Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 28 (2008) 2501–2507
www.elsevier.com/locate/jeurceramsoc

Preparation, characterization and electrical properties of spinel-type environment friendly thick film NTC thermistors

Shweta Jagtap [a,b], Sunit Rane [a,*], Suresh Gosavi [c], Dinesh Amalnerkar [a]

[a] *Thick Film Materials and Electronics Packaging Division, Centre for Materials for Electronics Technology, Panchawati, Off Dr. Bhabha Road, Pune 411008, India*
[b] *Department of Electronic Science, University of Pune, Pune 411007, India*
[c] *Department of Physics, University of Pune, Pune 411007, India*

Received 10 March 2008; accepted 26 March 2008
Available online 23 May 2008

Abstract

Environment friendly thick film NTC thermistors based on spinel-type semiconducting electroceramics of different compositions $Mn_{1.85}Co_{0.8}Ni_{0.35}O_4$, and $Mn_{1.85}Co_{0.8}Ni_{0.35}O_4 + RuO_2$ were fabricated on alumina substrate. The basic bulk ceramics and the fired thick films were characterized by thermo-gravimetric analysis, X-ray diffraction, and scanning electron microscopy with energy depressive X-ray analysis. Thick film samples showed compact and homogeneous microstructure. The electrical parameters of the planar thick film NTC thermistors were determined. Depending on the ceramic composition, the prepared thick film NTC thermistors showed room temperature resistance in the range of 6–168 MΩ. The values of thermistor constant, $\beta_{25/300}$ ranged from 3600 to 4900 K.

Keywords: Powders-solid state reaction; Thick film; Sintering; Spinels; Eco-friendly; Thermistors; Sensors

1. Introduction

Oxides of manganese, nickel, and cobalt are the most interesting semiconductor ceramics used as negative temperature co-efficient (NTC) thermistor. These transition ceramics have been preferred for the preparation of a thermistor due to their electrical resistance, which decreases greatly with increasing temperature, and gentle slope of the β factor. These materials crystallize in spinel structure, i.e. cubic close packing of oxygen anions in which the cations are located on the tetrahedral sites (A) and the octahedral sites (B). The electrical phenomenon in these materials is interpreted in terms of a phonon-assisted jump of carriers among localised states, called hopping conductivity.[1] For thermistors, the characteristics such as room temperature resistance, thermistor constant, temperature co-efficient of resistance, activation energy, etc. are important from the viewpoint of technical applications. These parameters depend upon number of factors such as composition, homogeneity, microstructure, processing parameters, etc. As solids do not react with each other at room temperature over normal timescale, it is essential to heat them at higher temperature (normally ≥1000 °C) with an appreciable rate to facilitate the reaction which shows that both kinetic and thermodynamic factors are important in solid-state reaction.[2] Many researchers have synthesized the spinel thermistor materials >1000 °C and also for longer duration.[3–7]

The manganese-based spinel oxide materials commonly used in preparation of thick film NTC thermistors, showed non-linear *I–V* characteristics.[8] This non-linearity can be circumvented by mixing of small amount of precious metal with the spinel compound. The precious metals like copper, ruthenium dioxide, etc. are being used to achieve the linearity. Therefore, the present work is focussed into three directions:

1. The first objective of this investigation was to synthesize the NTC powder material at lower temperature, so that the structural and electrical parameters were satisfied.
2. Effect of addition of RuO_2 in the functional spinel material in order to vary its electrical resistance, thermistor constant, and activation energy.

* Corresponding author at: Thick Film Materials and Electronics Packaging Division, Centre for Materials for Electronics Technology, Panchawati, Off Dr. Bhabha Road, Pune 411008, India. Tel.: +91 20 25899273/8390/8141; fax: +91 20 25898180/8085.
E-mail address: sunitrane@yahoo.com (S. Rane).

0955-2219/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2008.03.027

3. Many researchers have studied the NTC thermistors in bulk form,[9–12] as well as in the form of thick films.[13–16]

Thick film consists of functional material, lead borosilicate glass frit and organic vehicle. The glass frits are based on high percentage of lead, cadmium in addition to glass forming agents such as boron, silicon, aluminium, etc. But the lead, cadmium and mercury are toxic and remain stable over time and hence hazardous for human being and also to the environment. Recently, the environmental protection and 'green' products are the issues more and more concern due to the strict RoHS guidelines. Some of the 'green' thick film products in particular conductor, solder and overglaze materials are now available commercially in electronic market. However, to our information the no 'green' resistor, thermistor materials are available as on date in the electronic market hence, the extensive literature on this topic is not available. Recently, some researchers have initiated the work to eliminate the hazardous elements from the thick film resistors[17–19] and thermistors.[20] During the course of this work, we have prepared the environment friendly thick film NTC thermistors and studied their electrical properties.

