on the Curie temperature T_C of $BaTiO_3$-based PTC

In the experiment, it was worth noting that the T_C of $BaTiO_3$-based PTC doped just limiting amount of NBT slightly increased with respect to pure $Ba_{0.92}Sr_{0.08}TiO_3$, and the T_C was greatly improved with the increasing of the NBT contents. Table 2 shows T_C of samples with different contents of NBT. The T_C of materials increased to 110 °C from 97 °C when 0.1 mol% NBT were added into $Ba_{0.92}Sr_{0.08}TiO_3$-based PTC, and the T_C of adding 0.5, 1, 1.5 mol% NBT, respectively, reached 118, 127 and 150 °C, which was a quite unusual result. The value of *c*/*a* was increased with the increasing of NBT added into $BaTiO_3$, which indicated that the stabilization of the ferroelectric phase was occurring when NBT was incorporated in $BaTiO_3$ (Fig. 3).

Why did the T_C increase so much only limiting amount of NBT added into $BaTiO_3$-based PTC materials? There were two reasons for explaining it. Firstly, We all know that the melting point of Bi_2O_3 (820 °C) is very low, namely the Bi–O bands is very weak. So A–O bonds were weakened, which induced that Ti–O bonds were strengthened correspondingly after NBT were doped, and then the interactions between Ti^{4+} (a departure of center) and its near O^{2-} were so strong that Ti^{4+} could not resume its seat unless the tetragonal ferroelectric were wrecked at higher temperature, hence the Curie temperature of $BaTiO_3$-based PTCR ceramics was clearly improved. Secondly, in the perovskite-type (ABO_3) structure, A-site ion is at the center of oxygen dodecahedron, and there are oxygen octahedron held down directly by A-site ion. In addition, more oxygen octahedrons are held down indirectly by A-site ion. So although a few of A-site iron are replaced, there will be vast Ti–O bonds to be influenced, namely the Curie temperature T_C of materials is going to be changed if a few of A-site iron are replaced [18].

It was a pity that all samples for NBT concentration more than 1.5 mol% were dielectric material when they were sintered in air. However, the semiconducting sample H was sintered at 1275 °C for 2 h in reducing atmosphere, but they have not PTC effect. As shown in Fig. 4 the resistivity fell with the increasing of temperature, and the resistivity was nearly linear with the temperature, which was a byproduct in the experiment.

Table 2
T_C of samples with different contents of NBT

Samples	T_C (°C)
A	97
B	110
C	118
D	127
E	150

3.3. Effects of NBT on the PTC effect of $BaTiO_3$-based materials

Fig. 5 represents the ρ–T curves of samples with different contents of NBT, and it clearly revealed the PTC properties of samples. The PTC effects of the materials doped with NBT improved greatly at the cost of the room temperature resistivity, as shown in Table 3. The temperature coefficients α in Table 3

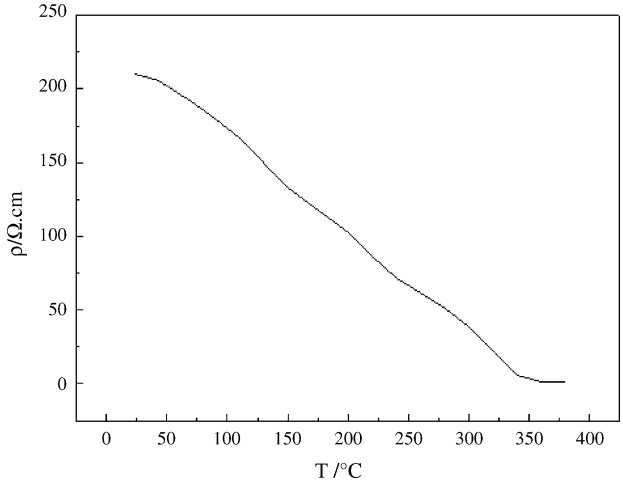

Fig. 4. The ρ–T curve of sample H sintered at 1275 °C for 2 h in reducing atmosphere.

