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Effect of sintering procedure on the resistivity of $(1-x)BaTiO_{3-x}(Bi_{0.5}Na_{0.5})TiO_3$ ceramics

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ABSTRACT

The experimental results on the effect of sintering procedure on the resistivity of high Curie point $(1-x)BaTiO_{3-x}(Bi_{0.5}Na_{0.5})TiO_3$ ($x = 0.5, 2, 4, 6, 8, 10, 15, 20$ mol%) ceramics, are reported. The sample with $x = 0.5$ mol% could be semiconducting in air atmosphere sintering, with the Curie point about 149.7 °C. The samples with $x \geq 2$ mol% must be sintered at reducing atmosphere. The highest Curie point (about 192 °C) with superior PTC effect could be obtained at the sample with $x = 4$ mol% when sintered at 1290 °C for 20 min and added 5 g graphite in the crucible for reducing atmosphere. Samples with more BNT contents could not be semiconducting by this sintering procedure. The samples with weak NTC effect could be obtained by firstly air or reducing atmosphere sintering and then different reducing atmosphere treatment. At last, all of the samples with different BNT contents could be semiconducting according to changing sintering atmosphere and procedure.

1. Introduction

Barium titanate ($BaTiO_3$, BT) is a typical ferroelectric material [1–4] with perovskite structure [5]. The donor doped $BaTiO_3$ possesses a ferroelectric–paraelectric transition around its Curie temperature (Tc) about 120 °C [3]. This phenomenon is widely used in BT-based ceramics as the main components in many kinds of electroceramic devices such as multilayer capacitors (MLCs) [6] and positive temperature coefficient of resistors (PCTR) [7–9]. The significant feature of the PTCR ceramics is an abrupt increase in their electrical resistance above Tc, and this property is widely applied for several electric devices, for example, temperature sensors, current control elements, over-current protection devices, and self-controlled heaters. It is well known that BT-based electric devices perform at temperatures less than its Curie temperature, 120 °C. In order to come up to the demands of special applications using at a temperature above 120 °C, $PbTiO_3$ (PT) is usually added to the BT ceramics to shift the Tc to high temperature. However, Lead had been prohibited to use in the electric devices, considering the environmental protection problems. Recently, some other kinds of perovskite-type compounds [10–12] were doped into BT to replace the traditional PT, in order to increase the Curie temperature of BT-based PTCR ceramics.

$(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) is one kind of perovskite-type ferroelectric materials that possess relatively higher Curie temperature (Tc = 320 °C) [5] and can form finite solid solutions with BT. The BT-BNT ceramics demonstrated excellent PTCR behaviors, i.e. low room-temperature resistivity and anomalous resistivity change near Tc [13], by sintering at a low oxygen partial pressure and including additives [14]. So recently, it has been considered to be the most ideal lead-free dopants to fabricate high Tc BT-based PTCR ceramics, therefore a lot of researches have been done on this subject [15–17]. The mechanism of BNT on improving the Curie point of BT-based ceramics is that Bi^{3+} ions can substitute Ba^{2+} ions in BT lattice. Owing to its bigger c/a ratio with a broad oxygen octahedron vacancy and the weakness of Bi–O bonds, Ti^{4+} could not resume its seat unless the tetragonal ferroelectric is wrecked at high temperature [18]. However, the room-temperature resistivity of BT-BNT ceramics would be increased so rapidly with BNT content increasing that the samples would be difficult to semiconducting, thus reducing atmosphere protection sintering with certain procedure was necessary when BNT contents bigger than 2 mol% from our experiments.

In the present study, a series of $(1-x)BaTiO_{3-x}(Bi_{0.5}Na_{0.5})TiO_3$ ($x = 0.5, 2, 4, 6, 8, 10, 15, 20$ mol%) ceramics were fabricated by conventional mixed-oxide technique. The crucible must be sealed perfectly to prevent Bi_2O_3 from volatilizing excessively when the samples were sintered at air atmosphere (in Fig. 1(a)), while some graphite were added at the bottom of the crucible to make reducing atmosphere (in Fig. 1(b)) during sintering when the BNT-doping contents bigger than 2 mol%. The fireclay refractory powders were selected to seal the crucible and decrease the reaction velocity of