2. Experimental methods

2.1. Preparation of manganite powders

The powder of semiconducting oxides was prepared by mixing high purity (99%) oxides such as MnO_2, CoO and NiO. The desired semiconducting oxide system was prepared by taking appropriate molar ratios of such oxides. The prepared system was $(Mn_{1.85}Co_{0.8}Ni_{0.35})O_4$. The prepared mixture was then ground in an agate mortar to have a homogenized powder mixture. The mixture was subsequently sintered at 1000 °C with a heating rate (10 °C/min) for dwell time of 4 h. The sintered mass was again crushed and pulverised to obtain the fine powder. The prepared powder was then characterized by thermo-gravimetric, X-ray diffractometric, and microstructure analyses.

2.2. Formulation of thick film thermistor paste

Thick film thermistor pastes were prepared by blending the desired amount of semiconducting oxide powder, RuO_2, lead-free glass (calcium–barium borosilicate glass) and an organic vehicle in an agate mortar. The composition of inorganic to organic vehicle was kept as 70:30 wt.%. The pastes formulated using these compositions were found to have good thixotropy and printability. Planar thermistor structure was designed with suitable geometry for custom design so that measurable range of resistances could be obtained. The schematic of the thick film thermistor pattern is shown in Fig. 1. The resistance values were calculated using the following equation:

$$R = R_s \times N, \quad \text{where}$$

R_s = sheet resistance and N is the aspect ratio.

The prepared thick film thermistor pastes were then screen printed on to a 96% alumina substrate (1 in.^{2}) with pre-fired

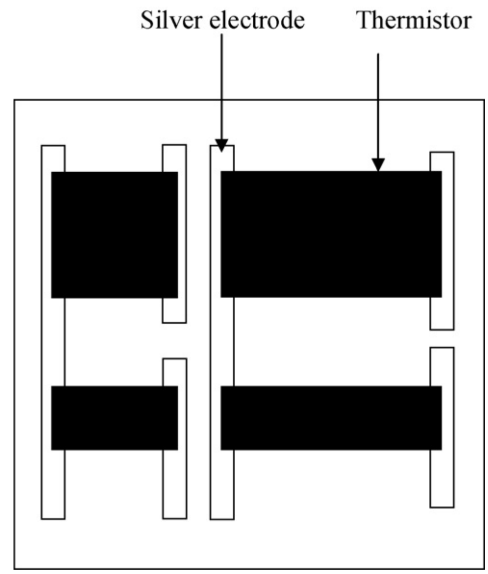

Fig. 1. Schematic of the thick film thermistor pattern.

Table 1
Summary of the samples prepared

Sample code	Compositions
TA1C	$Mn_{1.85}Co_{0.8}Ni_{0.35}O_4$
TA2C	$Mn_{1.85}Co_{0.8}Ni_{0.35}O_4 + RuO_2$ (15 wt.%)
TA3C	$Mn_{1.85}Co_{0.8}Ni_{0.35}O_4 + RuO_2$ (30 wt.%)

lead-free 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 (BTU make) at 850 °C at dwell of 15 min using the firing profile of 60 min. Thickness of the fired films was 25 ± 5 μm measured by Tallysurf thickness profiler. The resistance versus temperature measurement was carried out using Agilent 4.5 digit multimeter (Model U1252A) in the temperature range of 25–300 °C. The samples prepared are summarised in Table 1.

