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Research Article

NTCR Behavior of La-Doped $BaBiO_3$ Ceramics

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The influence of the composition on the microstructure and electrical properties of $BaBi_{1-x}La_xO_3$ $(0 \leq x \leq 0.1)$ NTC thermistors was investigated. A single phase of $BaBi_{1-x}La_xO_3$ with a monoclinic structure was prepared by solid state reaction method. The relationship between the resistivity and the reciprocal of absolute temperature of the prepared NTC thermistors was linear, indicative of NTC characteristics. The resistivity and the coefficient of temperature sensitivity first decreased with increasing x in the range of $x < 0.03$ and then increased with further increase in x. However the alpha parameter value increased to a maximum value and then decreased again.

1. Introduction

Negative temperature coefficient (NTC) thermistors are thermally sensitive resistors whose resistance decreases with increasing temperature. They are mainly used in electronics for the suppression of in-rush current, for temperature measurement and control, and for compensation for other circuit elements [1, 2]. There is a large choice of NTC materials, but those most used in practice are based on solid solutions of transition metal oxides, such as Mn_3O_4, Co_3O_4, and NiO, with the spinel structure of the general formula AB_2O_4 [3].

$BaBiO_3$ has a monoclinic crystal structure with a breathing- and a tilting-mode lattice distortion of BiO_6 octahedra [4], and it shows semiconducting behavior despite the theoretical calculation predicting metallic behavior [5]. The distortion produces inequivalent Bi sites and is believed to cause a possible valence disproportionation (or charge density wave) of Bi^{3+} and Bi^{5+}. $BaBiO_3$ is semiconducting material and shows a good NTC effect [6].

The selection of a given metal oxide material for applications of NTC thermistors is mainly determined by the required electrical properties and low cost of manufacturing of the thermistors. And those most used in practice are based on solid solutions of transition metal oxides with high sintering temperature. The sintering temperatures of $BaBi_{1-x}La_xO_3$ ceramics are only about 750°C. At the same time in our research it has been found that $BaBi_{1-x}La_xO_3$ ceramics show a good NTC effect. It is interesting to study the crystalline structure and the electronic properties of $BaBi_{1-x}La_xO_3$ ceramics as a new NTC materials system.

2. Experimental Procedures

$BaBi_{1-x}La_xO_3$ ceramic samples were prepared by solid state reaction method. The nominal composition of analytical grade $BaCO_3$, La_2O_3, and Bi_2O_3 powders was mixed in ethanol with an Al_2O_3 mortar. The obtained mixture was calcined in air at 800°C for 8 hours followed by pressing the powder into disc shape pellet. The disc was sintered at 750°C for 4 hours followed by a cooling rate of 200°C/h in air.

The crystalline structure of the prepared samples was analyzed by an X-ray diffractimeter (BRUKERD8-ADVANCE) using Cu K_α radiation with 40 KV, 35 mA, at a scanning rate of 6°/min. The microstructure of the samples was investigated by using a scanning electron microscope (Model: JSM5610LV). The Ag pastes with thickness of about 15 μm were spread on opposite surfaces of the sintered samples using a screen printer. After the pastes were dried at room temperature, the samples were heated at 550°C for 30 minutes. The electronic resistance of the samples in the furnace was measured with a digital multimeter (Fluke 45) in steps of 20°C. The accuracy of the furnace measurements was ±0.5°C.

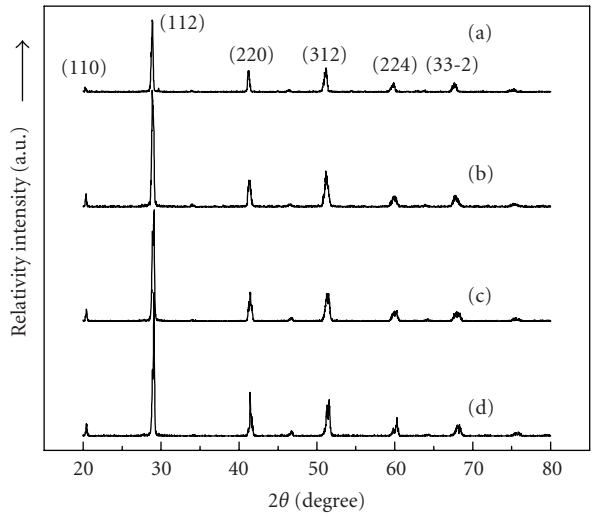

Figure 1: XRD patterns for (a) $BaBi_{0.99}La_{0.01}O_3$, (b) $BaBi_{0.97}La_{0.03}O_3$, (c) $BaBi_{0.95}La_{0.05}O_3$, and (d) $BaBi_{0.90}La_{0.10}O_3$.

