Electrical properties of $\text{Ba}_{0.7}\text{Bi}_{0.3}\text{Fe}_{0.9}\text{Sn}_{0.1}\text{O}_3\text{--BaCo}_{0.02}^{\text{II}}\text{Co}_{0.04}^{\text{III}}\text{Bi}_{0.94}\text{O}_3$ thick film thermistors with wide-range adjustable parameters

CHANGLAI YUAN*, YUN YANG, YING LUO¹, LING YANG, GUOHUA CHEN and XINYU LIU

School of Material Science and Engineering, Guilin University of Electronic Technology, Guilin 541 004, People's Republic of China

¹Guilin Academy of Air Force, Guilin 541 004, People's Republic of China

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Abstract. A novel $(1-x)\text{Ba}_{0.7}\text{Bi}_{0.3}\text{Fe}_{0.9}\text{Sn}_{0.1}\text{O}_3\text{--}x\text{BaCo}_{0.02}^{\text{II}}\text{Co}_{0.04}^{\text{III}}\text{Bi}_{0.94}\text{O}_3$ ($0.2 \leq x \leq 0.9$) negative temperature coefficient (NTC) thick film thermistors with high thermistor constant was prepared by screen printing. The values of room-temperature resistivity, thermistor constant and activation energy of the thick film thermistors, increasing with the addition of $\text{Ba}_{0.7}\text{Bi}_{0.3}\text{Fe}_{0.9}\text{Sn}_{0.1}\text{O}_3$, are in the range of $35.5 \Omega\cdot\text{cm}$ – $1.34 \text{ M}\Omega\cdot\text{cm}$, 2067 – 6139 K and 0.177 – 0.527 eV , respectively. This means that the electrical properties of the thick films are adjustable at a wide range, depending on the compositions. Impedance analysis shows that the magnitude of thick film bulk resistance is mainly attributed to the contribution of grain boundary.

Keywords. Thick film thermistors; microstructures; electrical properties; impedance spectroscopy.

1. Introduction

Thermistors with negative temperature coefficient (NTC) of resistance have been widely used in various industrial and domestic applications pertaining to temperature monitoring, control and compensation, etc (Sachse 1975; Lavenuta 1997). However, the continuous development in applying microcontrollers to control equipments requires a large number of low-cost, highly-reliable, size-reduction temperature sensors. Thick film fabricated by screen printing offers a good opportunity for resolving the problems. In the thick film technology, it is well known that three essential components in thick film thermistor pastes are a functional phase, a glass frit and an organic viscous fluid also known as the organic vehicle (Jagtap *et al* 2008). The functional phases are generally composed of semiconductor metal oxides with general spinel-type formula AB_2O_4 (Park and Bang 2003; Schmidt *et al* 2004; Zhuang *et al* 2004; Song *et al* 2005; Varghese *et al* 2008). In order to decrease the room-temperature resistivity of thermistor films, it is general to add a conductive phase into the functional phase. The glass phase is mixed with the target film materials to keep the adhesion with the alumina substrate or make the thick film surface smoother.

Nowadays, the glass phases are mainly based on high percentage of lead and cadmium besides glass-forming agents such as boron, silicon and aluminum. The added conductive material is often high-cost RuO_2 powder in the preparation process of thick films. Jagtap *et al* (2008, 2010a, b, 2011) developed a few kind of thick film thermistors

