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Effect of Cu and Fe addition on electrical properties of Ni–Mn–Co–O NTC thermistor compositions

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Abstract

The effect of addition of Cu and Fe on the electrical properties of Ni–Mn–Co–O based NTC thermistor compositions is studied. Compositions with very low resistivity were prepared by co-doping of very small amounts of Cu along with Co in $NiMn_2O_4$, without affecting the sensitivity very much. Compositions with high resistivity and good sensitivity were achieved by co-doping Fe with Co in $NiMn_2O_4$. The effect of sintering temperature on electrical properties was investigated and it was found that the resistivity and material constant increase with sintering temperature. The reliability characteristics of the compositions were studied by the accelerated thermal aging method. All the compositions exhibited very good reliability.
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Keywords: Thermistor; NTC; Reliability; Nickel manganite

1. Introduction

In the recent years, negative temperature coefficient (NTC) thermistors have grown as the most influential components in the thermal sensor industry. NTC thermistors have been extensively used for various industrial and domestic applications such as circuit compensation, aerospace, cryogenic, automotive, temperature measurement and control applications [1,2]. Due to the enormous commercial success of NTC thermistors, there has been an exceedingly growing interest in improving the performance and reliability of NTC thermistor devices. Nickel manganite based compositions are the most widely used NTC materials. They belong to the class of controlled valence semiconductors in which the electrical resistance decreases exponentially with the increasing temperature [1–6]. Nickel manganite ($NiMn_2O_4$) has a cubic spinel crystal structure with a structural formula AB_2O_4. This spinel structure has a cubic close packing of oxygen atoms with cations distributed in tetrahedral A-sites and octahedral B-sites. The electrical properties of nickel manganite have been explained in terms of a phonon assisted hopping of charge carriers between Mn^{3+} and Mn^{4+} ions in octahedral B-sites [1,7]. The electrical properties strongly depend on the composition of metal oxides and the microstructure of the ceramic material, which affect the distribution of cations in the spinel structure [8].

Ni–Mn–Co–O ceramic system has already been identified as an excellent choice of NTC composition for many applications [9–11]. The electrical properties can be fine tuned by co-doping various transition metal ions including Cu, Fe, Zn, etc. along with Co in $NiMn_2O_4$. In most of the earlier works, the co-doping was carried out as a substitution for Co, keeping the Ni:Mn ratio constant [12–14]. In $NiMn_2O_4$ the major contribution to the electrical conductivity is from the Mn ions in the octahedral sites. Hence it will be worthwhile to investigate the effect of substitution of Mn in Ni–Mn–Co–O system by keeping the Ni:Co ratio constant. Even though some works were already carried out in this direction [8,15,16], a systematic study including the reliability aspect of the compositions would be a noteworthy attempt.

In the present work, $Ni_{0.7}Mn_{2.3}O_4$ was taken as the base composition and Mn was substituted using Co and Cu or Fe. The effect of dopant concentration and sintering

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temperature on electrical properties are investigated. Reliability characteristics as a measure of drift in resistance after accelerated aging are also reported.

2. Experimental

2.1. Synthesis of NTC compositions

Three sets of compositions based on $Ni_{0.7}Mn_{2.3-x}Co_xO_4$ ($0 \le x \le 0.7$), $Ni_{0.7}Mn_{1.8-x}Co_{0.5}Cu_xO_4$ ($0 \le x \le 0.05$) and $Ni_{0.7}Mn_{1.8-x}Co_{0.5}Fe_xO_4$ ($0 \le x \le 0.7$) were prepared by solid state route. Starting materials such as nickel carbonate basic hydrate, manganese carbonate, Fe_2O_3, CuO and Co_3O_4 (Sigma Aldrich, USA) were of high purity (> 99%) in order to ensure higher quality and reproducibility of the synthesized thermistor compositions. The raw materials were accurately weighed and ball milled using isopropyl alcohol as solvent and yttria stabilized zirconia balls as grinding media for 24 h to get a uniform mix. The powder mix was then calcined at 1173 K for 3 h. The calcined powder was then ground by ball milling for 48 h to achieve a narrow particle size distribution. The powder after grinding was passed through ASTM 400 mesh size sieve so as to make sure that only particles of uniform size were present in the resulting powder after drying. Crystal structure of the resulting composition was analyzed by X-ray diffraction (XRD) analysis (Bruker AXS D5005, Germany).

