Preparation and electrical properties of perovskite ceramics in the system BaBi$_{1-x}$Sb$_x$O$_3$ (0 ≤ x ≤ 0.5)

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ABSTRACT

The effect of the composition on the electrical properties of BaBi$_{1-x}$Sb$_x$O$_3$ (0 ≤ x ≤ 0.5) negative temperature coefficient (NTC) thermistors was studied. Major phases present in the sintered bodies of BaBi$_{1-x}$Sb$_x$O$_3$ (0 < x < 0.5) ceramics were BaBi$_{0.5}$Sb$_{0.5}$O$_3$ compounds with a rhombohedral structure and BaBiO$_3$ compounds with a monoclinal structure. Most pores were located in the grains of BaBiO$_3$ and BaBi$_{0.5}$Sb$_{0.5}$O$_3$ ceramics. It was apparent that the ρ_{25} and B$_{25/85}$ constant of the thermistors increased with increasing Sb content.

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1. Introduction

Negative temperature coefficient (NTC) thermistors are thermally sensitive resistors whose resistance decreases with increasing temperature [1]. 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 [2–4]. 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$_3$O$_4$, Co$_3$O$_4$, and NiO, with the spinel structure of the general formula AB$_2$O$_4$ [5–8].

However, their application is commonly limited to temperatures below 200 °C. Rare earth oxide (Sm, Tb, Y ...) can be used for measurements at high temperature. The conduction of such oxide is dependent on the atmosphere (P$_{O_2}$) and densification [9]. These effects can be limited by doping. Wang et al. have studied the doping of Y$_2$O$_3$ by ZrO$_2$ and CaZrO$_3$ for NTC high temperature components [10]. Their high resistivity (some MΩ at 800 °C) and B value around 24,000 K are not applicable for ambient to 1000 °C applications. Feltz and Pölzl have proposed a system of compositions Fe$_x$Ni$_y$Mn$_{3-x-y}$O$_4$ based on the spinel structure for high temperature applications. Yet *B* values are not stable for temperatures below 400 °C, which limits the temperature range for applications [11].

Oxide ceramic semiconductors based on the perovskite type structure are expected to be more available. Relatively high conductivity values and low activation energies or even metallic behavior are often found for perovskites. PTC ceramics based on donor doping, e.g. by substitution of a rare earth metal M^{3+} for Ba^{2+} in the series Ba$_{1-x}$M$_x^{3+}$Ti$_{1-x}^{4+}$Ti$_x^{3+}$O$_3$ provide even a lower value, e.g. σ_{25} = 2 Ω^{-1} cm^{-1} [12,13]. LaCoO$_3$ has a room temperature conductivity of about 100 Ω^{-1} cm^{-1} with metallic behavior above 330 °C [14,15]. Commonly, the thermistor sensitivity for temperature measurement is entirely insufficient.

BaBiO$_3$ has a monoclinic crystal structure with a breathing- and a tilting-mode lattice distortion of BiO6 octahedra, and it shows semiconducting behavior despite the theoretical calculation predicting metallic behavior [16]. 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+} [17].

Recently, in our research it has been firstly found that BaBi$_{1-x}$Sb$_x$O$_3$ (0 ≤ x ≤ 0.5) materials only show NTC effect over a wide temperature scale. In the present study, the influence of composition on the electrical properties of BaBi$_{1-x}$Sb$_x$O$_3$ NTC thermistors was investigated.

2. Experimental

High-purity BaCO$_3$, Sb$_2$O$_3$ and Bi$_2$O$_3$ powders were weighed in appropriate proportions, as shown in Table 1. The weighed powders, alcohol and toluene were ball-milled for 24 h in teflon jar using ZrO$_2$ as grinding media. The ball-milled slurries were dried at 120 °C in an oven for 2 h. The dried powders were ground carefully

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Table 1
Chemical composition of the samples designed in this study.