based on the compositions spinel + RuO_2 . In their reports, the addition of RuO_2 plays surely the key role on decreasing the room-temperature resistivity of thick films. In order to reduce and even remove the use of high-cost RuO_2 , some Ru-free thick films are also studied as such the systems of $\text{NiMn}_2\text{O}_4 + \text{LaNiO}_3$, $\text{BaY}_x\text{Bi}_{1-x}\text{O}_3$, $\text{Cu}_{0.2}\text{Ni}_{0.5}\text{Zn}_{1.0}\text{Mn}_{1.3}\text{O}_4$, $\text{SrFe}_{0.9}\text{Sn}_{0.1}\text{O}_{3-\delta} + \text{BaBiO}_3 + \text{CuO}$ and Sr-Bi-Mn-Fe-O (Yuan *et al* 2010, 2011a; Luo *et al* 2011; Kang *et al* 2012; Aleksic *et al* 2013). In order to reduce Pb content in the glass phases, sometimes, the low-melt material like the Bi_2O_3 is partly introduced into the thick films (Kanade and Vijaya Puri 2008). Eventhough, many works in the thick film preparations have been done by researchers, only partial success is obtained in this area. Currently, the following shortcomings from the thick films are still the key issues and need to be resolved: (i) the hazardous elements from the glass phases should be restricted; (ii) the addition of RuO_2 in thick films leads to the higher cost in the preparation process of low-resistance thick films and weak linearity of $\log R\text{--}1/T$ curve and (iii) for the thick film thermistors, the high B constant is still difficult to obtain. For overcoming the problem, one kind of thick film thermistor with high thermistor constant and acceptable room-temperature resistivity needs to be investigated in the next work.

For the foregoing thick film thermistors containing RuO_2 , it is very difficult to obtain the thermistor constant of over 5000 K when the room-temperature resistivity is lower than $1.0 \text{ M}\Omega\cdot\text{cm}$. For the thick film systems of $\text{BaY}_x\text{Bi}_{1-x}\text{O}_3$, $\text{Cu}_{0.2}\text{Ni}_{0.5}\text{Zn}_{1.0}\text{Mn}_{1.3}\text{O}_4$, $\text{SrFe}_{0.9}\text{Sn}_{0.1}\text{O}_{3-\delta} + \text{BaBiO}_3 + \text{CuO}$ and Sr-Bi-Mn-Fe-O , to our information, the thermistor properties of the thick film thermistors are basically in agreement with the thick film thermistors

*Author for correspondence (yclguet@yahoo.com)

containing RuO_2 . However, the novel $\text{NiMn}_2\text{O}_4 + \text{LaNiO}_3$ composite system shows the higher thermistor constant of 5000 K when the room-temperature resistivity is 35 k Ω -cm. In thick film preparation process, it is crucial to employ the composite technology by the conjunction of high-constant thermistor materials and low-resistance thermistor phases.

In the earlier work, we found that the perovskite-type $\text{BaCo}_{0.02}^{\text{II}}\text{Co}_{0.04}^{\text{III}}\text{Bi}_{0.94}\text{O}_3$ thick film showed good NTC thermistor characteristics, low room-temperature resistivity ($\approx 4 \Omega$ -cm) and low sintering temperature (below 720 °C) (Yuan *et al* 2011b). We deduce that the material is expected to replace Pb-based glass frit and Ru-based conductive phase for the fabrication of lead-free and low-cost thick films. It was also found that the perovskite-structured $\text{Ba}_{0.7}\text{Bi}_{0.3}\text{Fe}_{0.9}\text{Sn}_{0.1}\text{O}_3$ ceramic was a good NTC thermistor with high thermistor constant (not published). Thus, in present work, a novel Pb-free, Ru-free and high-constant thick film NTC thermistor based on composite functional phases $\text{BaCo}_{0.02}^{\text{II}}\text{Co}_{0.04}^{\text{III}}\text{Bi}_{0.94}\text{O}_3 + \text{Ba}_{0.7}\text{Bi}_{0.3}\text{Fe}_{0.9}\text{Sn}_{0.1}\text{O}_3$, was prepared by screen-printing on alumina substrate. Compared with the current reported studies obtained by the other workers, the novel $\text{BaCo}_{0.02}^{\text{II}}\text{Co}_{0.04}^{\text{III}}\text{Bi}_{0.94}\text{O}_3 + \text{Ba}_{0.7}\text{Bi}_{0.3}\text{Fe}_{0.9}\text{Sn}_{0.1}\text{O}_3$ thick films show high thermistor constant and acceptable room-temperature resistivity comparable with that of the $\text{NiMn}_2\text{O}_4 + \text{LaNiO}_3$ composite system.

