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PTCR behaviour of Ba_2LaBiO_6-doped $BaTiO_3$ ceramics

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Abstract

The influences of Ba_2LaBiO_6 content on the electrical property and the microstructure of $BaTiO_3$-based materials have been studied. At a low dopant concentration the grain size is influenced significantly by the donor concentration. With an increase in Ba_2LaBiO_6 content the grain size decreases rapidly. All the prepared Ba_2LaBiO_6 doping $BaTiO_3$-based thermistors show typical PTC effect. As the amount of Ba_2LaBiO_6 added in $BaTiO_3$-based ceramics increases, the room temperature resistivity appears to exhibit a minimum value. At high Ba_2LaBiO_6 content ($\geq$0.15), the room temperature resistivity increased again with increasing Ba_2LaBiO_6 content. At a given content of Ba_2LaBiO_6, the influence of sintering temperature on the electrical properties of samples has been investigated. A maximum of ρ_{max}/ρ_{min} ratio was obtained at the sintering temperature equal to 1270 °C at a given content of Ba_2LaBiO_6.

Keywords: PTC; Ba_2LaBiO_6; Microstructure; Electrical property

1. Introduction

Positive temperature coefficient (PTC) thermistors are characterized by an increase in the electrical resistance with temperature. Apart from special polymer composites (so-called Polyswith-PTCs), commercial PTC-components are based on a doped, polycrystalline, n-semiconducting barium-titanate ($BaTiO_3$) ceramic. Insulating $BaTiO_3$ (with a conductivity of around $10^{-3}\ \Omega^{-1}\ cm^{-1}$) can be transformed into semiconducting material by small additions of donor dopants, such as La^{3+} at the Ba^{2+} site or Nb^{5+} at the Ti^{4+} site [1–3]. Controlled incorporation of donor dopants in combination with an optimized ceramic process lead to positive temperature coefficient resistivity (PTCR) materials [4,5].

Heywang explained the PTCR effect in terms of double Schottky barriers at the grain boundaries. According to this model, these barriers result from electron trapping by acceptor states at the interfaces [6]. Later on, Jonker extended the model considering the influence of polarization on the resistivity below the Curie point [7–9].

The donor dopants in $BaTiO_3$-based ceramics are often a tripostive or pentapositive valence state oxides. Sometimes they are the mixture of tripostive and pentapositive valence state oxides. Recently, in our research it was firstly found that $BaTiO_3$ materials doped with Ba_2LaBiO_6 compounds showed typical PTC characteristic. As a kind of donor dopant, Ba_2LaBiO_6 can simultaneously supply two kinds of different valence ions (La^{3+} and Bi^{5+}). There are many other compounds also to contain tripostive and pentapositive valence state ions like Ba_2LaBiO_6. According to this research there are more compounds to be selected as donor dopants in $BaTiO_3$-based ceramics. In the present study, the influence of composition on the microstructure and electrical properties of $BaTiO_3$-based PTC thermistors was studied.

2. Experimental

Analytical grade $BaTiO_3$, Ba_2LaBiO_6, $Mn(NO_3)_2$, Al_2O_3, SiO_2, and TiO_2 powders were weighed in appropriate proportions, as shown in Table 1. The weighed powders were agate milled in planetary for 24 h in alcohol. The ball-milled slurries were dried at 120 °C in an oven for 6 h. The dried powders were ground carefully in mortar and passed through a 250-mesh sieve. Subsequently, the mixture of powders was pressed at 175 MPa into 18 mm diameter and about 2.5 mm high cylindrical pellets. Pellets were sintered at 1290 °C for 1 h in air, and then furnace cooled. The Ag pastes with thickness of about 15 μm were spread on opposite-side surface of the sintered samples using a screen printer.

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Table 1
Chemical composition of the samples designed in this study

Sample	Composition (molecular ratio)
N1	$100BaTiO_3 + 0.100Ba_2LaBiO_6 + 0.03Mn(NO_3)_2 + 3(3Al_2O_3 + 3SiO_2 + TiO_2)$
N2	$100BaTiO_3 + 0.125Ba_2LaBiO_6 + 0.03Mn(NO_3)_2 + 3(3Al_2O_3 + 3SiO_2 + TiO_2)$
N3	$100BaTiO_3 + 0.150Ba_2LaBiO_6 + 0.03Mn(NO_3)_2 + 3(3Al_2O_3 + 3SiO_2 + TiO_2)$
N4	$100BaTiO_3 + 0.175Ba_2LaBiO_6 + 0.03Mn(NO_3)_2 + 3(3Al_2O_3 + 3SiO_2 + TiO_2)$
N5	$100BaTiO_3 + 0.200Ba_2LaBiO_6 + 0.03Mn(NO_3)_2 + 3(3Al_2O_3 + 3SiO_2 + TiO_2)$

After the pastes were dried at room temperature, the samples were heated at 600 °C for 30 min.