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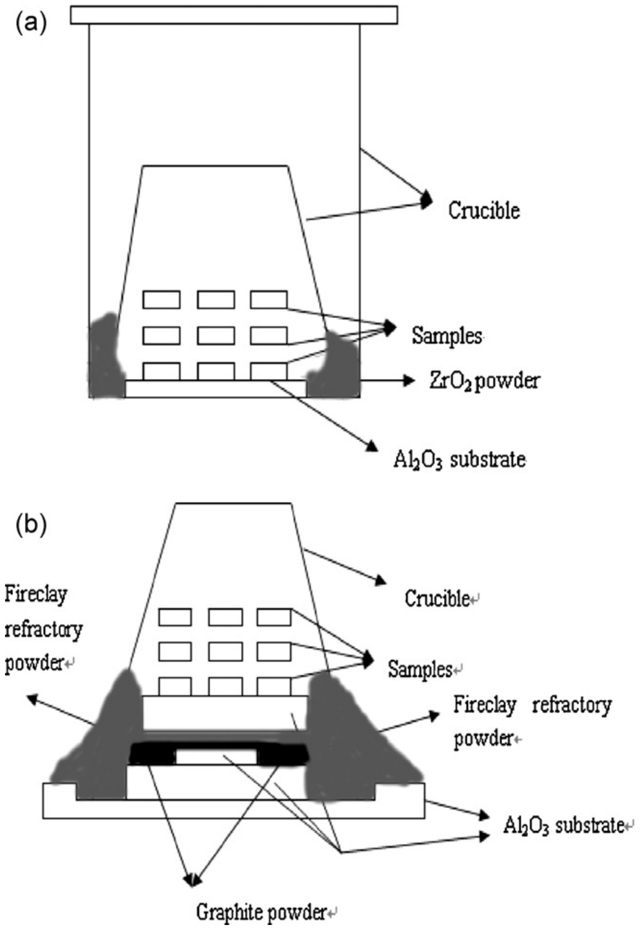

Fig. 1. The schematic graph of (a) air atmosphere and (b) reducing atmosphere sintering equipment.

graphite with air, because the powders, together with some Bi_2O_3 volatilizing from the samples, could become dense enough after high temperature sintering. The influence of sintering atmosphere and procedure on the room-temperature resistivity and PTC property of these samples were investigated at last.

2. Experimental procedure

(1−x)BaTiO$_{3-x}$(Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ (x = 0.5, 2, 4, 6, 8, 10, 15, 20 mol%) ceramics were prepared by the conventional powder processing route. Reagent grade Bi_2O_3, TiO_2 and Na_2CO_3 were weighed with proper amounts and mixed by ball milling for 4 h. The amounts of Bi_2O_3 were calculated based on the whole reaction process of BNT:

$$Bi_2O_3 + Na_2CO_3 + 4TiO_2 \rightarrow 4(Bi_{1/2}Na_{1/2})TiO_3 + CO_2 \tag{1}$$

by the molar ratio of Bi_2O_3:Na_2CO_3:TiO_2 = 1.005:1:4, a little of Bi_2O_3-excess to offset its volatilization at high temperature. The dried powders were then synthesized at 780 °C for 2 h to pre-calcine BNT.

In the first stage, we prepared BT PTCR ceramics with Tc about 120 °C. (1) High purity (99.9%) basic starting materials of $BaCO_3$, TiO_2, Sb_2O_3, and Nb_2O_5 powders, in the molar ratio of 1:1.01:0.00046:0.0010 were mixed by ball milling for 4 h, dried at 120 °C in an oven and then calcined at 1050 °C for 2 h. (2) In succession, 0.11 wt‰MnO_2 were added to the starting materials to improve their PTC property and re-milled for 6 h and dried. After granulation with polyvinyl alcohol (PVA), the powders were pressed into discs with 15 mm in diameter and about 2 mm in thickness at a pressure of 190 MPa. (3) The green discs were sintered at 1290, 1300 and 1310 °C, respectively for 20 min in air atmosphere. Then the ohmic aluminum electrodes were constructed on the two grinded surfaces and treated at 580 °C for 10 min. In the second stage, we studied the property of (1−x)BT-xBNT ceramics. A certain amounts of pre-calcined BNT obtained above were doped in procedure (1), and after the above (1) and (2) synthesizing procedures, the samples were sintered at 1270 and 1290 °C, respectively for 20 min in air or reducing atmosphere.