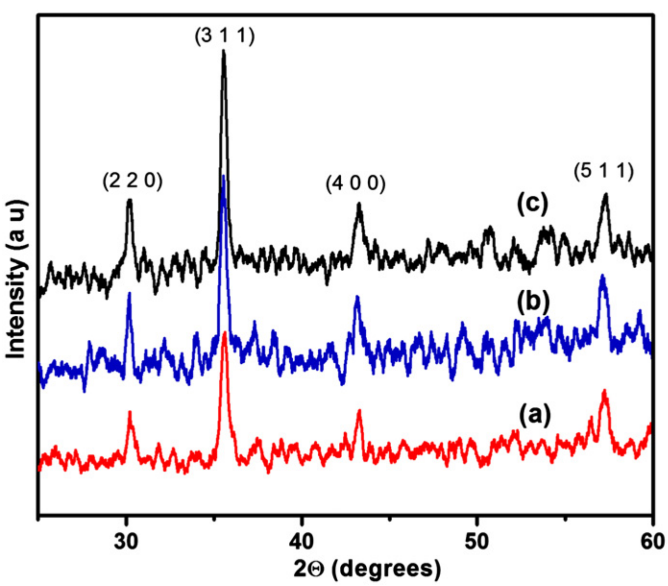

Fig. 1. XRD patterns of the compositions calcined at 1173 K: (a) $Ni_{0.7}Mn_{1.8}Co_{0.5}O_4$, (b) $Ni_{0.7}Mn_{1.5}Co_{0.5}Fe_{0.3}O_4$ and (c) $Ni_{0.7}Mn_{1.77}Co_{0.5}Cu_{0.03}O_4$.

2.2. Preparation of disc thermistors

The NTC powder was granulated using 5% PVA solution and green discs of 10 mm diameter and 1.7 mm thickness were made by uniaxial compaction. The green discs were then sintered at 1473 K, 1493 K, 1523 K and 1553 K for 3 h and controlled cooling was given. Sintered discs were electroded using silver paste (Shoei-H-5698, Japan) and cured at 1023 K in a conveyor belt furnace. The speed of the conveyor was adjusted so as to keep the sample at the peak temperature for 10 min. After curing, the discs were kept at a temperature of 393 K for 2 days, to ensure thermal stability. The microstructure of the sintered discs was studied by Scanning Electron Microscopy (SEM).

2.3. Electrical characterization and reliability studies

Electrical resistance of the disc samples were measured at 298 K and 358 K in a calibrated constant temperature silicon oil bath (Model 7340, Hart Scientific, USA) with a temperature uniformity of ± 0.005 °C, using a precise digital multimeter (Fluke 8808A, USA) with 0.03% dc current accuracy. The electrical characteristics of the thermistors such as resistivity, material constant, temperature coefficient of resistance and activation energy were calculated.

The disc thermistors were subjected to reliability studies by accelerated aging method. The discs were kept at 393 K for 168 h and the drifts in resistance (at 298 K) of the discs before and after the thermal aging test were measured. The percentage drift in resistance was taken as the measure of its reliability.

3. Results and discussion

3.1. X-ray diffraction studies and microstructure analysis

The XRD patterns of representative samples from all the three sets of compositions are given in Fig. 1. It is obvious from the XRD patterns that all the compositions maintain

