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Effect of additives on the electrical properties of a $(Ba_{0.92}Sr_{0.08})TiO_3$-based positive temperature coefficient resistor

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Abstract

In the present work, the effects of the additives (BN, $Y_2O_3+Nb_2O_5$, $Sb_2O_3+Nb_2O_5$, and Cr) on the electrical properties of $(Ba_{0.92}Sr_{0.08})TiO_3$-based positive temperature coefficient resistor (PTCR) were investigated. It was noted that the addition of BN lowered the sintering temperature of the material system studied. A proper amount of BN could enhance the PTC effect, but the room-temperature resistivity would increase with increasing the content of BN. The addition of double donor $Sb_2O_3+Nb_2O_5$ could lead to a lower room-temperature resistivity than that of $Y_2O_3+Nb_2O_5$. Metal Cr was also added to further reduce the resistivity. The low room-temperature resistivity and PTC behavior was achieved by controlling both the metallic Cr content and the process of reducing sintering and oxidation treatment. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: BN; Electrical conductivity; Electrical properties; $(Ba,Sr)TiO_3$-based; PTC devices

1. Introduction

Since its discovery in 1954, the positive temperature coefficient resistor (PTCR) has been extensively used in various fields as an over-current protector, self-regulating heater, or temperature sensor, due to its particular properties[1]. Used as an over-current protector, the PTC component is connected in series with the protected circuit. Normally, due to its low resistance, the voltage divided on the PTC component is much smaller than that distributed on the protected circuit, which makes sure that the circuit works with enough voltage. When over-current occurs, the PTCR will bear nearly all the voltage, because the PTC component is heated by the over-current and its resistance increases sharply and achieves several orders of magnitude higher as the temperature increases. As a result, the circuit can be protected. It can be noted that low room-temperature resistivity and strong PTC effect are both required for the application of over-current protection. In microelectronic application, the requirement of low room-temperature resistivity shows a more prominent position due to the applied lower voltage. Therefore, lowering the room-temperature resistivity of PTC materials becomes an important research field.

The room-temperature resistivity and the PTC effect depend on the material compositions and structures. Barium titanate has long been used as a principal PTC material because of its high temperature coefficient and good stability.[2] However, pure $BaTiO_3$ is an insulator and no PTC effect can be observed. The additives play a crucial role in the fabrication of $BaTiO_3$-based PTCR. Basically, there are three kinds of additives: donor additives, acceptor additives, and additives for property modification. The semiconducting ceramic grains can be achieved by donor doping, which is a prerequisite for preparing PTC ceramics. The donor additives are usually trivalent (La^{3+}, Y^{3+})[2–7] or pentavalent (Nb^{5+}, Ta^{5+}) ions.[8–11] In our earlier work,[12] double donor $Sb_2O_3+Nb_2O_5$ was added to $(Ba,Pb)TiO_3$-based ceramics and a lower room-temperature-resisitivity component, compared with the single donor Nb_2O_5, was achieved. As acceptor additives, Mn^{2+} or Mn^{4+} ion[2, 4, 7, 13] is usually added in PTC materials. It is expected that the acceptors are located at the grain boundaries to enhance the PTC effect.[14, 15] The additives for property modification, in general, include Pb^{2+} or Sr^{2+} ions,

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which move the Curie temperature (T_C) of $BaTiO_3$,[16] and AST (the mixture of Al_2O_3, SiO_2, and TiO_2), which is used as a sintering aid to lower the sintering temperature[17]. Ho and Hsieh[6] have reported that the sintering temperature of PTC material can be lowered tremendously by using BN as a sintering aid. To further lower the resistivity, recently in our earlier work,[18] a metallic additive, Cr, was added in $(Ba,Pb)TiO_3$-based ceramics.[18] Low room-temperature resistivity (1.33 Ω cm) and PTC effect ($\rho_{max}/\rho_{min} = 10$) were achieved.