3. Results and discussion

3.1. Thermo-gravimetric analysis

The thermo-gravimetric analysis of the prepared powder (TA1C) was carried out in the temperature range of 30–900 °C at a heating rate of 10 °C/min in nitrogen medium. This gives the idea of the qualitative prediction of various phases could be formed while sintering at 1000 °C for 4 h. Fig. 2 shows the TG and DTG of the sintered powder (TA1C). The thermogram indicates the weight loss due to the removal of water molecules, which might be present due to environment. The total weight loss is nearly 6%. In DTG, the peaks at 460, 530 °C and 580, 670 °C indicate the occurrence of a phase transformation. The first could be the oxidation state of Mn from +4 to +3 state (i.e. MnO_2 to Mn_2O_3). The exothermic peaks around 530 and 600 °C could be due to the reaction between MnO_2 and CoO to form binary spinel-type oxide of possible $CoMn_2O_4$ or $MnCo_2O_4$ and change of oxidation state from Co^{2+} to Co^{3+}, i.e. CoO to Co_2O_3

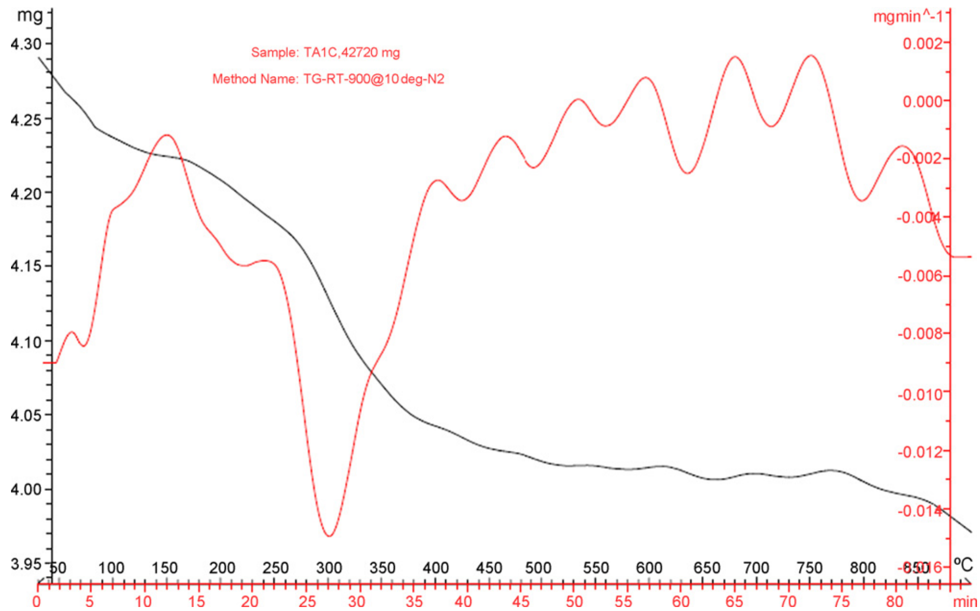

Fig. 2. Thermogram of the sintered thermistor powder.

and the expected formation of phase could be $CoMn_2O_4$. This indicates that Mn^{3+} has a preference for occupying octahedral sites over Co^{2+}. Additionally, the exothermic peaks similar to the above region indicates the phase formation due to reaction between NiO and Mn_2O_3, where Ni^{2+} prefers tetrahedral site and the most favoured reaction is the formation of $NiMn_2O_4$ phase. Also the exothermic peaks around 750 and 840 °C indicate a reaction between Ni^{2+} and Co_2O_3 leads to the formation of favourable $NiCo_2O_4$ phase. Therefore, it can conclude from the TG and DTG plot that the formation of $NiMn_2O_4$, $CoMn_2O_4$ and $NiCo_2O_4$ phases in the manganite on sintering at 1000 °C for 4 h.

3.2. X-ray diffraction analysis

X-ray diffractometry analysis of the complex powder and films was carried out using Cu Kα radiation at an angle $2\theta = 20–80°$. The X-ray diffractograph for the powder sintered at 1000 °C for 4 h is shown in Fig. 3a. The reflections at $d = 2.53$, 2.48, 2.44 A° correspond to maximum intensity peaks of $NiMn_2O_4$, $CoMn_2O_4$, (Co,Mn)(Co,Mn)$_2$O$_4$ and $NiCo_2O_4$ phases respectively, which indicates that manganite is possibly the solid solution of the above four crystalline spinel phases.[1] The existence of spinel phases is shown in Fig. 3a and detailed analysis of the phases is also given in Table 2.