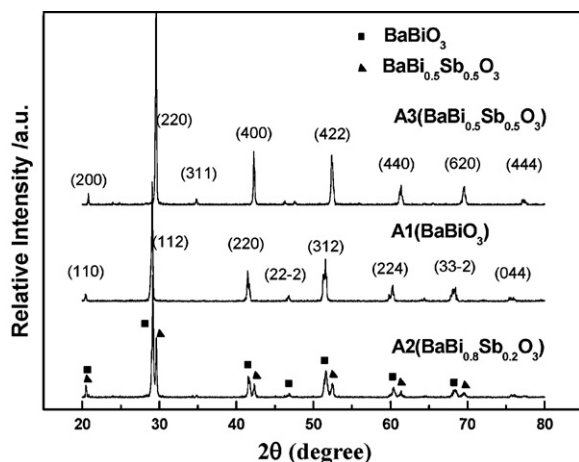| Sample	Chemical composition
A1	$BaBiO_3$
A2	$BaBi_{0.8}Sb_{0.2}O_3$
A3	$BaBi_{0.5}Sb_{0.5}O_3$

in mortar and passed through a 250-mesh sieve. The mixture was subsequently calcined at 850 °C with a heating rate (10 °C/min) for dwell time of 4 h. The sintered mass was again crushed and pulverized to obtain the fine powder. Subsequently, the fine powders was pressed at 175 MPa into 18 mm diameter and about 2.5 mm high cylindrical pellets. Pellets of samples A1, A2, and A3 were sintered at 900, 1000, and 1100 °C for 2 h in air, respectively. Ag pastes with thickness of about 15 μm were spread on opposite-side surface of the sintered samples using a screen printer. After the pastes were dried at room temperature, the samples were heated at 600 °C for 30 min.

The crystalline structure of samples was analyzed by an X-ray diffractometer (BRUKERD8-ADVANCE) using Cu K_α radiation with 40 KV, 35 mA, at a scanning rate of 6°/min. The microstructure of samples was investigated using a scanning electron microscope (Model: JSM5610LV). The average grain size of the samples was estimated 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 °C to 350 °C in steps of 20 °C. The accuracy of the furnace measurements is ±0.5 °C.
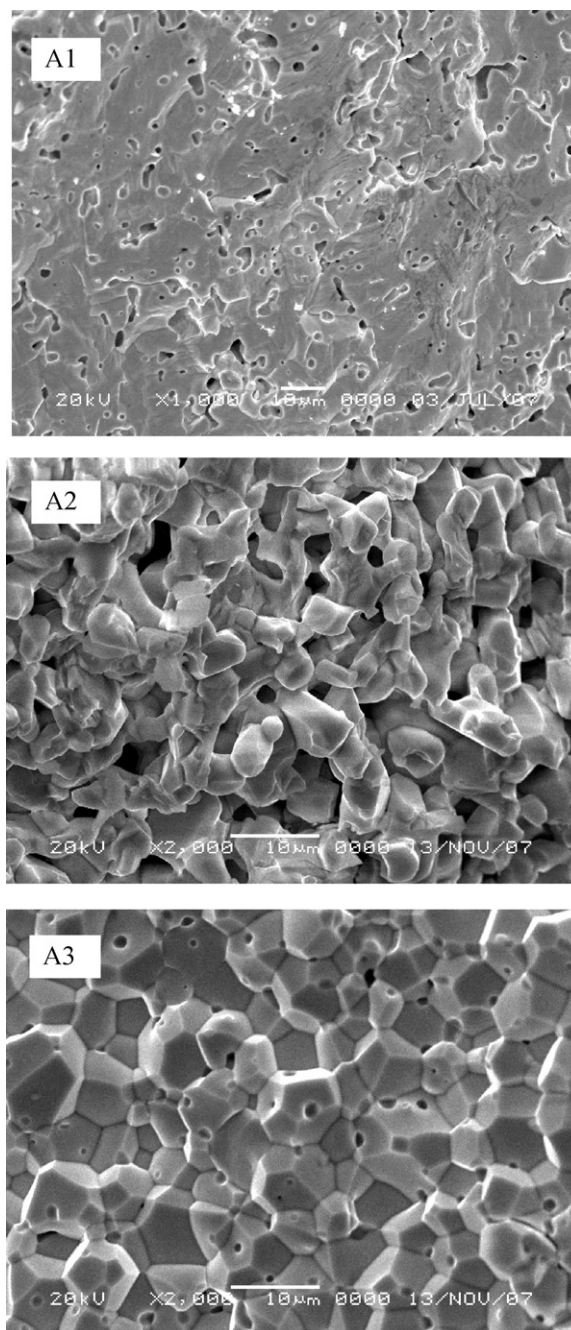
3. Results and discussion