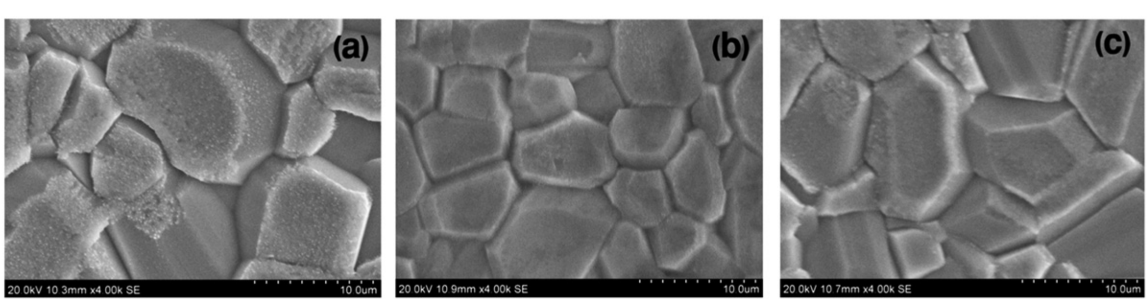

Fig. 2. SEM images of disc thermistors sintered at 1473 K: (a) $Ni_{0.7}Mn_{1.8}Co_{0.5}O_4$, (b) $Ni_{0.7}Mn_{1.5}Co_{0.5}Fe_{0.3}O_4$ and (c) $Ni_{0.7}Mn_{1.77}Co_{0.5}Cu_{0.03}O_4$.

the cubic spinel structure even after doping with various metal ions. No secondary phase is observed. This observation is also complimented by the SEM images of sintered discs as shown in Fig. 2. All the compositions have a uniform microstructure with densely packed grains. No porosity or formation of secondary phase is noticed. The homogeneous microstructure of the sintered body is a well desired property for NTC thermistors.

3.2. Influence of dopants on the electrical characteristics

The main electrical properties of NTC thermistors are, room temperature resistivity (ρ_{298}), material constant (B-value) and temperature coefficient of resistance (α). The electrical parameters, B-value and 'α' can be derived from the resistance temperature characteristics. These parameters determine the condition under which a given thermistor material may be utilized [2]. The resistance (R) and temperature (T) relationship of an NTC thermistor can be represented as

$$R = A\exp(q/kT) \quad (1)$$

where A is a constant related to the device dimensions and resistivity (ρ). 'q' is the activation energy for the hopping process and 'k' is Boltzmann's constant. B-value is simply 'q/k' and is usually calculated using

$$B_{298/358} = (T_{298}T_{358}\ln(R_{298}/R_{358}))/(T_{358}-T_{298}) \quad (2)$$

where R_{298} and R_{358} are the resistance values at 298 K (T_{298}) and 358 K (T_{358}), respectively. The temperature coefficient of resistance (α) is defined as the rate of change of resistance (R) with temperature (T) to the resistance at a specified temperature and is given by

$$\alpha_{298} = ((1/R)\,dR/dT) = -B/T^2 \quad (3)$$

Fig. 3 shows a linear dependence of logarithm of resistivity with reciprocal of absolute temperature over a wide temperature range for the aged disc thermistors, which is an indication of excellent NTC thermistor characteristics.

3.2.1. Effect of cobalt concentration in $Ni_{0.7}Mn_{2.3-x}Co_xO_4$

To understand the effect of Co doping in the composition $Ni_{0.7}Mn_{2.3-x}Co_xO_4$, x was varied from 0 to 0.7. The electrical characteristics including room temperature resistivity, material constant (B-value), activation energy, temperature coefficient of resistance and percentage drift in resistance after aging are given in Table 1. The resistivity and B-value decrease with the increasing Co content (Fig. 4). This observation is well expected as the Co^{2+} and Co^{3+} ions can also occupy the octahedral sites and contribute to the electrical conductivity along with

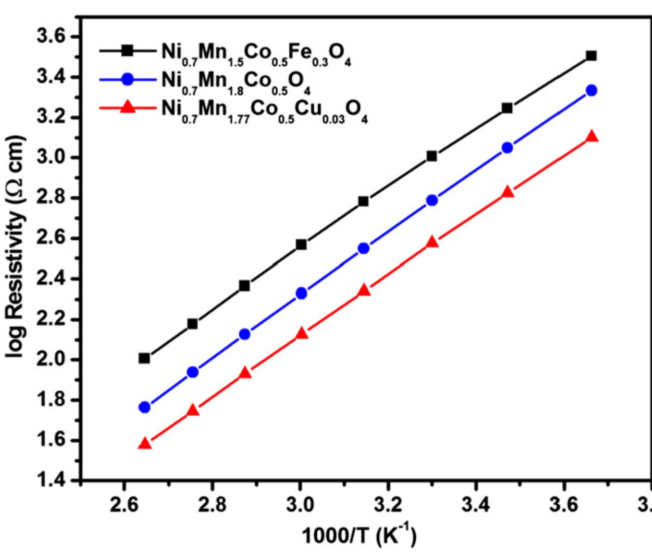

Fig. 3. Relationship between log resistivity and $1/T$ for disc thermistors.