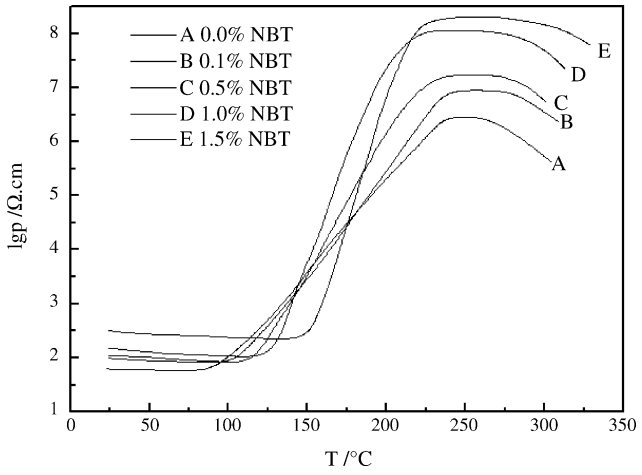

Fig. 5. The ρ–T curves of samples with different contents of NBT.

Table 3
PTC properties of samples with different contents of NBT

Contents of NBT (mol%)	Room resistivity (Ω cm)	Magnitude ($\times 10^4$)	Resistivity temperature factor (% °C^{-1})
0	63.1	5.0	8.1
0.1	97.7	11.2	9.3
0.5	104.28	21.4	11.6
1	151.36	114.8	18.9
1.5	316.23	95	21.9

were calculated by the following formula [19]:

$$\alpha = 2.303 \times \frac{\lg(R_2/R_1)}{T_2 - T_1} \quad (2)$$

T_1 equals the Curie temperature T_C, and T_2 ($T_2 > T_C$) corresponds to a point on the tangent of the ρ–T curve in Fig. 5, and R_1 and R_2 are, respectively, opposite resistance.

Doping with NBT led to a consequent decrease in the grain size. The grain size without NBT was between 5 and 10 μm, and the size with 0.1 mol% NBT was between 3 and 6 μm, and the grain size was about 1 μm when 1.0 mol% NBT was added. The