X-ray diffractometry analysis of the powder was carried out using Cu Kα radiation at an angle $2\theta = 20$–80°. The XRD patterns from the samples A1, A2, and A3 are shown in Fig. 1. The sample A1 was consisted of single phase $BaBiO_3$ with a monoclinic structure, and the sample A3 was consisted of single phase $BaBi_{05}Sb_{0.5}O_3$ with a rhombohedral structure. Major phases present in the sample A2 were $BaBiO_3$ phase and $BaBi_{0.5}Sb_{0.5}O_3$ phase. In $BaBi_{0.5}Sb_{0.5}O_3$ compounds the +5 oxidation state of Sb is more stable than that of Bi. Therefore, the valence states of bismuth and antimony can be assigned as Bi (+3) and Sb (+5) [18]. The system $BaBi_{0.8}Sb_{0.2}O_3$ was consisted of $BaBiO_3$ phase and $BaBi_{0.5}Sb_{0.5}O_3$ phase. So $BaBi_{0.5}Sb_{0.5}O_3$ phase cannot be achieved by Sb^{5+} ions replacing the Bi^{5+} ions in the lattices of $BaBiO_3$ phase.

The SEM images of cross-section of ceramics samples A1, A2, and A3 are shown in Fig. 2. The $BaBi_{1-x}Sb_xO_3$ ceramics were relatively dense, ranging from 93% to 97% of the theoretical density. Most pores were located in the grains of ceramics samples A1 and A3. Because ceramics samples A1 and A3 were consisted of single phase $BaBiO_3$ and $BaBi_{05}Sb_{0.5}O_3$, respectively. And no second phases or impurities were present at the grain boundaries. Air in


Fig. 2. SEM images obtained from the cross-section of as-sintered samples A1 ($BaBiO_3$), A2 ($BaSb_{0.2}Bi_{0.8}O_3$), and A3 ($BaSb_{0.5}Bi_{0.5}O_3$).

the samples A1 and A3 was enclosed and leaved in the grains when the samples were sintered at high temperature with a quick heating rate.

Fig. 3 shows plots of the resistivity (ρ) against the reciprocal of the absolute temperature ($1/T$) for the system $BaBi_{1-x}Sb_xO_3$ NTC thermistors with different Sb content. It was found that the NTC thermistors operated steadily with the straight line relationship between the electrical resistivity and the temperature over a wide temperature range, indicating NTC thermistor characteristics. $BaBiO_3$ shows 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+} [17]. X-ray photoemission [19] and X-ray absorption spectroscopy [20] point to a minimal charge transfer between the two Bi sites. Sb^{5+} and Bi^{5+} are similar in the electron

Fig. 1. XRD patterns for samples $BaBi_{1-x}Sb_xO_3$ ($x = 0$, 0.2, and 0.5).

Table 2
Resistivity at 25 °C, $B_{25/85}$ constant, and activation energy of the prepared $BaBi_{1-x}Sb_xO_3$ ($0 \leq x \leq 0.5$) NTC thermistors.