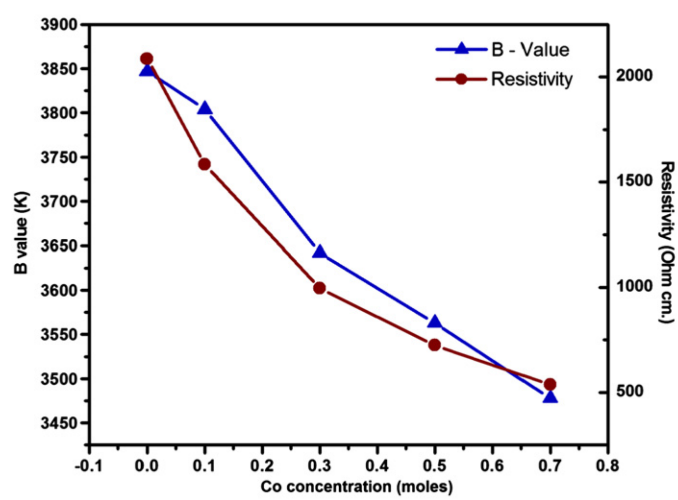

Fig. 4. Effect Co concentration on B-value and resistivity of the system $Ni_{0.7}Mn_{2.3-x}Co_xO_4$.

Table 1
Electrical characteristics of $Ni_{0.7}Mn_{2.3-x}Co_xO_4$ NTC compositions.

Code	Composition	Resistivity (ρ_{298}) (Ω cm)	$B_{298/358}$ (K)	Activation energy, q (eV)	Temperature coefficient of resistance (α_{298}), (%/K)	Drift in R_{298} after aging (ΔR), (%)
A1	$Ni_{0.7}Mn_{2.3}O_4$	2087	3847	0.331611	−4.332012	0.52
A2	$Ni_{0.7}Mn_{2.2}Co_{0.1}O_4$	1584	3804	0.327905	−4.283591	0.39
A3	$Ni_{0.7}Mn_2Co_{0.3}O_4$	996	3642	0.313940	−4.101167	0.31
A4	$Ni_{0.7}Mn_{1.8}Co_{0.5}O_4$	725	3563	0.307131	−4.012207	0.34
A5	$Ni_{0.7}Mn_{1.6}Co_{0.7}O_4$	538	3478	0.299804	−3.916490	0.23

Mn^{3+}/Mn^{4+} ion pairs in the octahedral sites [14]. This results in the decrease of resistivity and *B*-value. As expected, the activation energy and temperature coefficient of resistance also decreased with increase in Co content.

The drift in resistance at room temperature (ΔR) after accelerated aging was found to be less than 0.6% in all the cases which is an indication of excellent reliability of the thermistor compositions.

3.2.2. Effect of Cu co-doped with cobalt in $Ni_{0.7}Mn_{1.8-x}Co_{0.5}Cu_xO_4$

For many practical applications such as inrush current limiters, NTC thermistors with low resistance and moderate sensitivity are required. Copper is normally added as a dopant to reduce the resistivity of NTC thermistor compositions. But the addition of copper in large amounts has a harmful effect as it causes low sensitivity to temperature excursions [17–19]. In this study, in order to obtain NTC compositions with low resistivity without affecting very much the thermal sensitivity, very low concentrations of Cu are added to the $Ni_{0.7}Mn_{1.8-x}Co_{0.5}Cu_xO_4$ system where x is varied from 0 to 0.05.

The effect of Cu content of the composition on *B*-value and resistivity is given in Fig. 5. As expected, the resistivity was considerably lowered (from 725 Ω cm to 354 Ω cm) by the addition of very low concentrations of copper but the temperature sensitivity, i.e., *B*-value and α values were not affected much. As the concentration of Cu increases, the Mn^{3+}/Mn^{4+} pairs in the octahedral sites increases. Moreover, in addition to the Mn^{3+}/Mn^{4+} cation pairs, the Cu^{+}/Cu^{2+} ions in the octahedral site also take part in conduction [7] which results in the decrease of resistivity and *B*-value. As seen in Table 2, the drift in resistance after aging is less than 0.7% in all the compositions and thus exhibit very good reliability. Hence these compositions are suitable for practical devices which need low resistivity, good sensitivity and excellent reliability.