The analysis of films was carried out in the similar way as that of the powder. Fig. 3b shows the XRD pattern of the thick films. It is noted that in addition to the spinel phase of $NiMn_2O_4$, and oxides of calcium and aluminium from the glass frit is reacted with the spinel compound occurred in the phases as $CaMn_2O_4$, $CaCo_2O_4$ and $NiAl_2O_4$. It is also observed that the crystallinity of the compound is increased in the film. The Ag_2O phase is also observed due to the termination line only. It may be noted here that we have not observed any penetration of silver into the thermistor composition. Also there is no reaction occurred between

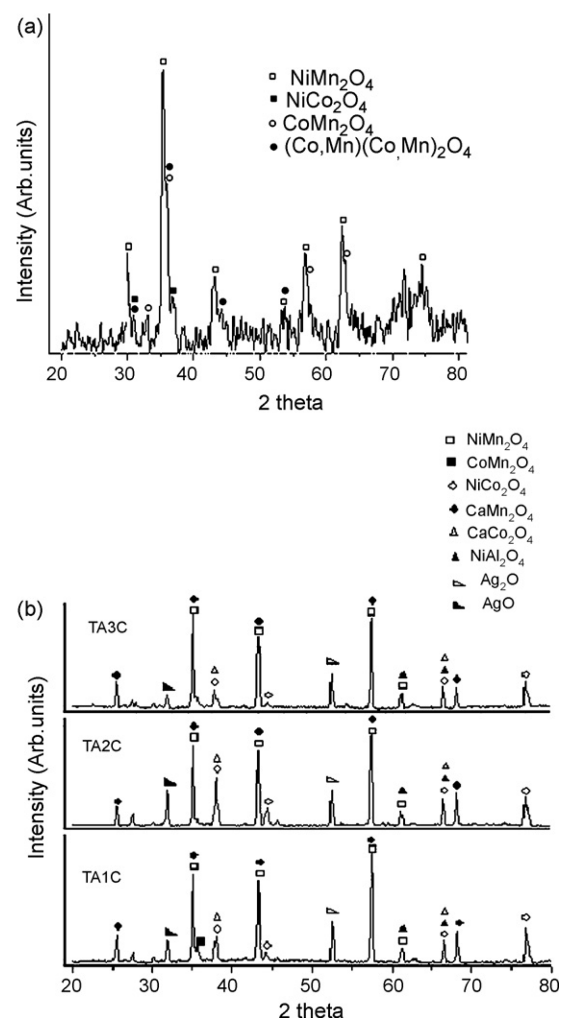

Fig. 3. X-ray diffractogram of (a) synthesized powder (TA1C) and (b) fired thermistor thick films.

Table 2
Details of phases for spinel powder system (TA1C)

TA1C		$NiMn_2O_4$		$CoMn_2O_4$		$NiCo_2O_4$		$(Co,Mn)(Co,Mn)_2O_4$	
d	*I*/I0	*d*	*I*/I0	*d*	*I*/I0	*d*	*I*/I0	*d*	*I*/I0
2.9741	38	2.97	30						
2.8677	14					2.86	25	2.86	16 [10]
2.7088	13			2.71	20 [12]				
2.5370	100	2.53	100						
2.4826	57			2.48	100 [57]			2.47	100 [57]
2.4428	19					2.44	100 [19]		
2.4162	18	2.41	25						
2.0915	26	2.09	50						
2.0456	19			2.04	10 [6]	2.02	25 [5]	2.03	35 [20]
1.7190	15	1.71	8					1.71	14 [8]
1.6205	33	1.61	40			1.65	8 [2]		
1.5978	15			1.60	13 [8]				
1.5878	13			1.57	13 [8]				
1.4882	45	1.48	60	1.49	10 [6]				
1.2900	20	1.28	8						
1.2711	32			1.27	10 [6]				
1.2611	24	1.26	12					1.26	8 [5]
1.2266	19					1.23	16 [4]		
1.2076	15	1.21	8						
1.1145	17	1.12	4			1.13	2 [1]		

the spinel compound and the conducting oxide, i.e. RuO_2. It may be noted here that the present thick film (consisting spinel compound and lead-free glass) is a complicated system and hence the exact quantitative determination of different phases is difficult and therefore, only qualitative description is possible in the present system.

3.3. Microstructure analysis

Fig. 4 represents the SEM images of the prepared functional spinel powder (TA1C) and the RuO_2 powder used. The particle size of the powder is approximately in the range of 300–500 nm. However, few larger particles are also seen in case of RuO_2. The morphology of the fired films was observed under scanning electron microscopy (SEM). Fig. 5 shows the backscattered SEM images obtained from the surface of fired thick films. The SEM reveals the denser and smoother surface of the films, with connected grain boundaries but with some pores on the surface. The oxide particles are grown due to the firing of the film and homogeneously dispersed in the glassy matrix. The glass phase is normally added in thick films for adhesion, enhancement of sintering conditions and improvement of particle packing.[21] It is seen from the SEM pictures that the organic binders used in the paste creates some pores/holes on the surface due to the burning of organics and also due to complex reaction between the constituents (functional material and glass frit) during the firing of the films. Some grey particles are also seen in the matrix, which are nothing but the conducting RuO_2 grains (Fig. 5b) as confirmed by energy depressive X-ray (EDAX) analysis.