In the present work, $(Ba,Sr)TiO_3$-based ceramics were fabricated in an attempt to obtain low-resistivity PTCR at a lower sintering temperature. BN was used as the sintering aid to lower the sintering temperature. The effect of BN content on resitivity and PTC effect is discussed. Two kinds of double donors, $Y_2O_3 + Nb_2O_5$ and $Sb_2O_3 + Nb_2O_5$, were added separately, and their doping effects on the room-temperature resistivity of the materials are compared. To further lower the room-temperature resistivity, metallic Cr was added to a selected material system. The effects of the metal content and the sintering atmosphere on the electrical properties of $(Ba,Sr)TiO_3$-based materials were investigated.

2. Experimental procedure

2.1. Raw materials

Commercially available reagent-grade powders were used as starting materials. $BaCO_3$, $SrCO_3$ and TiO_2 were used to form the principal crystal phase of $(Ba,Sr)TiO_3$. Y_2O_3, Sb_2O_3, Nb_2O_5, MnO_2, SiO_2, Al_2O_3, BN and Cr were used as the additives.

2.2. Processing

The material compositions designed in the present work are shown in Table 1. Throughout the present work, the materials prepared are termed as Samples 1–8 based on the compositions shown in this table. The weighted powders for each composition were mixed for 24 h using a Restch planetary ball miller. After milling, the resultant slurry was dried in an oven and then the powders were calcined at 1000 °C for 2 h in a Carbolite high-temperature furnace. After sieved, the calcined powders were subjected to uniaxial pressure of 150 MPa to form pellets. The compacts (Samples 1–6) were sintered in air at different sintering temperatures (1220–1260 °C) for 20 min in the high-temperature furnace. The Cr-containing compacts (Samples 7 and 8) were first sintered at 1250 °C for 20 min in a reducing atmosphere, which was created by covering the compacts with graphite powder. They were then subjected to oxidation in air at 600 °C for 20 min. The heating and cooling rates for all the samples were 5 and 10 °C/min, respectively.

2.3. Characterization

The resistance-temperature property of the sample obtained was measured by a KATO X-Y functionally testing apparatus. The density of the sample was measured using the Archimedes method. A JSM scanning electron microscopy (SEM) was used to observe the microstructure of samples.

3. Results and discussion

3.1. Effect of BN

As the sintering aid, BN was added in the $(Ba_{0.92}Sr_{0.08})TiO_3$-based material system. From the colors of the sintered samples, i.e. grey blue, it is noted that good semiconducting materials were achieved in the sintering temperature range of 1220 to 1260 °C.[19] It was reported that the typical sintering temperature for PTC ceramics was above 1300 °C.[2, 7, 11] Therefore, in the present work, PTC materials were obtained at lower sintering temperatures due to the addition of BN. Ho and Hsieh[6] attributed this sintering promotion effect to the oxidation of BN at 900 °C and a formation of a boron-containing liquid phase.

Three compositions, i.e. Samples 1–3, were used to evaluate the effect of BN content on the material elec-

Table 1
Compositions of designed materials

Sample number	Composition
1	$(Ba_{0.92}Sr_{0.08})TiO_3 + 0.0010Y_2O_3 + 0.0005Nb_2O_5 + 0.0004MnO_2 + 0.1AST + 0.02BN$
2	$(Ba_{0.92}Sr_{0.08})TiO_3 + 0.0010Y_2O_3 + 0.0005Nb_2O_5 + 0.0004MnO_2 + 0.1AST + 0.05BN$
3	$(Ba_{0.92}Sr_{0.08})TiO_3 + 0.0010Y_2O_3 + 0.0005Nb_2O_5 + 0.0004MnO_2 + 0.1AST + 0.10BN$
4	$(Ba_{0.92}Sr_{0.08})TiO_3 + 0.0010Sb_2O_3 + 0.0005Nb_2O_5 + 0.0004MnO_2 + 0.1AST + 0.02BN$
5	$(Ba_{0.92}Sr_{0.08})TiO_3 + 0.0010Sb_2O_3 + 0.0005Nb_2O_5 + 0.0004MnO_2 + 0.1AST + 0.05BN$
6	$(Ba_{0.92}Sr_{0.08})TiO_3 + 0.0010Sb_2O_3 + 0.0005Nb_2O_5 + 0.0004MnO_2 + 0.1AST + 0.10BN$
7	$(Ba_{0.92}Sr_{0.08})TiO_3 + 0.0010Sb_2O_3 + 0.0005Nb_2O_5 + 0.0004MnO_2 + 0.1AST + 0.05BN + 0.15Cr$
8	$(Ba_{0.92}Sr_{0.08})TiO_3 + 0.0010Sb_2O_3 + 0.0005Nb_2O_5 + 0.0004MnO_2 + 0.1AST + 0.05BN + 0.25Cr$