3.2.3. Effect of Fe co-doped with cobalt in $Ni_{0.7}Mn_{1.8-x}Co_{0.5}Fe_xO_4$

Owing to the fact that Fe ion has some specialities, such as changeable valency Fe^{2+} and Fe^{3+}, the flexible occupation of A-site and B-site in spinel structure, Fe ion has complicated influence on electrical properties of electroceramics [8]. Introduction of Fe^{3+} ion into the Ni–Mn–Co–O system may arouse an interesting change in electrical properties of NTC thermistors. Some reports were published with Fe substituting the Co in Ni–Mn–Co–O systems [12,13]. In this work, Fe is substituted for Mn by keeping the Ni:Co ratio constant.

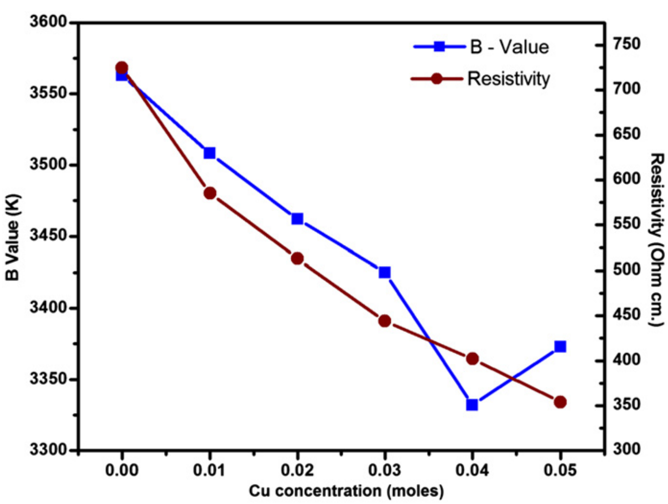

Fig. 5. Effect of Cu concentration on *B*-value and resistivity of the system $Ni_{0.7}Mn_{1.8-x}Co_{0.5}Cu_xO_4$.

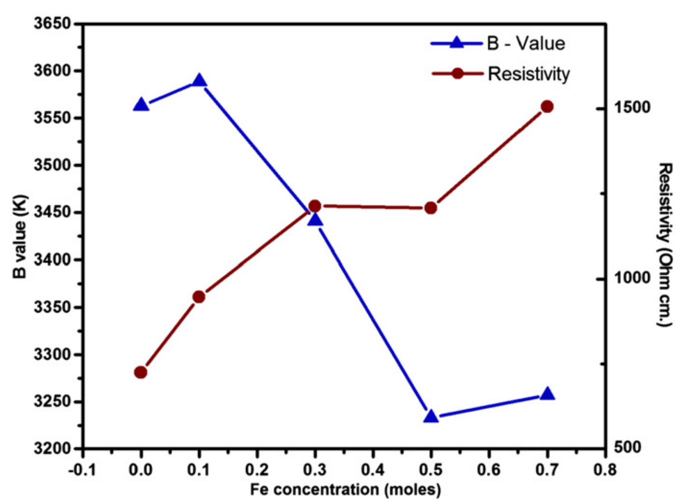

Fig. 6. Effect of Fe concentration on *B*-value and resistivity of the system $Ni_{0.7}Mn_{1.8-x}Co_{0.5}Fe_xO_4$.

Table 2
Electrical characteristics of $Ni_{0.7}Mn_{1.8-x}Co_{0.5}Cu_xO_4$ NTC compositions.

Code	Composition	Resistivity (ρ_{298}) (Ω cm)	$B_{298/358}$ (K)	Activation energy, q (eV)	Temperature coefficient of resistance (α_{298}), (%/K)	Drift in R_{298} after aging (ΔR), (%)
B1	$Ni_{0.7}Mn_{1.8}Co_{0.5}O_4$	725	3563	0.307131	−4.012207	0.34
B2	$Ni_{0.7}Mn_{1.79}Co_{0.5}Cu_{0.01}O_4$	585	3508	0.302390	−3.950273	0.30
B3	$Ni_{0.7}Mn_{1.78}Co_{0.5}Cu_{0.02}O_4$	513	3462	0.298424	−3.898473	0.18
B4	$Ni_{0.7}Mn_{1.77}Co_{0.5}Cu_{0.03}O_4$	444	3425	0.295235	−3.856808	0.44
B5	$Ni_{0.7}Mn_{1.76}Co_{0.5}Cu_{0.04}O_4$	402	3332	0.287218	−3.752083	0.45
B6	$Ni_{0.7}Mn_{1.75}Co_{0.5}Cu_{0.05}O_4$	354	3373	0.290753	−3.798252	0.64

Table 3
Electrical characteristics of $Ni_{0.7}Mn_{1.8-x}Co_{0.5}Fe_xO_4$ NTC compositions.