3. Results and Discussion

Figure 1 displays the XRD patterns of $BaBi_{1-x}La_xO_3$, respectively, showing that a single phase of $BaBi_{1-x}La_xO_3$ was prepared in the range $0 \leq x \leq 0.1$. The ion radius of La^{3+}, Bi^{3+}, and Ba^{2+} are 1.15 Å, 1.03 Å, and 1.35 Å, respectively. And Bi^{3+} is more similar to La^{3+} in the radius than Ba^{2+}. So Bi^{3+} was replaced by La^{3+} in the lattices prior to Ba^{2+}. From the facts that Bi does not occupy the Ba site [7] and that the BaO phase is not observed in the XRD pattern, it is demonstrated that the La ion does not occupy the Ba site but the Bi site.

The SEM images obtained from the surface of as-sintered samples $BaBi_{1-x}La_xO_3$ are shown in Figures 2(a)–2(d), respectively. With an increase in La content the grain size decreases rapidly. The influence of La content in the samples on grain size was attributed to La^{3+} ions substituting for Bi^{3+} ions in the lattices. And the melting point of La_2O_3 is much higher than Bi_2O_3. With an increase in La content the melting point of $BaBi_{1-x}La_xO_3$ increases. Under the same sintering temperature diffusion of ions in material becomes more difficult with higher melting point. So grains in material with low melting point grow up easily.

The resistivity versus $1/T$ curves of $BaBi_{1-x}La_xO_3$ materials with different La contents sintered at 750°C is shown in Figure 3. The relationship between the resistivity and the reciprocal of absolute temperature of the prepared NTC thermistors is linear, indicative of NTC characteristics. Furthermore, the resistivity measured at other temperatures showed basically the same behavior as at room temperature, irrespective of the measuring temperature. $BaBiO_3$ shows, at room temperature, a distorted perovskite lattice with a monoclinic unit cell (*I2/m*) characterized by two different B sites, occupied, respectively, by Bi^{3+} and Bi^{5+}. X-ray photoemission [8] and X-ray absorption spectroscopy [9] point to a minimal charge transfer between the two Bi sites.

Table 1: Resistivity at 25°C, $B_{25/125}$ constant, and temperature coefficient of resistance for the samples sintered at 750°C.

Sample	Resistivity at 25°C (Ω·cm)	$B_{25/125}$ constant (K)	Alpha parameter-value (%/°C)
$BaBiO_3$	3756	3513	−0.029
$BaBi_{0.99}La_{0.01}O_3$	1104	3275	−0.027
$BaBi_{0.97}La_{0.03}O_3$	388	2998	−0.025
$BaBi_{0.95}La_{0.05}O_3$	2561	3626	−0.030
$BaBi_{0.90}La_{0.10}O_3$	6450	3969	−0.033

The data on the electrical parameters such as room temperature resistivity, thermistor constant, and temperature coefficient of resistance are given in Table 1. The resistivity and the coefficient of temperature sensitivity first decreased with increasing x in the range of $x < 0.03$ and then increased with further increase in x. Room temperature resistivity and B constant of materials are related to active energy. So the ρ_{25} and the $B_{25/125}$ show the same trend with an increase in La content of $BaBi_{1-x}La_xO_3$ compounds. However the alpha parameter values of samples increased to a maximum value and then decreased again. The alpha parameter value of NTC materials is related to B constant. And the alpha parameter value decreases with an increase in B constant.

La substitution introduce electrons into the conduction band which is ascribed to the Bi(La)6s-O2p hybridized band [10]. And Shiro Kambe pointed out that the decrease in resistivity was due to the increase in the formal Bi valence in the solid solutions of $BaBiO_3$ compounds [11]. So with an increase in La content the resistivity of samples decreased. However the microstructure of samples became another main factor to affect the resistivity of them with further increasing La content. Grain size decreased rapidly with an increase in La content, and crystal boundary area enlarged. So the room temperature resistivity of samples increased when the La content in $BaBi_{1-x}La_xO_3$ compounds was high (>0.03).