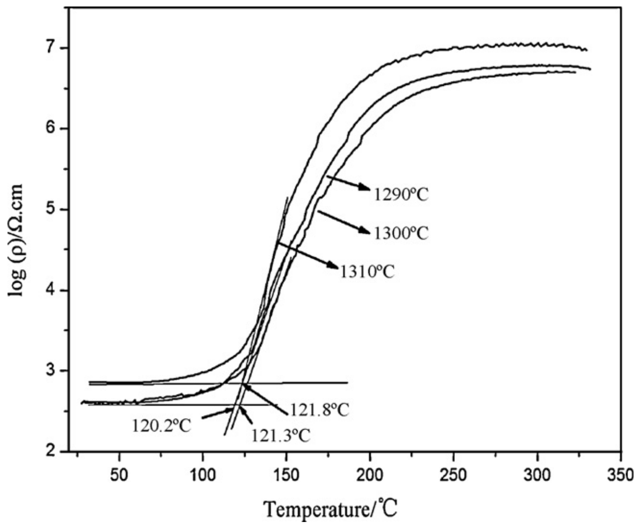

Fig. 2. The resistivity–temperature (ρ–T) curve of BT PTCR ceramics sintered at different temperature.

The microstructure of the samples was investigated by using an environmental scanning electron microscope (PHILIPS XL-30 ESEM). The electric resistance was measured using a temperature-programmable furnace controlled by a computer and a digital multimeter from room temperature to 400 °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:

$$\rho = \frac{R\pi d^2}{4h}. \tag{2}$$

3. Results and discussions

Fig. 2 shows the BT ceramics with PTC property prepared in this experiment. It is clearly that the samples doped with Sb_2O_3 and Nb_2O_5 had superior PTC property with the Tc about 121 °C. So we will study the Curie temperature increment base on this Tc after doping with certain amounts of BNT.

All the samples were firstly sintered at 1290 °C for 20 min in air atmosphere and their correspondingly room-temperature resistivity (ρ_{25}) was listed in Fig. 3.

It is clearly that the resistivity of samples with $x \geq 2$ mol% was very big when sintered at air atmosphere. The substitution of Bi^{3+}

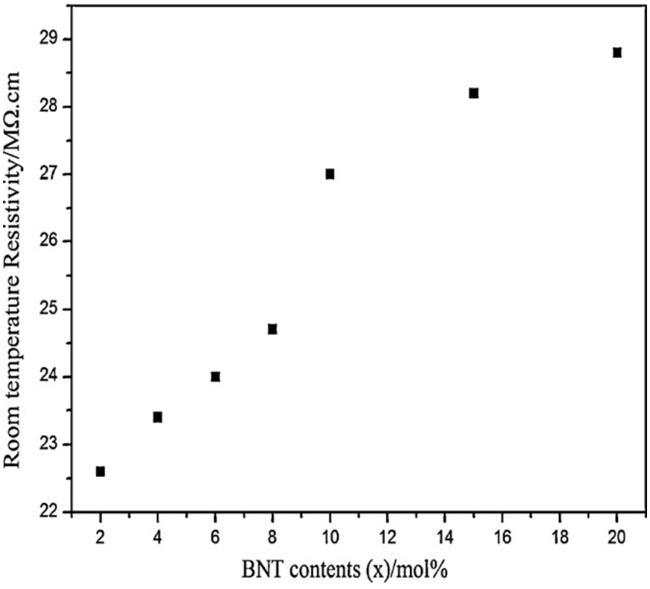

Fig. 3. The room-temperature resistivity (ρ_{25}) of samples sintered at air atmosphere.