For microstructural investigation the samples were mounted in epoxy in a cross-section orientation and then polished using standard metallographic techniques. The specimens were etched in HF solution (4% HF) for 10 s. The microstructure of the samples was investigated by using a scanning electron microscope (Model: JSM5610LV). The average grain size of the samples was estimated by using the line-intersecting method. The samples of each composition were prepared for measuring electrical resistance. The samples were held with a holder in a tube furnace, and their temperatures were measured with a digital thermometer. The electrical resistance of the samples in the furnace was measured with a digital multimeter (Fluke 45) from 25 to 350 °C in steps of 10 °C. The accuracy of the furnace temperature is ±0.5 °C.

3. Results and discussion

The SEM images obtained from the surface of as-sintered samples N1, N2, N3, and N5 are shown in Fig. 1(a–d), respectively. Fig. 1(a) reveals that its average grain diameters are ∼9.0 μm. Similarly in samples N2 and N3, their average grain diameters are ∼5.5 and ∼5.0, respectively. At a low dopant concentration the grain size is influenced significantly by the donor concentration. With an increase in Ba_2LaBiO_6 content the grain size decreases rapidly. However, in samples N5, a bimodal grain size distribution is observed. Grains of about 40 μm coexist with a fine-grained matrix (grain size about 1 μm). Exaggerated grain growth in $BaTiO_3$ ceramics, is frequently associated to a non-uniform distribution of the donor dopant in the $BaTiO_3$ powder [10]. Donor dopant restricts grain growth of $BaTiO_3$ at the sintering temperature and then, a strong inhibition of the grain growth in those dopant enriched regions is achieved.

With an increase in donor dopant concentration grain size decreased because of a significant dopant drag on the boundary mobility, and grain boundary volume increased [11]. This was harmful to conductivity. However, at small dopant concentrations, with an increase in dopant concentration donor incorporation by electronic compensation was helpful to increase the conductivity. And donor incorporation by electronic compensation was main factor to increase the conductivity. So the effect of grain size on the conductivity was covered up.