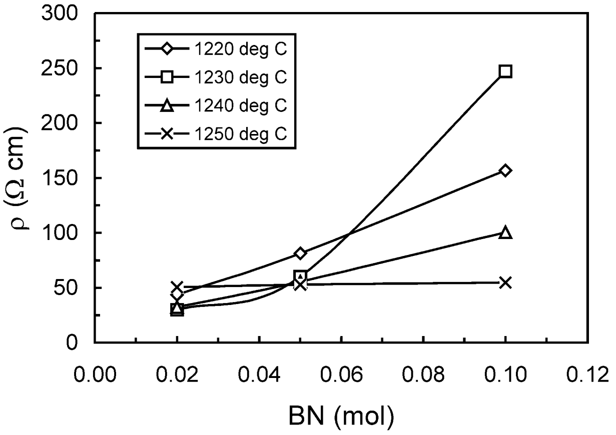

Fig. 1. Variations of room-temperature resistitvtiy with content of BN, where data of Samples 1 to 3 prepared at different sintering temperatures were used.

trical properties. Fig. 1 shows the variations of room-temperature resistivity with the content of BN. In the investigated sintering temperature range, it can be seen that the room-temperature resistivity of the sample obtained at a given sintering temperature increases with an increase in the content of BN. During sintering, as the content of BN increased, more boron-containing liquid phases had formed, which contribute to a higher resistivity.

Fig. 2 shows the variations of $\rho_{\max}/\rho_{\min}$ with the content of BN. A maximum of $\rho_{\max}/\rho_{\min}$ ratio was obtained at the BN content equal to 0.05 in the sintering temperature range. Based on the work reported by Ho,[2°] an improvement in the PTC effect up to 0.05 BN can be attributed to an increase in the surface acceptor state with the BN content. However, further addition of BN led to a weaker PTC effect due to the poor quality of grain boundaries arising from the occurrence of more boron-containing liquid phases during sintering.

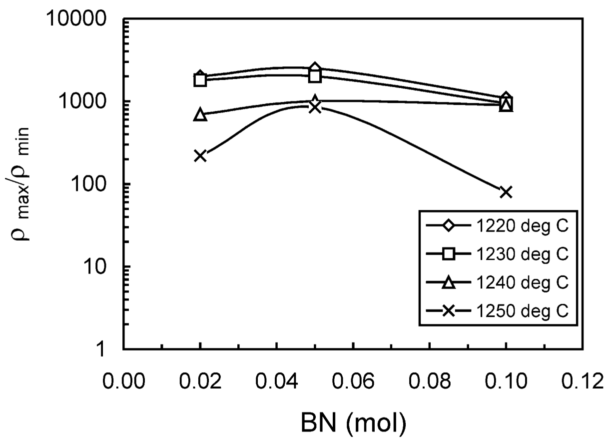

Fig. 2. Variations of $\rho_{\max}/\rho_{\min}$ with content of BN, where data of Samples 1–3 prepared at different sintering temperatures were used.

3.2. *Effect of double donors*

It was noted that double-donor doping was more effective than single-donor doping on lowering the resistivity of PTC materials.[12] In the present work, two double-donor systems, $Y_2O_3+Nb_2O_5$ and $Sb_2O_3+Nb_2O_5$, were selected for the $(Ba_{0.92}Sr_{0.08})TiO_3$-based material, and their doping effects on the resistivity are compared in this section.

Fig. 3 shows the room-temperature resistivities of Samples 2 and 5 sintered at different temperatures. In the investigated temperature range, it can be seen that at a given sintering temperature, the room-temperature resistivity of Sample 5 is always lower than that of Sample 2. This result indicates that the double donor $Sb_2O_3+Nb_2O_5$ provides a better resistance-reducing function than $Y_2O_3+Nb_2O_5$ for the present material system.