2. Experimental

$\text{BaCo}_{0.02}^{\text{II}}\text{Co}_{0.04}^{\text{III}}\text{Bi}_{0.94}\text{O}_3$ (abbreviated as BCCB) source powder was produced by mixing, grinding and firing the precursors BaCO_3 , Bi_2O_3 and Co_3O_4 . The mixtures were fired at 700 °C for 2 h. $\text{Ba}_{0.7}\text{Bi}_{0.3}\text{Fe}_{0.9}\text{Sn}_{0.1}\text{O}_3$ (abbreviated as BBFS) source powder was produced by firing the precursors BaCO_3 , Bi_2O_3 , Fe_2O_3 and SnO_2 for 4 h at 1000 °C. Thermistor pastes (ink) were prepared by mixing the desired amounts of produced $\text{BaCo}_{0.02}^{\text{II}}\text{Co}_{0.04}^{\text{III}}\text{Bi}_{0.94}\text{O}_3$ and $\text{Ba}_{0.7}\text{Bi}_{0.3}\text{Fe}_{0.9}\text{Sn}_{0.1}\text{O}_3$ source powders (as shown in table 1) with the organic vehicle in order to obtain printable pastes. Organic vehicle was a solution of ethyl cellulose, lecithin and 2-(2-butoxy

ethoxy-ethyl) acetate. The inorganic to organic ratio was kept at 70:30 (w/w%). The resultant thick film thermistor pastes were screen-printed onto a 96% alumina substrate using a stainless screen of 250 mesh size, then settled down and dried under IR lamp for 10–15 min. This printing process was repeated ten times and the thickness of each printing was 5–6 μm . The printed patterns were fired in a muffle furnace at 820 °C with a dwell time of 60 min. All the organic components were decomposed after printing the films during the sintering process of thick films.

Samples were routinely characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The thickness of the fired films was $55 \pm 4 \mu\text{m}$ as measured by XP-100 high resolution stylus-type surface profilometer. The d.c. electrical resistance of thermistor films was measured using a digital multimeter (Fluke 45) from 25 to 200 °C with a step of 5 °C. For all the thick films, impedance spectra were taken at room temperature using an Agilent (4294A) Impedance Analyzer with computer-controlled automated data collection, which increased the frequency logarithmically between 40 Hz and 10 MHz. The impedance spectra of BFBC-6 sample were also obtained as a function of frequency (40 Hz–2 MHz) at different temperatures (25–275 °C).

3. Results and discussion

XRD patterns of composite NTC thick films (Samples BFBC-1–BFBC-8) were shown in figure 1. From figure 1, it is seen that the thick films are mainly composed of BBFS and BCCB phases. Some residual aluminum bismuth iron oxide and Bi_2O_3 components are observed besides the BBFS and BCCB phases. The aluminum bismuth iron oxide and Bi_2O_3 are attributed to the contribution of the alumina substrate and the precursors of BBFS and BCCB compounds. This is a strong indication for the phase purity of the fired films and it may be concluded that no chemical reactions occur between $\text{BaCo}_{0.02}^{\text{II}}\text{Co}_{0.04}^{\text{III}}\text{Bi}_{0.94}\text{O}_3$ and $\text{Ba}_{0.7}\text{Bi}_{0.3}\text{Fe}_{0.9}\text{Sn}_{0.1}\text{O}_3$ source materials. The intensities of the diffraction peaks are an indicative of the percentages of the individual phases. With increasing BCCB content, the peak intensity of BCCB

Table 1. The resistivity at 25 °C, thermistor constant and activation energy of the thick film NTC thermistors.

Samples	Compositions (mole ratios)	Resistivity (ρ_{25}) at 25 °C (Ω -cm)	Thermistor constant ($B_{25/85}$) (K)	Activation energy (E_a) (eV)
BFBC-1	1 BBFS + 9 BCCB	35.5	2067	0.177
BFBC-2	2 BBFS + 8 BCCB	110	1958	0.168
BFBC-3	3 BBFS + 7 BCCB	218	2741	0.235
BFBC-4	4 BBFS + 6 BCCB	1894	3126	0.268
BFBC-5	5 BBFS + 5 BCCB	4935	3648	0.313
BFBC-6	6 BBFS + 4 BCCB	51.5 k	4858	0.417
BFBC-7	7 BBFS + 3 BCCB	406 k	5651	0.485
BFBC-8	8 BBFS + 2 BCCB	1.34 M	6139	0.527

Figure 1. XRD patterns of screen-printed thick films.

phase (marked ‘▲’) increases, while that of BBFS phase (marked ‘▼’) decreases. These indicate that the change of the peak intensities is in an agreement with the pre-designed compositions as shown in table 1.