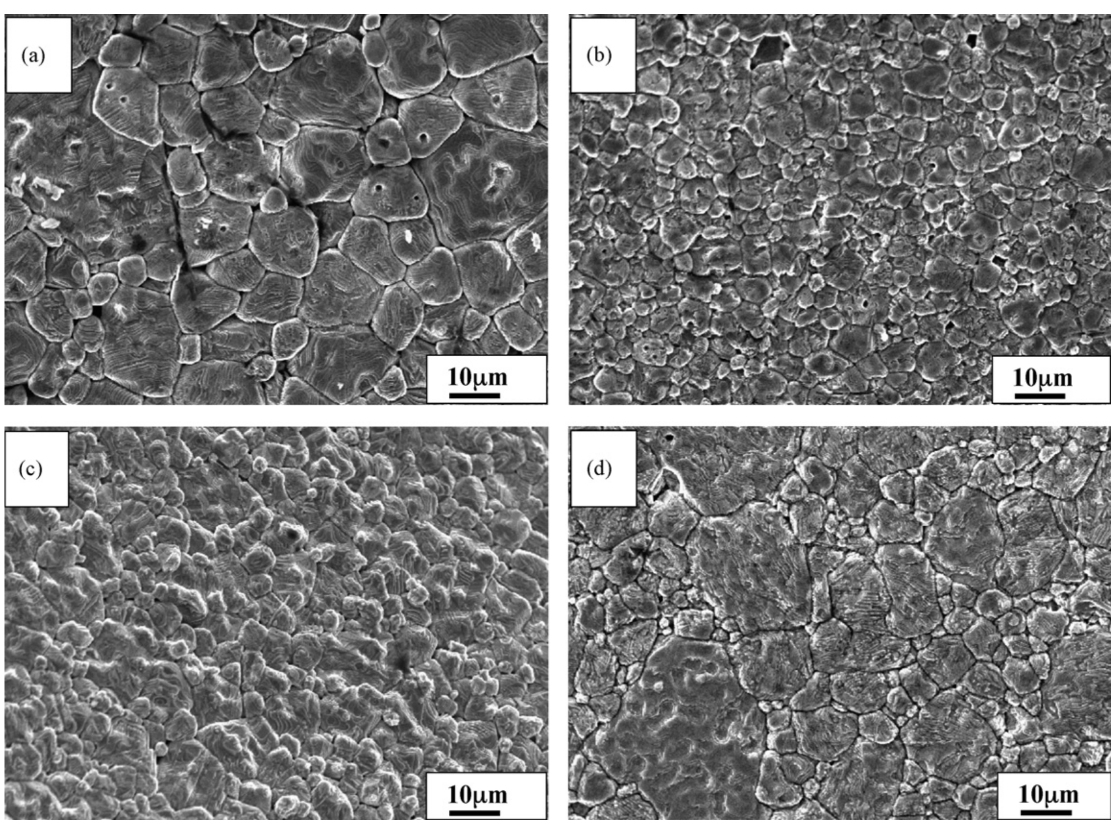

Fig. 1. SEM images of the surface of as-sintered samples (a) N1 (Ba_2LaBiO_6 = 0.100), (b) N2 (Ba_2LaBiO_6 = 0.125), (c) N3 (Ba_2LaBiO_6 = 0.150), and (d) N5 (Ba_2LaBiO_6 = 0.200).

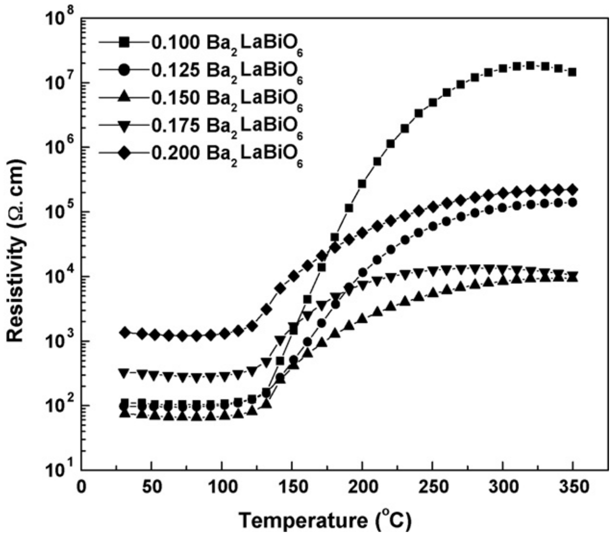

Fig. 2. Resistivity–temperature curves of the samples doped with different Ba_2LaBiO_6 content sintered at 1290 °C for 1 h.

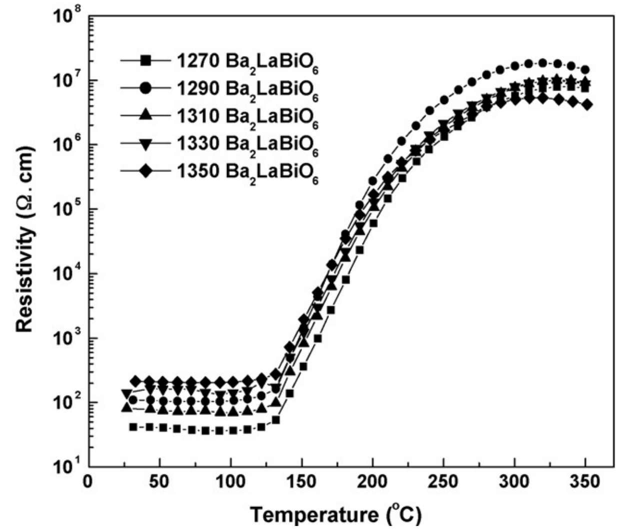

Fig. 3. Resistivity–temperature curves of N1 samples at different sintering temperature for 1 h.

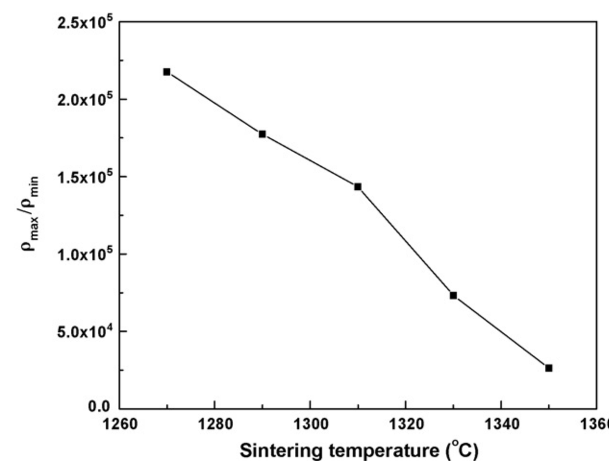

Fig. 4. Variation of ρ_{max}/ρ_{min} ratio of N1 samples with sintering temperature.