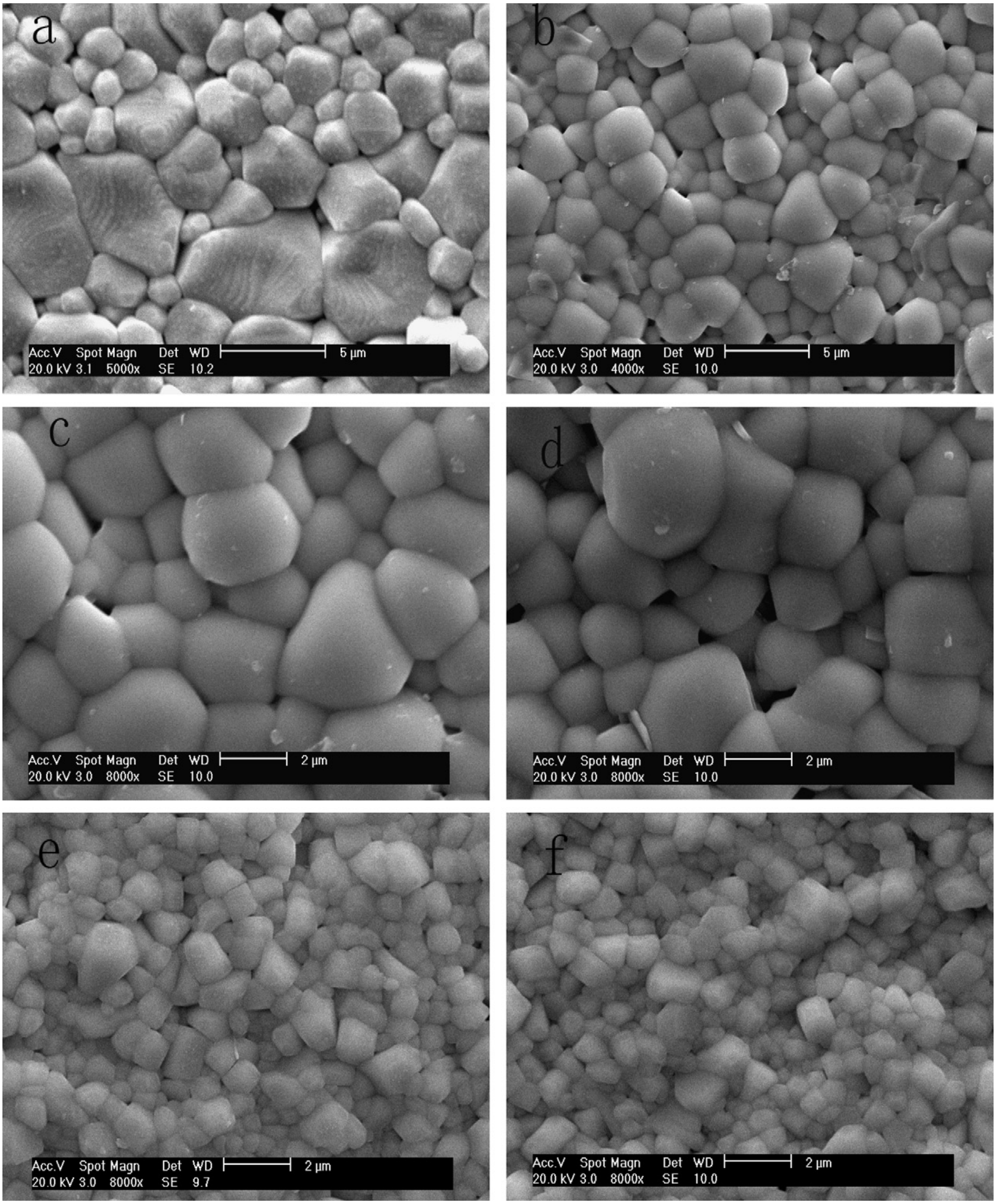

Fig. 4. (a–f) SEM images of the surface of as-sintered samples doped with different contents of BNT (a) 0.5, (b) 2, (c) 4, (d) 8, (e) 15, and (f) 20 mol%.

and Na^+ ions to Ba^{2+} ions was occurred during sintering. Owing to the low melting point of Bi_2O_3 (~820 °C), the pre-calcined BNT could be easily decomposed at lower temperatures, which facilitated the migration of the Na^+ ions through the lattice. The grain resistivity would be increased with the concentration of Na^+ ions (as an acceptor) in the lattice increasing. In addition, Na^+ ions could be easily segregated in the grain boundaries due to its small radius, leading to higher grain boundary resistivity. These two reasons caused the samples difficult to semiconducting.