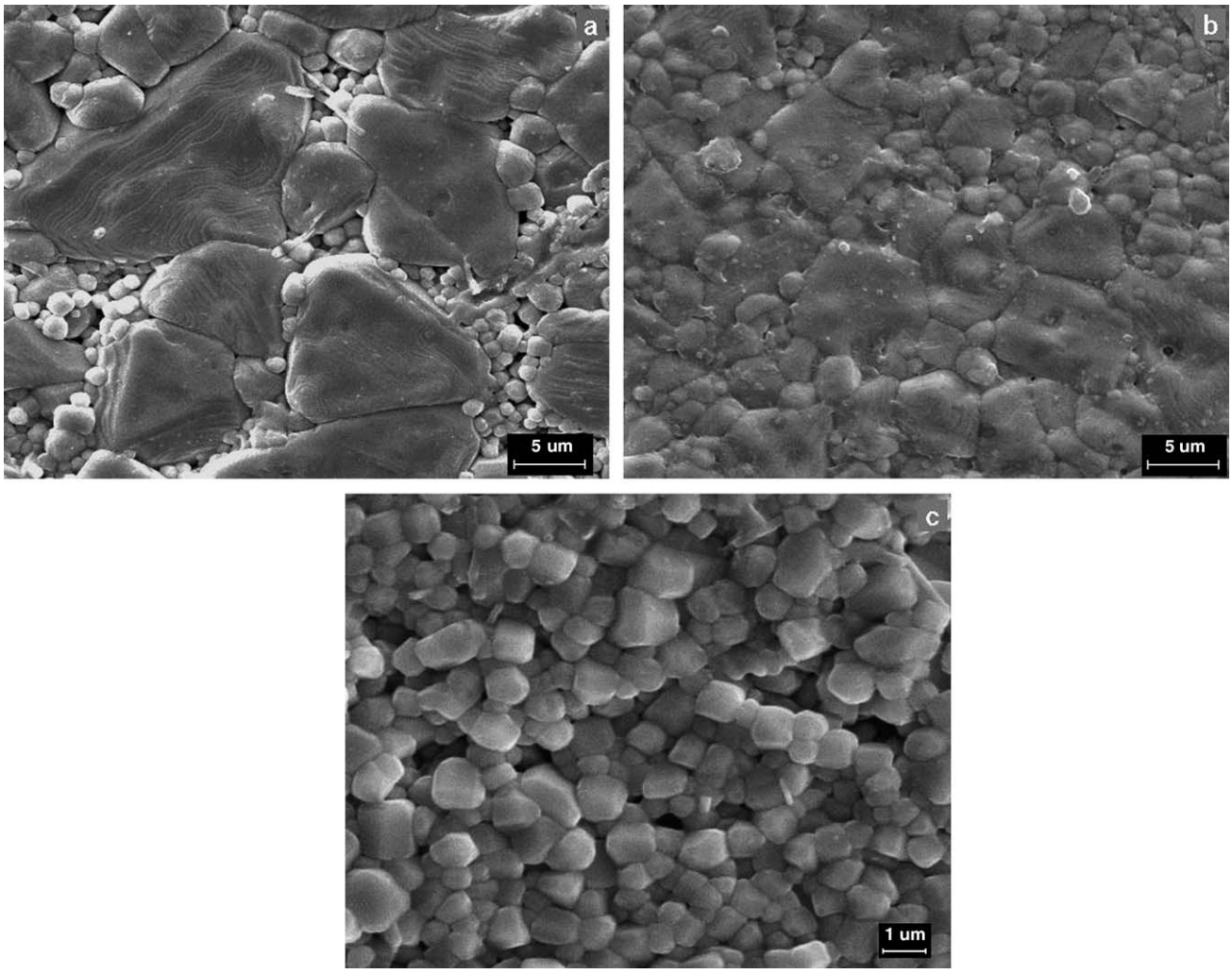

Fig. 6. SEM images of samples with different content of NBT (a) without NBT, (b) 0.1 mol% NBT added, and (c) 1.0 mol% NBT added.

less the grain size was, the more the mounts of grain boundaries were, so the effect of grain boundary was improved (Fig. 6).

And in addition, PTC effects of ceramics were meliorated, which attributed to vast electron capture centers formed through Bi_2O_3 that Bi_2O_3 was prone to volatilize during the sinter at 1275 °C acting with MnO [20]. A series of action formulas were shown as follows:

Under normal conditions,

$$MnO \xrightarrow{TiO_2} Mn''_{Ti} + O^{\times}_{O} + V^{\bullet\bullet}_{O} \quad (3)$$

Mn^{2+} could be oxidized into Mn^{3+}, and electron capture centers formed.

$$2Mn''_{Ti} + V^{\bullet\bullet}_{O} + \tfrac{1}{2}O_2 \rightarrow 2Mn'_{Ti} + O^{\times}_{O} \quad (4)$$

And then Mn^{3+} could combine in composite defects with oxygen and Bi_2O_3 that was disassembled from the NBT.

$$O_2 + 2MnO + Bi_2O_3 \xrightarrow{BaTiO_3} 2Bi^{\bullet}_{Ba} + 7O^{\times}_{O} + 2Mn'_{Ti} + V^{\times}_{Ba} \quad (5)$$

And then,

$$2Mn'_{Ti} + V^{\times}_{Ba} \rightarrow (2Mn_{Ti} \cdot V_{Ba})'' \quad (6)$$

So the concentration of valent manganese defects and correlative composite defects increased. Manganese could still promote the neuter barium vacancy and correlative composite defect to form. As follows:

$$\tfrac{1}{2}O_2 + MnO + Bi_2O_3 \xrightarrow{BaTiO_3} 2Bi^{\bullet}_{Ba} + 5O^{\times}_{O} + Mn''_{Ti} + V^{\times}_{Ba} \quad (7)$$

The format of shortening was that:

$$Mn''_{Ti} + V^{\times}_{Ba} \rightarrow (Mn_{Ti} \cdot V_{Ba})'' \quad (8)$$

4. Conclusion

The incorporation of NBT into $BaTiO_3$-based ceramics was studied, and doping NBT not only improved the PTC effects but also increased the Curie temperature (T_C). The T_C was obviously improved with the increasing of NBT content. When the amount of doped NBT was up to 1.5 mol%, the T_C increased from 97 to 150 °C. In addition, the magnitude had been improved greatly from 10^4 to 10^6, and the resistivity temperature factor was also enhanced, and the reproducibility of samples was very good, so it was possible to prepare the lead-free middle point PTC.

Though it was quite difficult to form semiconducting materials when the amount of NBT was over 1.5 mol%, it does not mean impossible, so inherent characteristic and the effects of the extrinsic factors should be further researched by us.

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Biographies

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