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Electrical properties of binder-free thick film $BaY_xBi_{1-x}O_3$ NTC thermistors

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ABSTRACT

The microstructure and electrical properties of $BaY_xBi_{1-x}O_3$ thick film negative temperature coefficient thermistors, fabricated by screen printing, were investigated. The sintered thick films were the single-phase solid solutions of the $BaY_xBi_{1-x}O_3$ compounds with a monoclinic structure. The added Y_2O_3 led to a significant decrease in the grain size of the thermistors. The resistivity and coefficient of temperature sensitivity for the $BaY_xBi_{1-x}O_3$ ($0 \le x \le 0.15$) thick film NTC thermistors decreased first with increasing x in the range of $x < 0.04$ and then increased with further increase in x.

1. Introduction

Sophisticated thick film hybrid circuits increase the need for simple means of temperature compensation [1,2]. The recent progress in applying microcontrollers to control equipments requires a large number of low cost, highly reliable, temperature sensors [3]. Thick film thermistor are expected to meet these requirements because of high reproducibility, flexibility and compatibility, apart from cost effective method of fabrication and above all highly conducive to planarization.

Although the concept of thick film NTC devices is quite attractive from a system design and manufacturing viewpoint they are not widely known and used [4]. Screen printing is a cost effective technology to produce planar components. Thick film sinters onto ceramic substrate to form an interlocked bond between the medium that leads to adhesion of the thick film with the substrate.

In thick-film technology, the target film material is mixed with a binder material such as glass. However, Addition of binder material leads to poor electrical properties or significantly increases the possibility of chemical interaction with the metal electrodes due to the presence of complicated phases in the thick film. A few binder-free materials systems have been investigated [5]. However, these thick films are sintered with high temperature.

$BaBiO_3$ has a monoclinic crystal structure with a breathing- and a tilting-mode lattice distortion of BiO_6 octahedra [6], and its meting point is about 1050 °C. The sintering temperature of thick film $BaBi_{1-x}Y_xO_3$ NTC thermistors is only about 750 °C. The thick films $BaY_xBi_{1-x}O_3$ NTC thermistors are sintered onto ceramic substrate to form an interlocked bond with binder-free. It is interesting to study the effect of composition on the electrical properties of binder-free thick film $BaY_xBi_{1-x}O_3$ NTC thermistors.

2. Experimental procedures

The powder of semiconducting oxide $BaY_xBi_{1-x}O_3$ was prepared by mixing analytical grade oxides such as $BaCO_3$, Y_2O_3 and Bi_2O_3. The desired semiconducting oxide system was prepared by taking appropriate molar ratios of such oxides. The prepared mixture was then ground in an agate mortar to have a homogenized powder mixture. The mixture was subsequently sintered at 700 °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. The prepared powder was analyzed by an X-ray diffract meter (BRUKERD8-ADVANCE) using Cu Kα 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).

A set of $BaY_xBi_{1-x}O_3$ ($x = 0$, 0.02, 0.04, 0.08, and 0.15) thick film NTC thermistors were prepared by screen printing. Thick film thermistor pastes were prepared by blending the desired amount of $BaY_xBi_{1-x}O_3$ powder and an organic vehicle in an agate mortar. The composition of $BaY_xBi_{1-x}O_3$ powder to organic vehicle was kept as 70:30 wt.%. The pastes formulated using these compositions were found to have good thixotropy and printability. The prepared thick film thermistor pastes were then screen printed on to a 96% alumina substrate with pre-fired silver electrodes. The printed patterns then dried under IR lamp for 10–15 min in order to settle down the film and removal of excess organics and then fired in a thick film-firing furnace at 750 °C at dwell of 2 h. Thickness of the fired films was about 100 μm calculated by weight difference method. The resistance versus temperature measurement was carried out using Fluke 45 digital multimeter.

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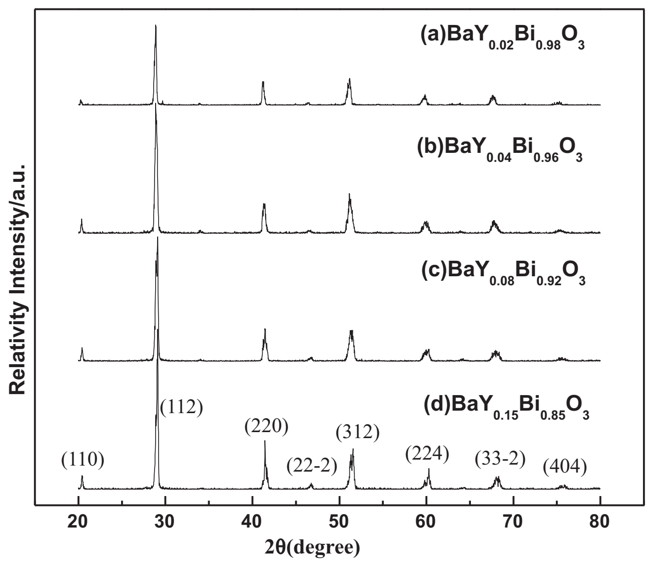