The SEM images obtained from the surface of as-sintered samples with 0.5, 2, 4, 8, 15, 20 mol% BNT contents are shown in Fig. 4(a–f), respectively. With an increase of BNT contents, the grain size was influenced significantly by the BNT concentration, which would be decreased rapidly. BNT 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.

The resistivity–temperature (ρ–T) curve of sample with $x = 0.5$ mol% was shown in Fig. 5. It could be found that the sam-

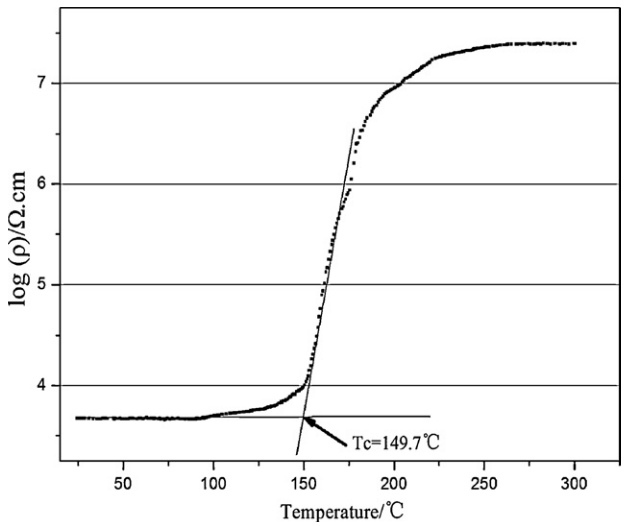

Fig. 5. The ρ–T curve of sample with $x = 0.5$ mol%.

ple showed a typical PTC effect. In order to obtain semiconducting ceramics with PTC behavior and increase its Curie point, light doping with foreign elements substituting at the Ba or Ti sites is required, which is associated to the formation of electrons as charge compensation defects. The perovskite BNT contains Bi^{3+} and Na^{+} ions in an ordered arrangement, which would substitute Ba^{2+} ions in the lattice. As mentioned above, Bi–O bond is very weak, so A–O bonds were weakened after Bi^{3+} ions substituted Ba^{2+} ions at A sites, which also induced that Ti–O bonds strengthened correspondingly. As a result, Ti^{4+} could not resume its seat unless the tetragonal ferroelectric was wrecked at high temperature. In addition, many oxygen octahedrons are held down directly or indirectly by A-site ions. Thus, although a few of A-site ions were substituted, there would be vast Ti–O bonds to be influenced. From these two aspects of reason, the Curie temperature could be improved rapidly by BNT doping [18].

In order to fabricate high Curie point PTC ceramics, a certain amount of graphite was added in a sealed crucible with a volume of 118 ml (Fig. 1(b)) to make reducing atmosphere. Three sintering procedures were adopted in the experiment, i.e. (a) the samples were firstly sintered at 1270 or 1290 °C for 20 min in reducing atmosphere (added with 5 g graphite) and then re-oxidizing at 850 °C for 2 h in air atmosphere; (b) the samples were firstly sintered at 1290 °C for 20 min in air atmosphere and then reducing atmosphere heat-treatment at 850 °C for 2 h (added with 5 g graphite); (c) the samples were firstly sintered at 1290 °C for 20 min in reducing atmosphere (added with three gram graphite) and then reducing atmosphere heat-treatment at 850 °C for 2 h (added with 5 g graphite).

The ρ_{25} of samples could be evidently decreased after adopting the above three sintering procedures. When sintered by procedure (a), the ρ_{25} of samples could be increased with the sintering temperature increasing and their PTC jump also be improved correspondingly. The re-oxidizing treatment after sintering induced the ρ_{25} and PTC jump to increase. Figs. 6 and 7 illustrate the ρ–T curves of samples with $x = 2$ and 4 mol%, respectively, sintered by procedure (a). The Curie point of the obtained samples was about 168 °C ($x = 2$ mol%) and 192 °C ($x = 4$ mol%). The other samples with more BNT contents could not be semiconductive by this sintering procedure. In reducing atmosphere, the oxygen loss with the creation of electrons (e′) by the following reaction could be occurred.