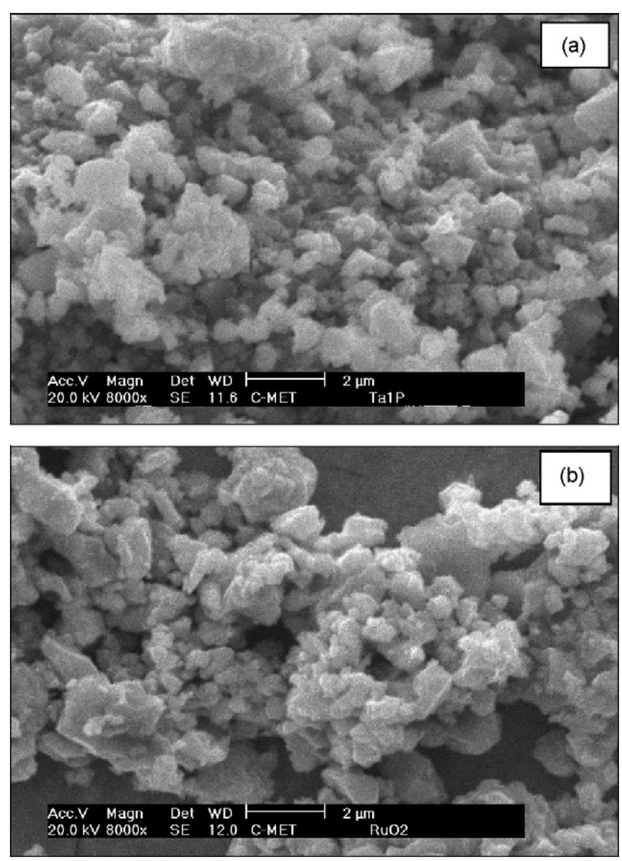

Fig. 4. Microstructure of the powders used for the preparation of thick film NTC thermistor (a) spinel powder (TA1C) and (b) RuO_2.

3.4. Electrical measurements

The resistance of the films was measured as a function of temperature. The resistance decreases exponentially as the tem-

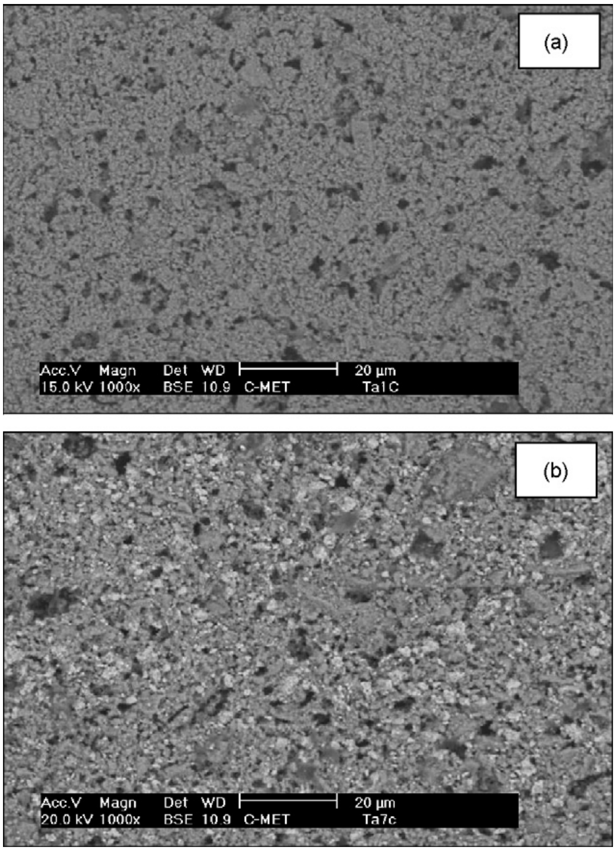

Fig. 5. Back-scattered images showing the microstructure thermistor films using: (a) TA1C and (b) TA3C.