The SEM pictures given in figure 2 show the difference in the surface density and the average grain size clearly. From figure 2 it can be concluded that the addition of BCCB phase led to the reduction of holes and pores between the film grains during the sintering process. With the rise in BCCB content, the surface of the thick films shows denser. Especially for samples BFBC-1, BFBC-2 and BFBC-3, fewer holes and pores are observed due to the introduction of large amounts of BCCB phases. It is believed that the addition of BCCB leads to the liquid-phase-sintering behaviour, and then significant improvement in the surface topography of thick films.

Figure 3(a) shows the relationship between the electrical resistivity (ρ) and Celsius temperature. The resistivity of all the films decreases exponentially with increase in temperature. For the thick film thermistor, the relationship between ρ and the reciprocal of absolute temperature ($1/T$) is shown in figure 3(b). From this figure, it is seen that a linear relation between the two parameters exists, an indicative of the NTC thermistor characteristics. On the basis of the linear relations, the thermistor constant ($\beta_{25/85}$) and activation energy (E_a) of the NTC thermistor films can be calculated by the following equations (Macklen 1979):

$$\beta_{25/85} = [\ln(\rho_{25}/\rho_{85})] / [(1/T_{25}) - (1/T_{85})], \quad (1)$$

$$E_a = \beta \cdot k_B, \quad (2)$$

where ρ_{25} and ρ_{85} are the resistivity measured at temperature T_{25} (25 °C) and T_{85} (85 °C), respectively. k_B is the Boltzmann constant.

The values of $\beta_{25/85}$ and E_a , obtained from (1) and (2), are listed in table 1, together with the resistivity at 25 °C (ρ_{25}).

This table indicates that the electrical properties of BBFS–BCCB composite NTC thick films strongly depend on the compositions. For all the thick films, the values of ρ_{25} , $\beta_{25/85}$ and E_a are in the wide range of 35.5 $\Omega \cdot \text{cm}$ –1.34 $\text{M}\Omega \cdot \text{cm}$, 2067–6139 K and 0.177–0.527 eV, respectively. From table 1, simultaneously, it is observed that, below the 80% BCCB content, the ρ_{25} of the thick films show the almost linear log decrease with increase in BCCB content. And then, the thick film resistivity shows little change with further increase of BCCB content, which denotes that the room-temperature resistivity of the composite films with higher BCCB content tends to be that of pure BCCB thick film. Based on the resistivity data of the thick film NTC thermistors, it is clear that the values of ρ_{25} and the $B_{25/85}$ constant can be adjustable depending on the compositions.

In polycrystalline materials, the resistive properties usually consist of several components, such as electrode-sample interface, grain boundary, intrinsic bulk contributions and grain shell, which can be separated and quantitatively determined in terms of their resistance and capacity by alternating current (a.c.) impedance spectroscopy measurements (Sinclair and West 1989; Irvine *et al* 1990). Thus, impedance spectroscopy is a powerful tool to investigate the intrinsic phenomena in thick film thermistors. Impedance spectroscopy data are commonly plotted as a complex plane plot of imaginary (Z'') vs real (Z') part of the impedance (Z^*), where in the ideal Debye case, each RC element is represented by a semicircle of radius $R/2$ with a maximum in Z'' at