Fig. 1. XRD patterns for (a) $BaY_{0.02}Bi_{0.98}O_3$, (b) $BaY_{0.04}Bi_{0.96}O_3$, (c) $BaY_{0.08}Bi_{0.92}O_3$, and (d) $BaY_{0.15}Bi_{0.85}O_3$.

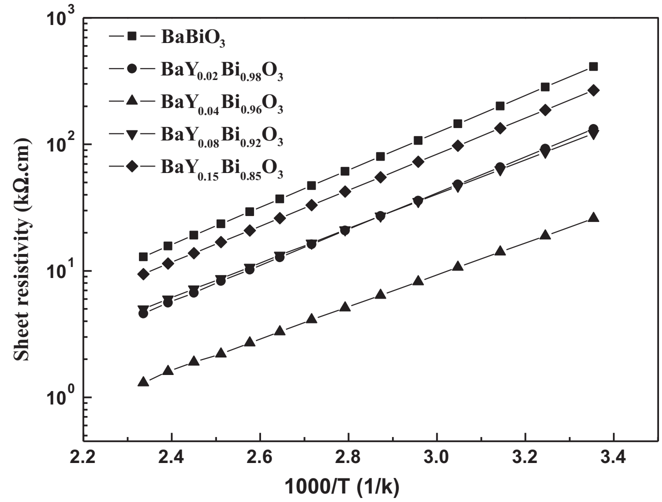

Fig. 3. Relationship between the sheet resistivity and the reciprocal of the absolute temperature for the thick film $BaBi_{1-x}Y_xO_3$ thermistors with different Y content.

3. Results and discussion

X-ray diffractometry analysis of the powder was carried out using Cu Kα radiation at an angle 2θ = 20–80°. The powder was the single-phase solid solutions of $BaY_xBi_{1-x}O_3$ with a monoclinic structure. As an example the XRD pattern from the $BaY_xBi_{1-x}O_3$ (x = 0.02, 0.04, 0.08, and 0.15) thick film sample is shown in Fig. 1. The ion radius of Y^{3+}, Bi^{3+}, and Ba^{2+} are 0.89 Å, 1.03 Å, and 1.35 Å, respectively. And Bi^{3+} is more similar to Y^{3+} in the radius than Ba^{2+}. So Bi^{3+} was replaced by Y^{3+} in the lattices prior to Ba^{2+}. From the facts that the Bi ions do not occupy the Ba site [7] and that the BaO phase is not observed in the XRD pattern, it is demonstrated that the Y ions do not occupy the Ba site but the Bi site.

Fig. 2 shows the SEM images obtained from the surface of the $BaY_xBi_{1-x}O_3$ thick films (a) x = 0.02, (b) x = 0.04, (c) x = 0.08, and (d) x = 0.15 sintered at 750 °C. It was found with increasing Y content the grain size decreased considerably. The influence of the Y content in the samples on the grain size is attributed to the Y^{3+} ions substituting for the Bi^{3+} ions in the lattices. And the melting point of Y_2O_3 is much higher than Bi_2O_3. With an increase in Y content the melting point of $BaY_xBi_{1-x}O_3$ increases. So at the same sinter-