perature increases (Fig. 6). The logarithm of resistance against the reciprocal of absolute temperature, which is a characteristic of the conduction process, is described in the Nernst–Einstein relation:

$$\sigma = \frac{1}{\rho} = \sigma_0 NC(1-C)\ \exp\left(\frac{E_H}{\kappa T}\right) \quad \text{with} \quad \sigma_0 = \frac{N_{oct} e^2 d^2 V_0}{\kappa}$$

where N_{oct} is the concentration of the octahedral sites, d is the jump distance for the charge carriers, V_0 is the lattice vibration frequency associated with conduction, κ is the Boltzmann's constant, e is the electronic charge, N is the concentration per formulae unit sites which are available to the charge carriers, C is a fraction of available sites which are occupied by the charge carriers, and E_H is a hoping energy. From Fig. 7, it is seen that almost all the NTC thermistors operate steadily with the straight-line relationships between these parameters over a wide temperature range, indicating a good thermistor characteristics. The thermistor with highest concentration of RuO_2 exhibits more linear nature than that of other two cases. The data on the electrical parameters such as sheet resistance, thermistor constant, temperature coefficient of ratio (TCR) and activation energy is given in Table 3. The thermistor constant (β) was calculated by the following equation:

$$\beta_{25-300} = \frac{\ln(R_{25}/R_{300})}{(1/T_{25}) - (1/T_{300})}$$

where R_{25} and R_{300} are the resistances measured at 25 °C and 300 °C, respectively. It is seen from Table 3, that the thermistor constant values are in the range of 3600–4900 K, which are sufficiently high and display higher sensitivity of the prepared lead-free thermistors. The addition of conducting phase, i.e. RuO_2, reduces the resistance as well as the thermistor constant. It is also noted that the thermistor constant is comparatively

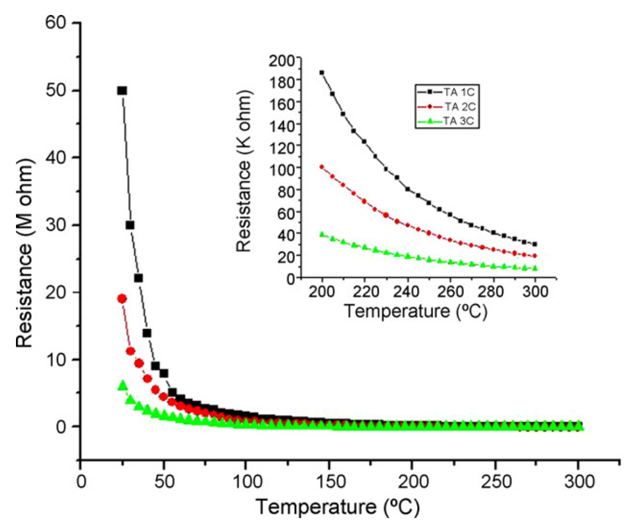

Fig. 6. NTC behavior of the investigated thick film compositions.

Table 3
Electrical properties of the environment friendly thick film NTC thermistor

Sample code	Sheet resistance (MΩ/□)	Aspect ratio	Thermistor constant (β) (K)	TCR (K^{-1})	Activation energy (eV)
TA1C	47.81	1	4344	−0.0132	0.3743
		1.75	4669	−0.0142	0.4023
		2	4842	−0.0147	0.4172
		3.5	4371	−0.0133	0.3766
TA2C	19.62	1	4000	−0.0121	0.3446
		1.75	3926	−0.0119	0.3383
		2	3866	−0.0117	0.3331
		3.5	3958	−0.0120	0.3410
TA3C	3.96	1	3869	−0.0117	0.3334
		1.75	3605	−0.0109	0.3106
		2	3806	−0.0115	0.3279
		3.5	3859	−0.0117	0.3325

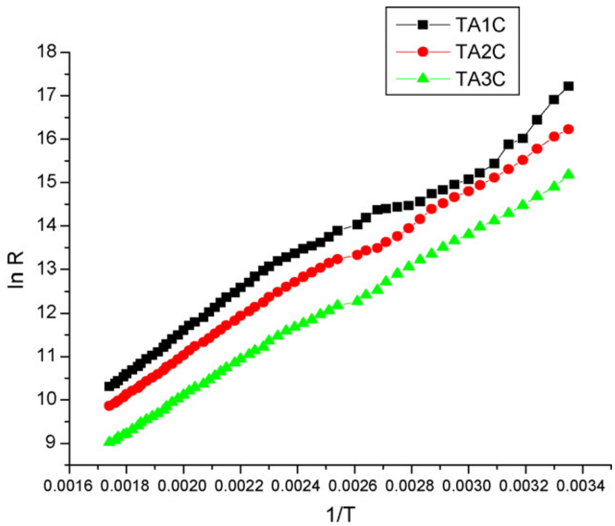

Fig. 7. Typical relationship between logarithm of resistance and inverse of absolute temperature of thick film thermistors.