$$O_O^x \rightarrow \frac{1}{2}O_2 + V_O^{\bullet\bullet} + 2e' \tag{3}$$

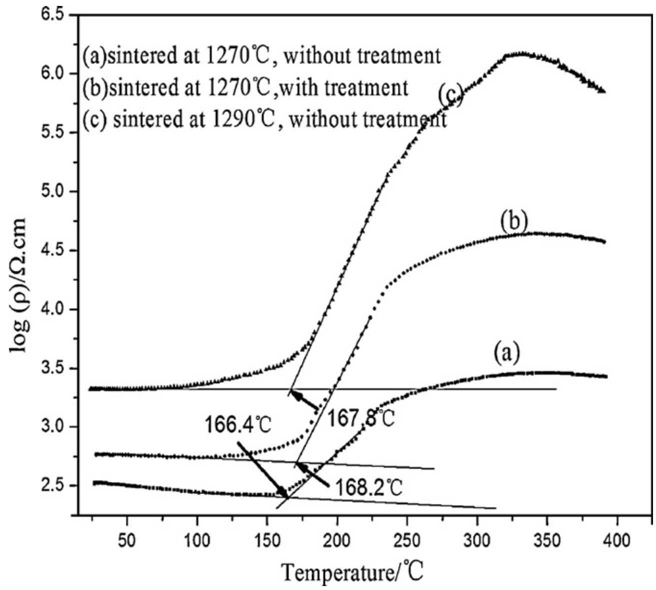

Fig. 6. The ρ–T curves of samples with $x = 2$ mol%, sintered by procedure (a).

These formed electrons contribute to the increase in charge carrier concentration, leading to the low resistivity at room temperature. On the other hand, this phenomenon leads to a decrease in the potential barrier because of an increase in the number of conduction electrons, degrading the PTC effect. During the re-oxidization treatment, the anion vacancies ($V_O^{\bullet\bullet}$) were filled, creating the electronic holes ($h^{\bullet}$) by the following reaction:

$$V_O^{\bullet\bullet} + \frac{1}{2}O_2 \rightarrow O_O^x + 2h^{\bullet} \tag{4}$$

The resistivity could be raised again by exposing to O_2 atmosphere. Oxygen was adsorbed at the grain boundaries during treatment in air atmosphere, thus annihilating the oxygen vacancies created during reducing atmosphere sintering and significantly increasing the grain boundary resistivity. Therefore, the low room-temperature resistivity in reducing atmospheres might be caused by the decrease in potential barrier height, which originated

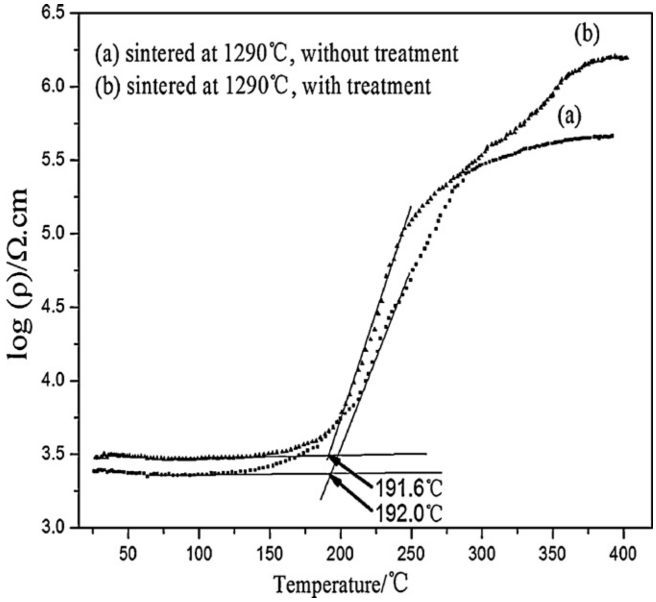

Fig. 7. The ρ–T curves of samples with $x = 4$ mol%, sintered by procedure (a).