Sample	Chemical composition	Resistivity at 25 °C(Ω cm)	$B_{25/85}$ constant (K)	Activation energy (eV)
A1	$BaBiO_3$	3756	3392	0.293
A2	$BaBi_{0.8}Sb_{0.2}O_3$	59352	4537	0.391
A3	$BaBi_{0.5}Sb_{0.5}O_3$	62186000	5762	0.497
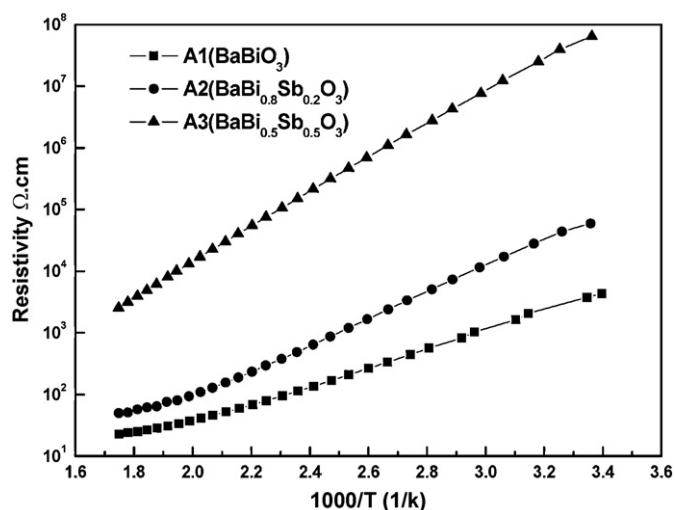
Fig. 3. Relationship between the resistivity and the reciprocal of the absolute temperature for the $BaBi_{1-x}Sb_xO_3$ thermistors.

structure. So $BaBi_{0.5}Sb_{0.5}O_3$ ceramic also shows semiconductive effect.

The slope of ρ versus $1/T$ curve is taken generally as a measure of the activation energy of conductivity. The resistivity can be expressed by the following Arrhenius equation:

$$\rho = \rho_0 \exp\left(\frac{B}{T}\right) \tag{1}$$

where ρ_0 is the resistivity of the material at infinite temperature, T is the absolute temperature, and B is the B constant, sometimes called the coefficient of temperature sensitivity. The room temperature resistivity, B constant, and activation energy are tabulated in Table 2 for the system $BaBi_{1-x}Sb_xO_3$ thermistors. The $B_{25/85}$ constant can be calculated by the following equation [21]:

$$B_{25/85} = \frac{\ln(\rho_{25}/\rho_{85})}{1/T_{25} - 1/T_{85}} \tag{2}$$

where ρ_{25} and ρ_{85} are the resistivity measured at 25 and 85 °C, respectively. This table indicates that the electrical properties of $BaBi_{1-x}Sb_xO_3$ NTC thermistors strongly depend on the composition. And the ρ_{25} and $B_{25/85}$ of $BaBi_{1-x}Sb_xO_3$ ceramics increased with increasing x due to an increase in the content of $BaBi_{0.5}Sb_{0.5}O_3$ phase in the system $BaBi_{1-x}Sb_xO_3$. Because the

system $BaBi_{1-x}Sb_xO_3$ ($0 < x < 0.5$) was consisted of $BaBiO_3$ phase and $BaBi_{0.5}Sb_{0.5}O_3$ phase. And the ρ_{25} and $B_{25/85}$ of $BaBi_{0.5}Sb_{0.5}O_3$ ceramics are higher than those of $BaBiO_3$ ceramics.

4. Conclusion

The NTC thermistors composed of $BaBi_{1-x}Sb_xO_3$ ($0 \leq x \leq 0.5$) ceramics were successfully sintered. Major phases present in the sintered bodies of $BaBi_{1-x}Sb_xO_3$ ($0 < x < 0.5$) ceramics were $BaBi_{0.5}Sb_{0.5}O_3$ compounds with a rhombohedral structure and $BaBiO_3$ compounds with a monoclinic structure. $BaBi_{0.5}Sb_{0.5}O_3$ cannot be achieved by Sb^{5+} ions replacing the Bi^{5+} ions in the lattices of $BaBiO_3$ phase. With increasing Sb content, the resistivity and coefficient of temperature sensitivity for the $BaBi_{1-x}Sb_xO_3$ ($0 \leq x \leq 0.5$) NTC thermistors increased. The $BaBi_{1-x}Sb_xO_3$ thermistors provided much flexibility in tailoring the electrical properties by controlling the composition.

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