$$\omega_{\max} = \frac{1}{RC} = \frac{1}{\tau}. \quad (3)$$

For all the thick film thermistors, the impedance data were obtained by Agilent Impedance Analyzer. For the BFBC-1 sample, at the measured temperature $T_m = 25$ °C, the diagram in figure 4(a) exhibits two poorly overlapping arcs. The impedance plots at the measured temperatures, $T_m = 50$ °C and 80 °C for BFBC-1 film (as shown in figure 4(b and c)), however, they show only one arc due to the limit of measured frequency range. Simultaneously, the Z'' and M'' (the imaginary of modulus M^*) spectroscopic plots of sample BFBC-1 at three different temperatures are shown in figure 5. From figure 5, it is found that two apparent peaks in Z'' and M'' plots are observed at 25 °C and only one peak at 25–85 °C. According to the foregoing impedance characteristics of the BFBC-1 sample at 25 °C, a careful deconvolution analysis of the impedance data for the thick films has been done: two arcs corresponding to two components of grain (at higher frequency region) and grain boundary (at lower frequency region) are obtained at the measured temperature, 25 °C. At the measured temperatures, 50 °C and 80 °C, the peak of M'' plot in figure 5 is not the maximum value, which denotes that there is still one electrical component at higher frequencies. Hence, the impedance spectra of sample BFBC-1 at different measured temperatures can be fitted by two RC elements in series. For electroceramic response presented in the

Figure 2. SEM images of screen-printed thick films.

impedance notation, usually the non-Debye contribution of the resistance is neglected and the non-ideal capacitor is considered. In order to fit real system impedances, real resistance (R) and ideal capacitor (C) can be replaced by parallel RQ element to account for non-Debye behaviour, where Q can be depicted by the following equation:

$$Z_Q^* = \frac{1}{c^m(i\omega)^n}, \quad (4)$$

where c^m is the specific capacitance in modified units of $\text{Fs}^{n-1}\text{cm}^{-1}$, ω the angular frequency; $0 < n \leq 1$ and $i = \sqrt{-1}$. c^m tends to an ideal capacitance, when the exponent n tends

to the value of 1. The equivalent circuit of one electrical component is then made up of one RQ element with a specific impedance of (Macdonald 1987; Schmidt and Brinkman 2007):

$$Z_{RQ}^* = \frac{\rho_{dc}}{1 + \rho_{dc}c^m(i\omega)^n}, \quad (5)$$

where ρ_{dc} is the real resistivity in modified units of $\Omega\text{s}^{-n}\text{cm}$. On the basis of the non-ideal analysis, the corresponding equivalent circuit model of sample BFBC-1 at different measured temperatures is shown in the inset of figure 4(a). From figure 4, it is found that the three fitting impedance spectra

Figure 3. (a) Relationship between electrical resistivity (ρ) and temperature for the BBFS–BCCB composite NTC thick films. (b) Relationship between ρ and the reciprocal of absolute temperature for the BBFS–BCCB composite NTC thick films.

are well consistent with the experimental data by the equivalent circuit. The extracted resistive components and relaxation time (τ) by the fitted results are shown in figure 6. The relaxation times of electrical-component responses can be calculated by the equation $\tau = RC$, where τ is the relaxation time and C the real capacitance. It is seen that the values of grain boundary resistance (R_{gb}), grain resistance (R_g), grain relaxation time (τ_g) and grain-boundary relaxation time (τ_{gb}) show the almost linear logarithm increase with the inverse of absolute temperature, a typical NTC thermistor behaviour.

For the impedance spectra of samples BFBC-2–BFBC-8, the arc disappears and an almost symmetrical decentralization semicircle is observed in figures 7 and 8. For the samples, BFBC-6–BFBC-8, the impedance data in figure 8 are obtained by measuring at 250°C due to over-high room-temperature electrical resistance. For electroceramics,

Figure 4. Cole–Cole plot of BFBC-1 sample at different temperatures. Inset in (a) shows the equivalent circuit model.

the decentralization phenomenon is typically correlated to a distribution of relaxation time and this behaviour obeys an empirical Cole–Cole response (Cole and Cole 1941). Thus, one parallel RQ attributed to the contribution of grain

Figure 5. The frequency dependence of Z'' at various temperatures for the BFBC-1 sample.

Figure 6. (a) The resistance (R) and (b) relaxation time (τ) of grain boundaries, and that of grains from the BFBC-1 sample as a function of the reciprocal of absolute temperature.