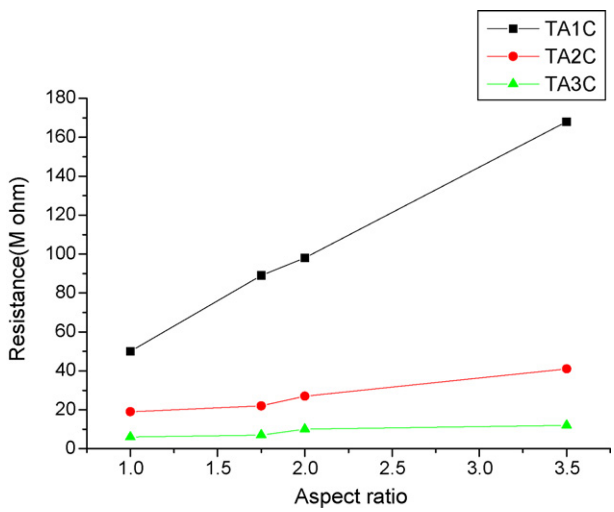

Fig. 8. Relation between resistance and the aspect ratio of thermistor.

more stable irrespective of the aspect ratio than that of thermistor without RuO_2. The change in resistance with respect to the aspect ratio of the thermistor pattern is reproduced in Fig. 8. As expected, the resistance changes with respect to the aspect ratio. Almost a linear variation of resistance was noticed with respect to aspect ratio.

4. Conclusion

NTC thermistor materials were prepared from mixtures of MnO_2, CoO and NiO by solid-state reaction technique at 1000 °C for 4 h. The X-ray diffraction analysis confirmed the formation of spinel phases, viz. $NiMn_2O_4$, $CoMn_2O_4$, $(Co,Mn)(Co,Mn)_2O_4$, and $NiCo_2O_4$. Additionally, $CaMn_2O_4$, $CaCo_2O_4$, $NiAl_2O_4$ phases were seen in the fired films. It is also observed that RuO_2 was not reacting with any other element to form spinel structure confirmed by X-ray analysis however, its presence in the films were confirmed by EDAX analysis and electrical properties. It is concluded that the sintering duration of 4 h was sufficient to form the appropriate spinel phases. We prepared environment friendly thick film NTC thermistors based on the spinel electroceramics for the first time. The planar thick film thermistors showed good microstructure, homogeneity, reproducibility of the electrical parameters, and high sensitivity with wide operating temperature range, which may be useful from the standpoint of fabricating accurate temperature sensors. Our eco-friendly thick film thermistor compositions revealed the room temperature resistance and thermistor constant in the range of 6–168 MΩ and 3600–4900 K, respectively.

Acknowledgments

We are grateful to Prof. R.C. Aiyer, Department of Physics, University of Pune, for her time to time help in this work. We also acknowledge Dr. U.P. Phadke, Advisor, Dr. Krishnakumar, Dr. U.C. Pande, Dr. V.C. Sethi, Senior Directors and Dr. S. Chatterjee, Director, Materials Component Division, Department of Information Technology, Ministry of Communication and Information Technology, Govt. of India, for the administrative help and generous funding.