4. Conclusion

A single phase of $BaBi_{1-x}La_xO_3$ with a monoclinic structure was prepared in the range $0 \leq x \leq 0.1$. The melting point of $BaBi_{1-x}La_xO_3$ increases with an increase in La content. The $BaBi_{1-x}La_xO_3$ compounds with different La content show typical NTC effect. As the amount of La in $BaBi_{1-x}La_xO_3$ compounds increases, the resistivity at room temperature decreases to a minimum value. At high La content (>0.03), the resistivity increased again with increasing La content.

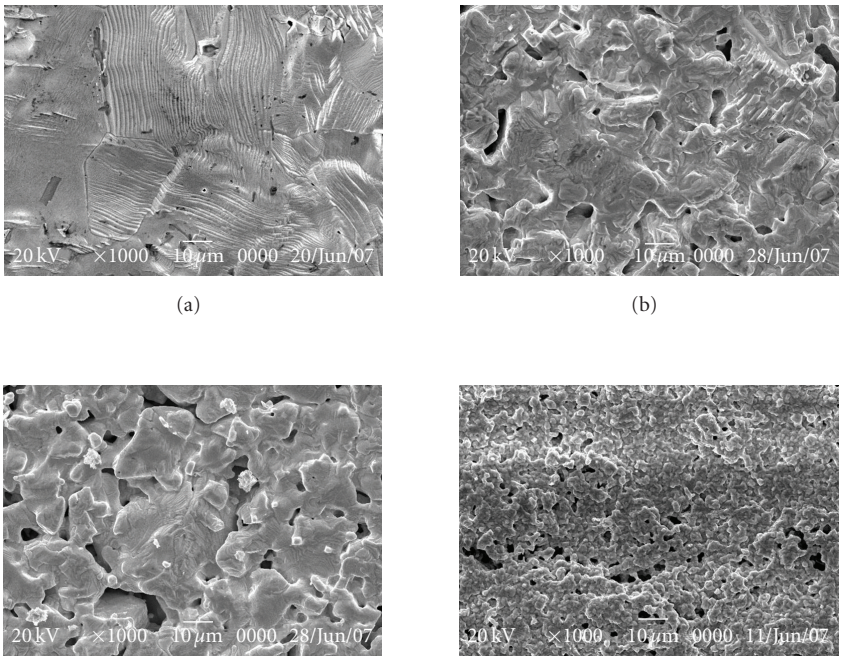

Figure 2: SEM images of as-sintered samples: (a) $BaBiO_3$, (b) $BaBi_{0.99}La_{0.01}O_3$, (c) $BaBi_{0.97}La_{0.03}O_3$, and (d) $BaBi_{0.90}La_{0.10}O_3$.

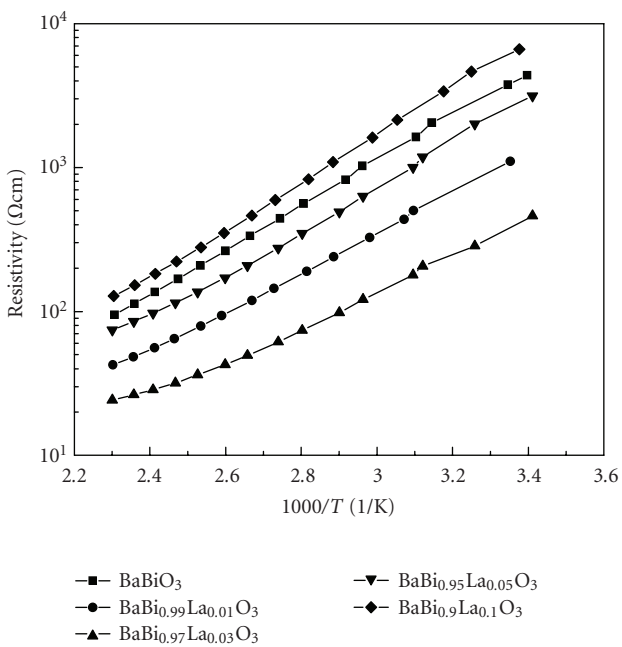

Figure 3: Resistivity-1/T curves of $BaBi_{1-x}La_xO_3$ ceramics sintered at 750°C for 4 hours.

Acknowledgment

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