Figure 7. Cole–Cole plots of the samples (a) BFBC-2 and BFBC-3 and (b) BFBC-4 and BFBC-5 at room temperature.

boundary (as shown in inset of figure 8a) is used to fit the impedance data of samples, BFBC-2–BFBC-8. Both the impedance data and theoretical fitting attained in different BCCB content are shown in figures 7 and 8. The points on the diagrams are the experimental data, while the continuous line represents the theoretical fitting. An excellent agreement between the experimental data and fitting curve is obtained. The electrical responses are well represented by one parallel RQ equivalent circuit.

Figure 8. Cole–Cole plots at 250 °C for the samples (a) BFBC-6 and (b) BFBC-7 and BFBC-8. Inset in (a) shows the equivalent circuit model.

Figure 9 shows the complex impedance plots of sample BFBC-6 measured at various temperatures from 150 to 275 °C. The shape of all the impedance diagrams shows similar characteristics with that of sample BFBC-6 at room temperature. Thus, the Z'' vs Z' curves are obviously composed of one semicircle attributed to the contribution of grain boundary. An equivalent circuit model same as the inset of figure 8(a) is used to fit the impedance data of sample BFBC-6 at different temperatures. Based on figure 9(a and b), the fitting lines are also in good agreement with the experimental data at various temperatures, which indicates that the semicircle is surely made up of one electrical response. The parameters of R_{gb} and C_{gb} at various measured temperatures are extracted from the fitting results. Based on the calculated results, the logarithmic values of R_{gb} and τ_{gb} as a function of reciprocal of absolute temperature ($1/T$) are plotted in figure 10. Both τ_{gb} and R_{gb} , decrease with increasing temperature, show typical NTC thermistor characteristics. This suggests that the conduction process from grain boundary is of the hopping type, in accordance with the NTC behaviour observed.

Figure 11 shows the variations of Z'' and M'' of BFBC-6 sample as a function of logarithmic frequency measured at different temperatures. The M'' curves tend to zero at low frequencies, which denote that the electrode polarization effect is absent or negligible. Both the curves of M'' and Z'' in figure 11 show only a peak at the measured frequencies. The

Figure 9. Cole–Cole plots at temperatures 150–275 °C for the BFBC-6 sample. Inset in (a) shows the corresponding equivalent circuit model.

Figure 10. Frequency dependence of Z'' and M'' of BFBC-6 sample at various temperatures.

Figure 11. Variation of grain-boundary resistance (R_{gb}) and relaxation time (τ_{gb}) with inverse of absolute temperatures for the BFBC-6 sample.

peak frequency of M'' and Z'' curves is shifted to higher frequency region with the increase in temperature. According to the shift of peak frequency in Z'' and M'' curves, it is possible to analyse the apparent polarization by inspection of the magnitude of mismatch between the peaks of both functions. The two functions will be simultaneously considered between localized (short range conduction associated with dielectric relaxation) and non-localized (long range) conduction. According to figure 11 and the equation $f = 1/2\pi\tau$, the two obvious peaks of Z'' and M'' curves at various temperatures are in complete accordance with the following relation: $\tau_Z = \tau_M$, i.e., there is a perfect match of peaks of M'' and Z'' . The match is further evidence of non-localized or long-range conduction (Gerhardt 1994). For the BFBC-1 sample, however, the two maximum peaks of M'' and Z'' curves in figure 5 are in complete disaccord with following order: $\tau_Z > \tau_M$. For the BFBC-1 sample, thus, the presence of mismatch between the maximum peaks of M'' and Z'' ($\tau_Z > \tau_M$) is an evidence of localized conduction (Cao and Gerhardt 1990; Gerhardt 1994).