At high dopant concentrations, with an increase in dopant concentration grain decreasing in size and donor incorporation by vacancy compensation, both were harmful to conductivity.

As the donor dopant, Ba_2LaBiO_6 was added in the $BaTiO_3$-based material system. From the colors of the sintered samples, i.e. grey blue, it is noted that good semiconducting materials were achieved [12]. The resistivity–temperature curves of the samples sintered at 1290 °C for 1 h are shown in Fig. 2. It can be found that the samples show typical PTC effect. In order to obtain semiconducting ceramics with PTCR behavior, light doping with elements substituting at the Ba or Ti site is required, which is associated to the formation of electrons as charge compensation defects. Ba_2LaBiO_6 contains La^{3+} and Bi^{5+} ions in an ordered arrangement. As the elements for achieving semiconducting grains, La^{3+} substituted for barium ions in the lattices and Bi^{5+} substituted for Ti ions [13]. The reaction occurred when Ba_2LaBiO_6 was added, as shown in the equation,

$$x\mathrm{Ba_2La^{3+}Bi^{5+}O_6} + 2\mathrm{BaTiO_3} = \left(\mathrm{Ba}^{2+}_{1-x}\mathrm{La}^{3+}_{x}\right)\left[\mathrm{Ti}^{4+}_{1-x}(\mathrm{Ti}^{4+}\cdot \mathrm{e})_x\right]\mathrm{O_3} + \mathrm{Ba}^{2+} \times \left[\mathrm{Ti}^{4+}_{1-2x}\mathrm{Bi}^{5+}_{x}(\mathrm{Ti}^{4+}\cdot \mathrm{e})_x\right]\mathrm{O_3} + x\mathrm{BaTiO_3} + 2x\mathrm{BaO} + \frac{x}{2}\mathrm{O_2}$$

As the amount of Ba_2LaBiO_6 added in $BaTiO_3$-based ceramics increases, the resistivity decreases to a minimum value probably. At high Ba_2LaBiO_6 content (≥0.150), the resistivity increased again with increasing Ba_2LaBiO_6 content. This resistivity dependence on doping Ba_2LaBiO_6 is similar to that of conventional $BaTiO_3$ ceramics [14]. At small concentrations, donor incorporation by electronic compensation explained the high conductivity. As the average dopant concentration increased the local donor concentration at the grain boundary increased rapidly because of segregation [15]. This had one important effect that dopant incorporation at the grain boundary shifted from electronic to vacancy compensation, resulting in the formation of highly resistive layers.

Fig. 3 shows resistivity–temperature curves of N1 samples sintered at 1270, 1290, 1310, 1330, and 1350 °C for 1 h. The samples exhibit good PTC characteristics. Fig. 4 shows the variations of ρ_{max}/ρ_{min} for samples N1 with the sintering temperature. A maximum of ρ_{max}/ρ_{min} ratio was obtained at the sintering temperature equal to 1270 °C at a given content of Ba_2LaBiO_6. The presence of second phases, especially liquid phases at the grain boundary, may enhance the defect diffusion rates, thus influencing the thickness and resistivity of the insulating region [11]. Elevation of the sintering temperature led to a weaker PTC effect due to the poor quality of grain boundaries arising from the occurrence of a larger amount of liquid phase during sintering.

4. Conclusion

$BaTiO_3$-based PTC thermistors doped with Ba_2LaBiO_6 showed typical PTC effect. As the elements for achieving semiconducting grains, La^{3+} substituted for Ba ions in the lattices and Bi^{5+} substituted for Ti ions. At a low dopant concentration the grain size is influenced significantly by the donor concentration because of a significant dopant drag on the boundary mobility. All the prepared Ba_2LaBiO_6 doping $BaTiO_3$-based thermistors show typical PTC effect. As the amount of Ba_2LaBiO_6 added in $BaTiO_3$-based ceramics increases, the room temperature resistivity appears to exhibit a minimum value. At high Ba_2LaBiO_6 content ($\geq$0.15), the room temperature resistivity increased again with increasing Ba_2LaBiO_6 content. A maximum of ρ_{max}/ρ_{min} ratio was obtained at the sintering temperature equal to 1270 °C at a given content of Ba_2LaBiO_6.

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