As the elements for achieving semiconducting grains, yttrium and antimony ions can substitute barium ions in the lattices. The chemical valence of yttrium is very stable, therefore, at high temperature it is very difficult for Y^{3+} to generate a different valence. On the contrary, when Sb^{3+} was added in, it substituted for Ba^{2+}. Simultaneously, part of Sb^{3+} changed into Sb^{5+} during sintering.[21] As a result, Sb^{5+}, as well as Nb^{5+}, substituted for Ti^{4+}. Three reactions occurred concurrently when $Sb_2O_3+Nb_2O_5$ were added, as shown in Equations (1)–(3),

$$\begin{aligned} x\mathrm{Sb_2O_3} + 2\mathrm{BaTiO_3} &= 2\left(\mathrm{Ba}^{2+}_{1-x}\mathrm{Sb}^{3+}_{x}\right)\left[\mathrm{Ti}^{4+}_{1-x}\left(\mathrm{Ti}^{4+}\bullet \mathrm{e}\right)_x\right]\mathrm{O_3} \\ &\quad + x/2\mathrm{O_2} + 2x\mathrm{BaO} \qquad (1) \end{aligned}$$

$$\begin{aligned} y\mathrm{Sb_2O_5} + 2\mathrm{BaTiO_3} &= 2\mathrm{Ba}^{2+}\left[\mathrm{Ti}^{4+}_{1-2y}\mathrm{Sb}^{5+}_{y}\left(\mathrm{Ti}^{4+}\bullet \mathrm{e}\right)_y\right]\mathrm{O_3} \\ &\quad + y/2\mathrm{O_2} + 2y\mathrm{TiO_2} \qquad (2) \end{aligned}$$

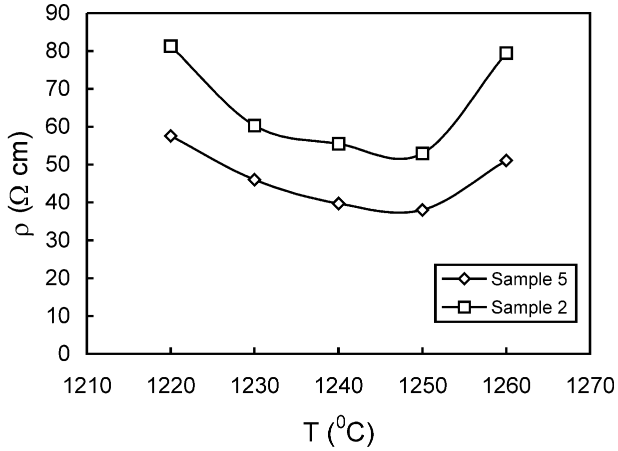

Fig. 3. Room-temperature resistivities of Samples 2 and 5 prepared at different sintering temperatures.

Table 2
Room-temperature resistivities of Samples 7 and 8 before and after oxidation

	Resistivity (Ω cm)	
	Sample 7	Sample 8
Before oxidation	6.3	0.73
Afteroxidation	1117.0	1.53

$$
\begin{aligned}
&z\mathrm{Nb_2O_5} + 2\mathrm{BaTiO_3} \\
&\quad = 2\mathrm{Ba}^{2+}\left[\mathrm{Ti}^{4+}_{1-2z}\mathrm{Nb}^{5+}_{z}\left(\mathrm{Ti}^{4+} \bullet \mathrm{e}\right)_z\right]\mathrm{O_3} \\
&\qquad + z/2\mathrm{O2} + 2z\mathrm{TiO_2} \qquad (3)
\end{aligned}
$$

where ($Ti^{4+}\bullet e$) is in a weak bound state, which is considered the origin for achieving semiconducting grains. For the $Sb_2O_3+Nb_2O_5$ doping PTC material system, three reactions contributed to the semiconducting process simultaneously, which led to a higher reaction entropy (highly disordered lattices) and hence a higher reaction activity of grains. As a result, the substitutive reactions proceeded completely and thoroughly and resulted in a lower room-temperature resistivity.