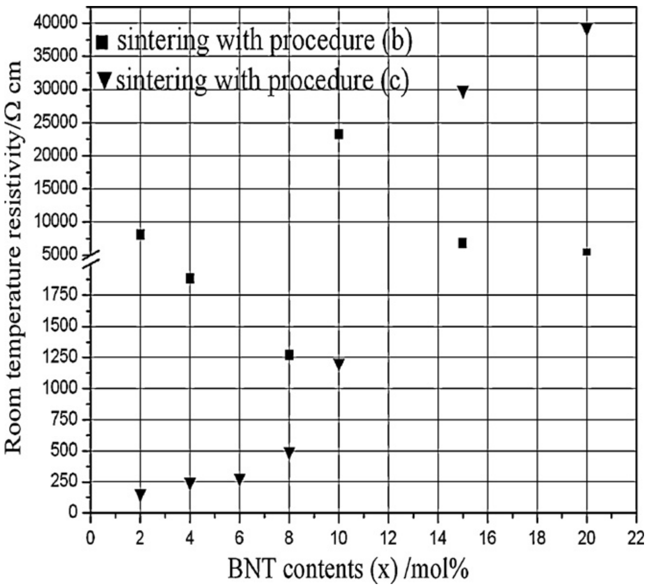

Fig. 8. The ρ_{25} of the samples sintered by procedure (b) and (c).

from an increase in the number of electrons owing to desorption of oxygen atoms at the grain boundaries. Also, the high room-temperature resistivity in oxidizing atmospheres might be caused by the increase in potential barrier height, which results from the adsorption of oxygen atoms at the grain boundaries [19,20]. A low oxygen partial pressure is required during the sintering process and then the samples should be sintered at air atmosphere to promote the grain boundary oxidation which is essential to the pronounced PTC effect [21]. In Fig. 6, for the same composition, a difference of 20 °C in the sintering temperature gave rise to the change of over two orders of magnitude in resistivity. This seemed to be striking and have something to do with a critical transition happened within that narrow temperature window of 20 °C. The PTCR effect is said to arise from the presence of a potential barrier at the grain boundaries; the barrier arising from the trapping of electrons by acceptor species at the grain boundary [22]. The barrier makes the grain boundary more resistive than the grain interior. As analyzed above, the high resistive grain boundary was aroused by the adsorption of oxygen atoms. So it is clearly that the oxygen pressure of sample sintered at 1290 °C was bigger than another. The characteristic of this sintering method was that if the sintering time was too long and the graphite used up, little amounts of air could penetrate into the crucible across the sealed materials without reacting, therefore the oxygen pressure increased. But when the oxygen pressure increased big enough, the semiconducting of the samples would become very difficult.

The ρ_{25} of the samples obtained by the procedure (b) and (c) were listed in Fig. 8. All of the samples could be semiconductive according to these two sintering procedures, although there was an evident difference between them. The ρ_{25} was increased steadily with the BNT contents increasing at procedure (c), while at procedure (b), it decreased with x increasing except for $x = 10$ mol%. It is clearly that, at procedure (b), the ρ_{25} was decreased from 8119.1 Ω cm ($x = 2$ mol%) to 1269.5 Ω cm ($x = 8$ mol%) and from 23187.8 Ω cm ($x = 10$ mol%) to 5232.4 Ω cm ($x = 20$ mol%). It was very absorbing and also seemed surprising that the resistivity would be decreased with BNT contents increasing using (b) procedure. This exceptional phenomenon might be resulted from the following reasons. All the samples were sintered at reducing atmosphere at first. From Fig. 3 we can see that their resistivity were all at MΩ cm orders of magnitude, and they also had comparable values, in addition to a larger increase at $x = 10$ mol%. Therefore, sintering in air atmosphere had little effect on the room-temperature resistivity of samples with different BNT contents. But when heat-treatment at 850 °C in reducing atmosphere, the higher Bi_2O_3 contents, the more crystal defects owing to the evaporation or segregation of Bi_2O_3 and Na_2O, which caused the loose structure of samples. This structure was more easily to lose its oxygen to create electrons, and increase the number of carriers, so the ρ_{25} could be decreased with the increasing of BNT contents.