Code	Composition	Resistivity (ρ_{298}) (Ω cm)	$B_{298/358}$ (K)	Activation energy, q (eV)	Temperature coefficient of resistance (α_{298}), (%/K)	Drift in R_{298} after aging (ΔR), (%)
C1	$Ni_{0.7}Mn_{1.8}Co_{0.5}O_4$	725	3563	0.307131	−4.012207	0.34
C2	$Ni_{0.7}Mn_{1.7}Co_{0.5}Fe_{0.1}O_4$	947	3589	0.309372	−4.041485	0.36
C3	$Ni_{0.7}Mn_{1.5}Co_{0.5}Fe_{0.3}O_4$	1213	3441	0.296614	−3.874825	0.29
C4	$Ni_{0.7}Mn_{1.3}Co_{0.5}Fe_{0.5}O_4$	1207	3233	0.278685	−3.640602	0.24
C5	$Ni_{0.7}Mn_{1.1}Co_{0.5}Fe_{0.7}O_4$	1506	3257	0.280753	−3.667628	0.21

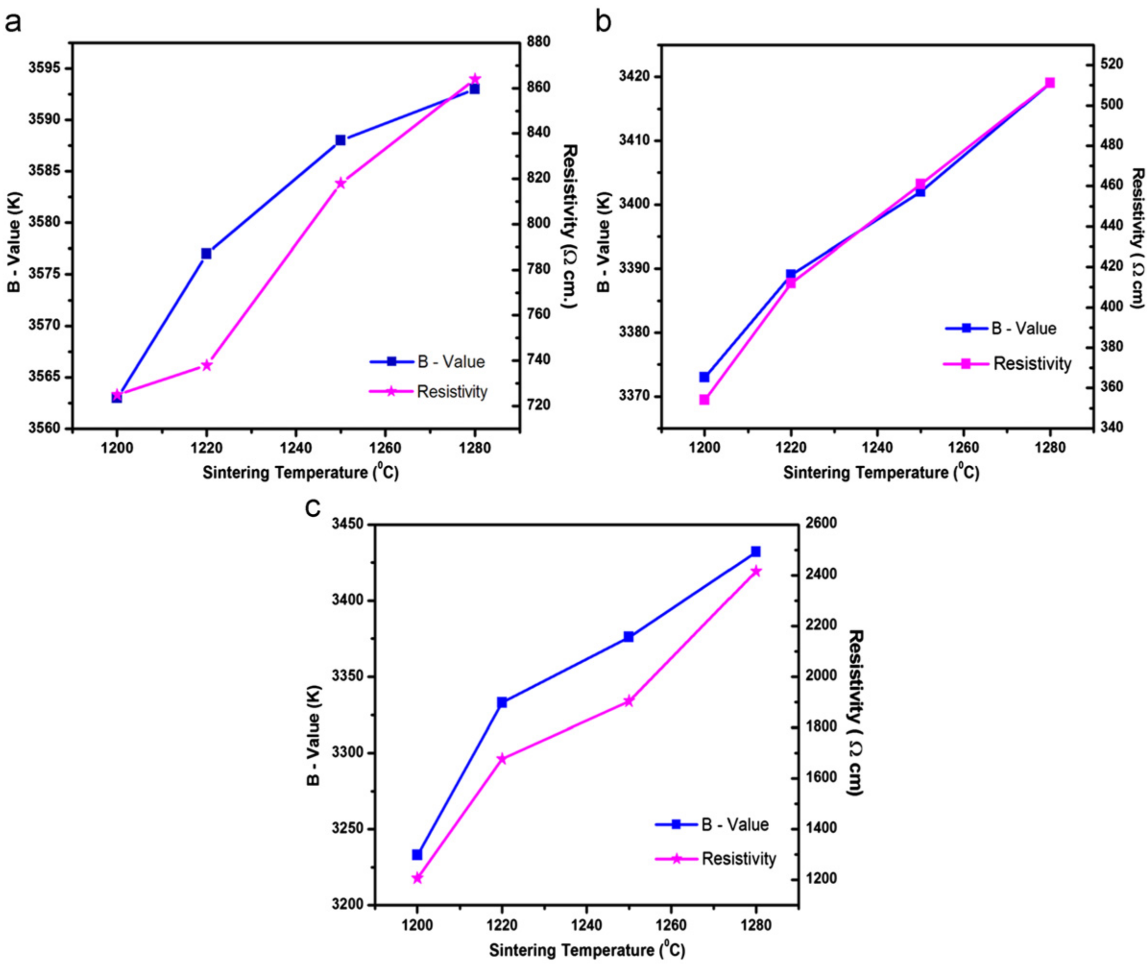

Fig. 7. Effect of sintering temperature on resistivity and B-value: (a) $Ni_{0.7}Mn_{1.8}Co_{0.5}O_4$, (b) $Ni_{0.7}Mn_{1.77}Co_{0.5}Cu_{0.03}O_4$ and (c) $Ni_{0.7}Mn_{1.5}Co_{0.5}Fe_{0.3}O_4$.

From Fig. 6, it can be seen that the resistivity increases with the increasing Fe content. The Fe^{3+} ions can occupy the octahedral sites of the spinel. As the amount of Fe^{3+} ions in octahedral sites increases, the amount of Mn^{3+} and Co^{2+} in octahedral sites, which are responsible for electrical conduction, decreases. Moreover the presence of Fe^{3+} ions in the octahedral sites increases the hopping distance between Mn^{3+} and Mn^{4+} ions. These cationic changes increase the resistivity [2]. Normally, in NTC compositions, if the resistivity is high the B-value will also be high. But in the present case, the B-value is found to be decreasing with increase in Fe content. This is because, as the Fe content increases, the Fe^{3+} ion concentration in the octahedral sites increases. Due to the dilution effect of Fe^{3+}, the hopping distance between Mn ions increases. This in turn decreases the hopping probability of Mn ions and thus the change in resistance with temperature decreases which indirectly results in decreasing B-value with increase in Fe content. This effect is more prominent in this system because we are substituting Mn with Fe and hence lesser amount of Mn ions are available for hopping in the octahedral sites.