3.3. *Effect of Cr*

As discussed in the previous sections, BN can lower the sintering temperature of PTC materials, and the double donor $Sb_2O_3+Nb_2O_5$ is better than $Y_2O_3+Nb_2O_5$ in lowering the room-temperature resistivity. Taking into account both the low resistivity and good PTC effect, the composition of Sample 5 was chosen for further investigation. the metal Cr was added to further lower the room-temperature resistivity. Samples 7 and 8 were obtained by reducing sintering (keeping a low resistance of the metal) and the oxidation treatment (enhancing PTC effect) process.

The measured resistivities are listed in Table 2. It can be seen that the room-temperature resistivity decreases distinctly with an increase in Cr in a reducing atmosphere. This is mainly attributed to the introduction of a low-resistance metallic phase to the ceramic matrix. After oxidation, the resistivity of Sample 8 increases slightly. But the resistivity of Sample 7 increases tremendously, and its value is much higher than even that of Sample 5 (without the addition of Cr). In our earlier work,[18] the relationship between the principal valence and the content of Cr after oxidation was discussed. It revealed that after oxidation the valence of the Cr element was +3 for a small amount of doping, but 0 for a large amount of doping. Due to its principal valence of +3, the abnormal increase in resistivity of Sample 7 resulted from the diffusion of partial Cr^{3+} into Ti^{4+} and hence a compensation between the acceptor, Cr^{3+}, and the donors, Nb^{5+} and Sb^{5+}. For Sample 8, low resisitivity was obtained because the principal valence of Cr was 0 and the resistivity only slightly increased due to the oxidation of Cr. The resistance-temperature properties of Samples 7 and 8 are shown in Figs. 4 and 5, respectively. It can be found that after oxidation, Sample 7 exhibits a negative temperature coefficient (NTC) effect, while Sample 8 shows a PTC effect. All the samples show NTC effects before oxidation. In our earlier work,[18] the above phenomena, i.e., the relationships between the resistance-temperature property and the sintering atmosphere factor, and the metallic content were explained in detail. In the present work, Sample 8 possesses both low room-temperature resistivity and PTC effect after oxidation. However, this PTC effect is weak compared with the Cr/(Ba,Pb)TiO_3-based system, as reported in our earlier work.[18]

Fig. 6 shows SEM images of Sample 8 sintered in reducing atmosphere and after oxidation treatment. Before oxidation, the bar-shaped Cr can be found, which is located at the grain boundary of the (Ba,Sr)-TiO_3-based ceramics. After oxidation, a more porous microstructure is shown due to the volume expansion of the metal during oxidation treatment. The density

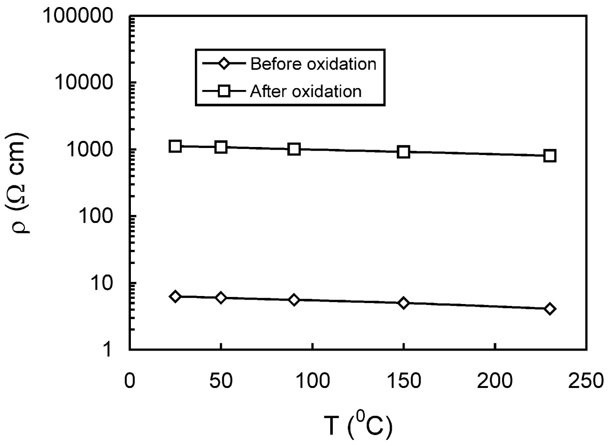

Fig. 4. Variations of resistivity with temperature of Sample 7 before and after oxidation.

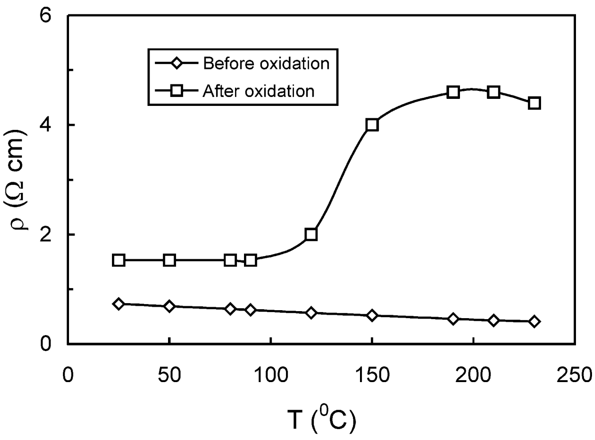

Fig. 5. Variations of resistivity with temperature of Sample 8 before and after oxidation.