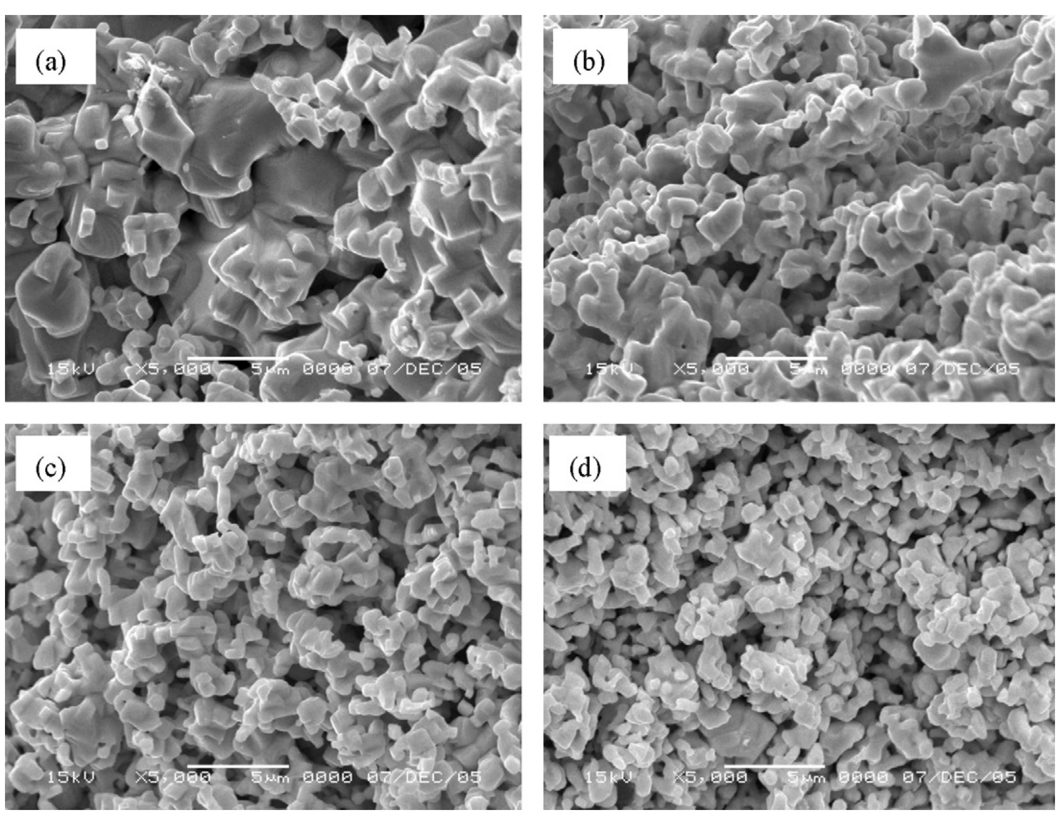

Fig. 2. SEM micrograph of the $BaBi_{1-x}Y_xO_3$ thick film thermistors (a) x = 0.02, (b) x = 0.04, (c) x = 0.08, and (d) x = 0.15.

Table 1
Electrical properties of the thick film thermistors.

Sample	Composition of thermistor	Sheet resistivity at 25 °C, kΩ cm	Thermistor constant ($B_{25/85}$) in K	Activation energy, eV
N1	$BaBiO_3$	411	3392	0.293
N2	$BaY_{0.02}Bi_{0.98}O_3$	132	3287	0.283
N3	$BaY_{0.04}Bi_{0.96}O_3$	26	2890	0.249
N4	$BaY_{0.08}Bi_{0.92}O_3$	122	3122	0.269
N5	$BaY_{0.15}Bi_{0.85}O_3$	267	3276	0.282

ing temperature the grains in samples grow up easily with low Y content.

Fig. 3 shows plots of the sheet resistivity (ρ) against the reciprocal of the absolute temperature ($1/T$) for the thick film $BaY_xBi_{1-x}O_3$ NTC thermistors with different Y content. It was found that the thick film 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, 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.

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:

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

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 1 for the thick film $BaY_xBi_{1-x}O_3$ thermistors. The $B_{25/85}$ constant can be calculated by the following equation [10]:

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

where ρ_{25} and ρ_{85} are the resistivity measured at 25 and 85 °C, respectively. This table indicates that the electrical properties of $BaY_xBi_{1-x}O_3$ thick film NTC thermistors strongly depend on the composition. The resistivity and coefficient of temperature sensitivity decreased first with increasing x in the range of $x < 0.04$ 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 $B_{25/125}$ show the same trend with an increase in Y content of $BaY_xBi_{1-x}O_3$ compounds.

4. Conclusion

The binder-free thick film NTC thermistors composed of $BaY_xBi_{1-x}O_3$ ceramics were successfully sintered at 750 °C. The thick films were the single-phase solid solutions of $BaY_xBi_{1-x}O_3$ with a monoclinic structure. With increasing Y content, the resistivity and coefficient of temperature sensitivity for the $BaY_xBi_{1-x}O_3$ ($0 \le x \le 0.15$) thick film NTC thermistors decreased to a minimum value and then increased again. The $BaY_xBi_{1-x}O_3$ thick film thermistors provided much flexibility in tailoring the electrical properties by controlling the composition.

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