From Table 3, it is clear that the compositions show very good reliability with less than 0.4% drift in resistance after aging.

3.3. Effect of sintering temperature

The effect of sintering temperature on the resistivity and *B*-value for representative samples of all the three sets of compositions under study is shown in Fig. 7. In all the compositions, the *B*-value and resistivity increases with sintering temperature. As the sintering temperature increases, oxygen loss from the sample can also take place, which changes the cation distribution in the spinel and the loss of one molecule of divalent oxygen will reduce two molecules of Mn^{4+} to Mn^{3+}, hence decreases the hopping probability [20]. At higher sintering temperatures the segregation or precipitation of impurities and additives at grain boundaries may form potential barriers, which also induce an increase in resistivity and *B*-value [4,7]. The samples sintered at all the four sintering temperatures exhibited excellent reliability.

4. Conclusions

The effect of addition of Cu and Fe on the electrical properties of Ni–Mn–Co–O based NTC thermistor compositions is studied. For applications such as inrush current limiters, NTC thermistors with low resistance and moderate sensitivity are required. Addition of Cu in large quantities for reducing the resistivity adversely affects the sensitivity. In this work, we could achieve compositions with very low resistivity without much affecting the sensitivity by the co-doping of very small amounts of Cu along with Co in $NiMn_2O_4$. Compositions with high resistivity and good sensitivity were achieved by co-doping Fe with Co in $NiMn_2O_4$. Fe was substituted for Mn by keeping the Ni:Co ratio constant. An increase in resistivity with the increasing Fe content was observed. There was an unusual decrease in *B*-value with Fe content. This may be due to the fact that Fe is substituted for Mn and hence the dilution effect of Fe^{3+} ions will be predominant in a Mn deficient system. All the compositions exhibited very good reliability.

Acknowledgment

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