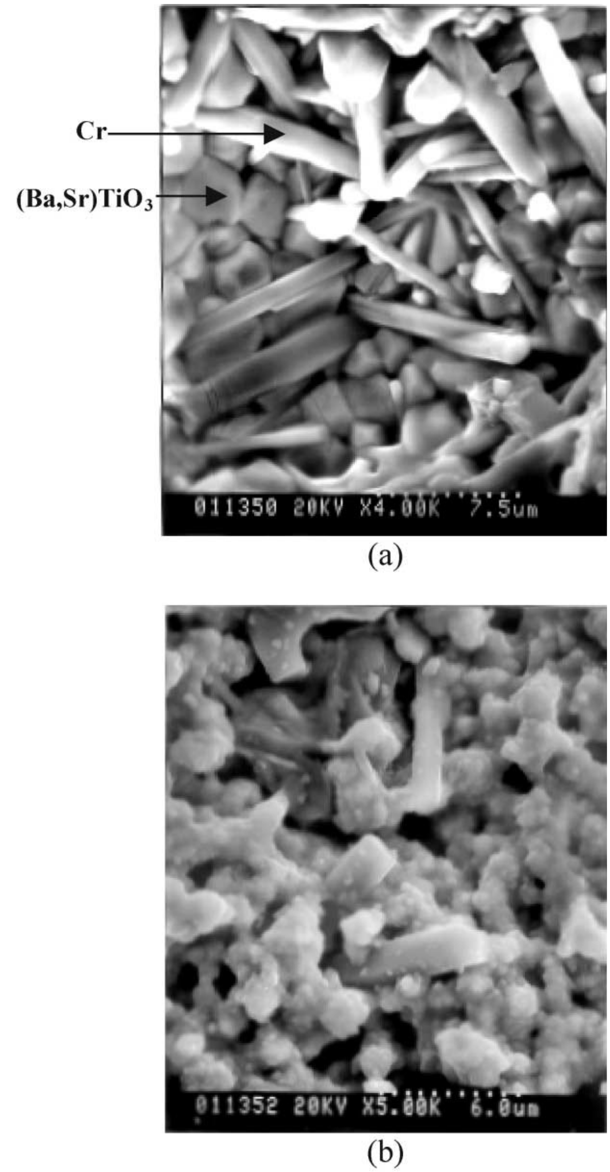

Fig. 6. SEM images of Sample 8 (a) before oxidation and (b) after oxidation.

measurement shows that the density of Sample 8 is 5.58 g/cm^3 before oxidation and 5.36 g/cm^3 after oxidation, respectively. This result is consistent with the SEM observation. The weak PTC effect could be attributed to the lower density obtained after oxidation, which resulted in a poor quality of grain boundaries and hence a low acceptor state density. The acceptor states located at grain boundaries are considered as the origin of the PTC effect.[14, 15]

4. Conclusions

The effects of the additives BN, $Y_2O_3 + Nb_2O_5$, $Sb_2O_3 + Nb_2O_5$, and Cr on the electrical properties of $(Ba_{0.92}Sr_{0.08})TiO_3$-based PTCR were investigated. It was shown that BN could be used as an effective aid to lower the sintering temperature of PTC materials. The addition of a suitable amount of BN could also enhance the PTC effect, but the room-temperature resistivity would increase with increasing BN content. Lower room-temperature resistivity can be achieved by the addition of the double donor $Sb_2O_3 + Nb_2O_5$ which is more effective than $Y_2O_3 + Nb_2O_5$. At a given Cr content and with a reducing sintering process, followed by an oxidation treatment, the (Ba,Sr)TiO$_3$-based material had a low room-temperature resistivity and a PTC effect. The PTC effect achieved, however, was weak, which was attributed to the lower density after oxidation, and hence a poor quality of grain boundaries of the material prepared.

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