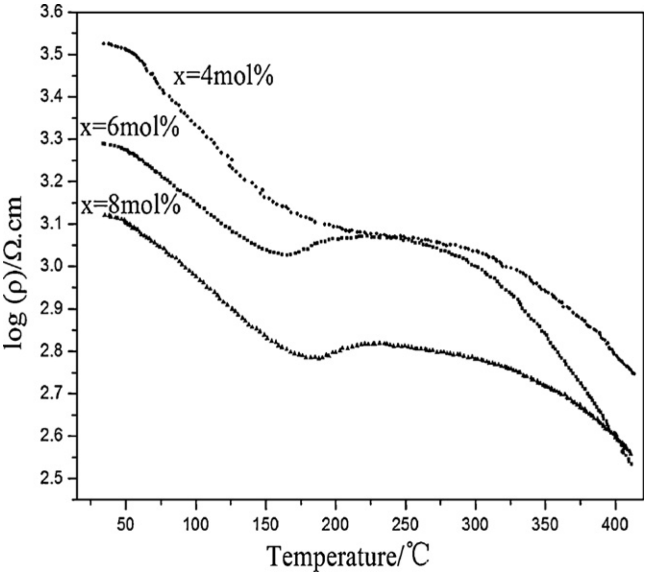

Fig. 9. The ρ–T curves of samples with $x = 4, 6, 8$ mol% sintered by procedure (b).

The ρ–T curves of the samples with $x = 4, 6, 8$ sintered by procedure (b) and (c) were demonstrated in Figs. 9 and 10.

A weak negative temperature coefficient (NTC) property was found in Fig. 9 that the resistivity could be decreased as the temperature increasing and the protuberant parts at the intermediate temperature (about 200 °C) were diminished with the BNT contents increasing. Compared with Fig. 9, these protuberant parts were distinctly augmented in Fig. 10, so the formation of these parts could be attributed to the reducing atmosphere during sintering. The increase of resistivity should be the PTC characteristic of the material itself, which was strongly reduction at reducing heat-treatment. The high potential barrier height formed at air

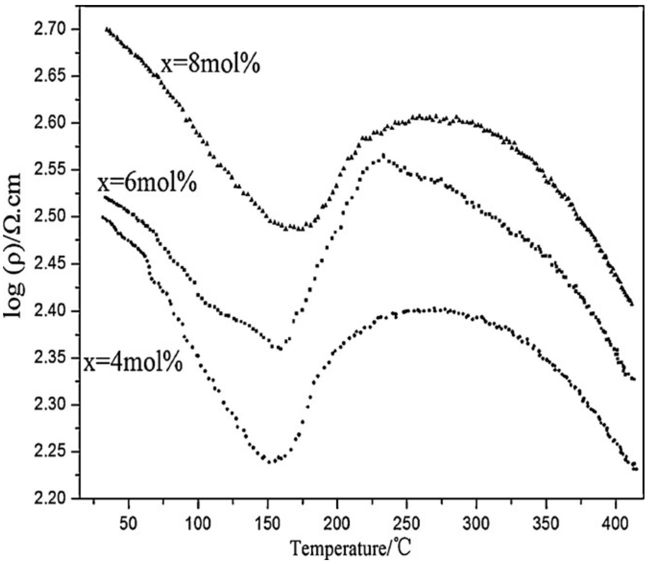

Fig. 10. The ρ–T curves of samples with $x = 4, 6, 8$ mol% sintered by procedure (c).

atmosphere sintering could be reduced strongly during reducing treatment, while the reducing atmosphere sintering would counteract the decreasing of potential barrier height to some extent. Owing to the big volume of oxygen vacancy, the firstly yielded oxygen vacancies during reducing sintering were distributed at the surface of the samples and this layer seemed to be a protective layer to prevent the interior oxygen in the crystal to lose, therefore the resistivity could not be decreased excessively. This could also be seen from Fig. 8 that the room-temperature resistivity of the sample $x = 15$ and 20 mol% sintered by procedure (c) was higher than those of procedure (b), different from the other parts.

4. Conclusion

A series of $(1-x)\text{BaTiO}_{3-x}(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramics with high Curie point were fabricated in this experiment. The sample with $x = 0.5$ mol% could be semiconductive in air atmosphere sintering and the obtained Curie point was about 149.7 °C. The samples with $x \geq 2$ mol% must be sintered at reducing atmosphere. The highest Curie point (about 192 °C) with superior PTC effect could be obtained at the sample with $x = 4$ mol% when sintered at 1290 °C for 20 min and added 5 g graphite in the crucible (118 ml). Sample with more BNT contents could not be semiconductive by this sintering procedure. In addition, the samples with weak NTC effect could be obtained by firstly air or reducing atmosphere sintering and then reducing atmosphere treatment.

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