4. Conclusions

Thick film NTC thermistors based on the compositions $\text{Ba}_{0.7}\text{Bi}_{0.3}\text{Fe}_{0.9}\text{Sn}_{0.1}\text{O}_3 + \text{BaCo}_{0.02}^{\text{II}}\text{Co}_{0.04}^{\text{III}}\text{Bi}_{0.94}\text{O}_3$ have been produced by screen printing on alumina substrate. The relation between the resistivity and the absolute temperature for the prepared thick film thermistor is well linear. Depended upon the ratios of $\text{BaCo}_{0.02}^{\text{II}}\text{Co}_{0.04}^{\text{III}}\text{Bi}_{0.94}\text{O}_3$ and $\text{Ba}_{0.7}\text{Bi}_{0.3}\text{Fe}_{0.9}\text{Sn}_{0.1}\text{O}_3$, the value of the room resistivity ρ_{25} and $\beta_{25/85}$ are adjustable to desired values within the frame $\rho_{25} = 35.5 \Omega\cdot\text{cm}$, $\beta_{25/85} = 2067 \text{ K}$ and $\rho_{25} = 35.5\text{--}1.34 \text{ M}\Omega\cdot\text{cm}$ at $\beta_{25/85}$ values up to 6139 K. This means that the performance of the composite thick films is comparable with that of the spinel NTC ceramics. The magnitude of thick film resistance is mainly attributed to the contribution of grain boundary except for the composition 1BBFS + 9BCCB. For the BFBC-1 sample, the observed polarization process is due to a localized conduction. For the thick film samples BFBC-2–BFBC-8, there is the presence of a non-localized conduction mechanism. The grain boundary

properties of the thick films exhibit thermistor parameters with a negative temperature coefficient characteristic, as well as that of the thick films.

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References

- Aleksic O S, Nikolic M V, Lukovic M D, Nikolic N, Radojicic B M, Radovanovic M, Djuric Z, Mitric M and Nikolic P M 2013 *Mater. Sci. Eng. B* **178** 202
- Cao W and Gerhardt R 1990 *Solid State Ionics* **42** 213
- Cole K S and Cole R H 1941 *J. Chem. Phys.* **9** 341
- Gerhardt R 1994 *J. Phys. Chem. Solids* **55** 1491
- Irvine J T S, Sinclair D C and West A R 1990 *Adv. Mater.* **2** 132
- Jagtap S, Rane S, Gosavi S and Amalnerkar D 2008 *J. Eur. Ceram. Soc.* **28** 2501
- Jagtap S, Rane S, Gosavi S and Amalnerkar D 2010a *J. Mater. Sci.: Mater. Electron.* **21** 861
- Jagtap S, Rane S, Aiyer R, Gosavi S and Amalnerkar D 2010b *Curr. Appl. Phys.* **10** 1156
- Jagtap S, Rane S, Gosavi S and Amalnerkar D 2011 *Microelectron. Eng.* **88** 82
- Kanade S A and Vijaya Puri 2008 *Mater. Res. Bull.* **43** 819
- Kang J E, Ryu J, Han G, Choi J J, Yoon W H, Hahn B D, Kim J W, Ahn C W, Choi J H and Park D S 2012 *J. Alloys Compd.* **534** 70
- Lavenuta G 1997 *Sensors* **14** 46
- Luo Y, Li X Q and Liu X Y 2011 *J. Alloys Compd.* **509** 463
- Macdonald J R 1987 *Impedance spectroscopy* (New York: Wiley)
- Macklen E D 1979 *Thermistors* (Ayr, Scotland: Electrochemical Publications Ltd.) p. 33
- Park K and Bang D 2003 *J. Mater. Sci.: Mater. Electron.* **14** 81
- Sachse H B 1975 *Semiconducting temperature sensors and their applications* (New York: Wiley)
- Schmidt R, Basu A and Brinkman A W 2004 *J. Eur. Ceram. Soc.* **24** 1233
- Schmidt R and Brinkman A W 2007 *Adv. Funct. Mater.* **17** 3170
- Sinclair D C and West A R 1989 *J. Appl. Phys.* **8** 3850
- Song S G, Ling Z and Placido F 2005 *Mater. Res. Bull.* **40** 1081
- Varghese J M, Seema A and Dayas K R 2008 *Mater. Sci. Eng. B* **149** 47
- Yuan C L, Wu X F, Huang J Y, Liu X Y and Li B 2010 *Solid-State Sci.* **12** 2113
- Yuan C L, Liu X Y, Liang M F, Zhou C R and Wang H 2011a *Sens. Actuators A* **167** 291
- Yuan C L, Liu X Y, Zhou C R, Xu J W and Li B 2011b *Mater. Lett.* **65** 836
- Zhuang J W, Chang A M, Zheng J, Zhuang S C and Jia D Z 2004 *Ceram. Int.* **30** 1661