References

1. Macklen, E. D., *Thermistors*. Electrochemical Publications Ltd., Ayr, Scotland, 1979.
2. West, A. R., *Solid State Chemistry and Its Applications*. John Wiley & Sons, 2003.
3. Ikegami, A., Arima, H., Tosaki, H., Matsuoka, Y., Ai, M., Minorikawa, H. and Asahino, Y., Thick film thermistors and it's applications. *IEEE Trans. Comp., Hybr. Manuf. Tech., CHMT-3*, 1980, **4**, 541–550.
4. Brunets, I., Mrooz, O., Shpotyuk, O. and Altenburg, H., Thick film NTC thermistors based on spinel type semiconducting electroceramics. In *Proceedings of the International Conference on Microelectronics, vol. 2*, 2004, pp. 503–506.
5. Abe, Y., Meguro, T., Yokoyama, T., Morita, T., Tatami, J. and Komeya, K., Electrical properties of sintered bodies composed of a monophase cubic spinel structure $Mn_{(15-0.5x)}Co_{(1+0.5x)}Ni_{0.5}O_4$ $(0 \le x \le 1)$. *J. Ceram. Process. Res.*, 2003, **4**(3), 140–144.
6. Sarkar, S. K., Sharma, M. L., Bhaskar, H. L. and Nagpal, K. C., Preparation, temperature and composition dependence of some physical and electrical properties of mixtures within the NiO–Mn_3O_4 system. *J. Mater. Sci.*, 1984, **19**, 545–551.
7. Golestani-Fard, F., Azimi, S. and Mackenzie, K. J. D., Oxygen evolution during the formation and sintering of nickel–manganese oxide spinels for thermistor applications. *J. Mater. Sci.*, 1987, **22**, 2847–2851.
8. Prudenziati, M., *Handbook of Thick Film Sensors, vol. 1*. Elsevier, 1994.
9. Martinez Sarrion, M. L. and Morales, M., Preparation and characterization of NTC thermistors based on $Fe_{2+\delta}Mn_{1-x-\delta}Ni_xO_4$. *J. Mater. Sci.*, 1995, **30**, 2610–2615.
10. Metz, R., Electrical properties NTC thermistors made of manganite ceramics of general spinel structure. *J. Mater. Sci.*, 2000, **35**, 4705–4711.
11. Martin De Vidales, J. L., Garcia-Chain, P., Rojas, R. M., Vila, E. and Garcia-Martinez, O., Preparation and characterization of spinel type Mn–Co–O negative temperature co-efficient ceramic thermistors. *J. Mater. Sci.*, 1998, **33**, 1491–1496.
12. Na, E. S., Paik, U. G. and Choi, S. C., The effect of sintered microstructure on the electrical properties of a Mn–Co–Ni–O thermistors. *J. Ceram. Process. Res.*, 2001, **2**(1), 31–34.
13. Park, K. and Bang, D., Electrical properties of Ni–Mn–Co–(Fe) oxide thick film NTC thermistor prepared by screen printing. *J. Mater. Sci. Mater. Electr.*, 2003, **14**, 81–87.

14. Park, K., Structural and electrical properties of $FeMg_{0.7}Cr_{0.6}Co_{0.7-x}Al_xO_4$ $(0 \le x \le 0.3)$ thick film NTC thermistors. *J. Eur. Ceram. Soc.*, 2006, **26**, 909–914.
15. Hrovat, M., Belavic, D., Holc, J. and Cilensek, J., The development of the microstructural and electrical characteristics of NTC thick film thermistors during firing. *J. Mater. Sci.*, 2006, **41**, 5900–5906.
16. Jagtap, S., Rane, S., Mulik, U. and Amalnerkar, D., Thick film NTC thermistor for wide range of temperature sensing. *Microelectr. Int.*, 2007, **24**(2), 7–13.
17. Rane, S., Prudenziati, M., Morten, B., Golonka, L. and Dziedzic, A., Structural and electrical properties of perovskite ruthenate based lead free thick film resistors on alumina and LTCC. *J. Mater. Sci. Mater. Electr.*, 2005, **16**, 687–691.
18. Rane, S., Prudenziati, M. and Morten, B., Environment friendly perovskite ruthenate based thick film resistors. *Mater. Lett.*, 2007, **61**, 595–599.
19. Kshirsagar, A., Rane, S., Mulik, U. and Amalnerkar, D., Microstructure and electrical performance of eco-friendly thick film resistor compositions fired at different firing conditions. *Mater. Chem. Phys.*, 2007, **101**, 492–498.
20. Jagtap, S., Rane, S., Mulik, U. and Amalnerkar, D., Eco-friendly thick film temperature sensors based on semiconducting electroceramics. In *Proceedings of the 12th National Seminar on Physics and Technology of Sensors*, 2007, pp. 131–133.
21. Schmidt, R., Stiegelschmitt, A., Roosen, A. and Brinkman, A., Screen printing of co-precipitated $NiMn_2O_{4+\delta}$ for production of NTCR thermistors. *J. Eur. Ceram. Soc.*, 2003, **23**, 1549–1558.