Electrical characterisation of $Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$ thermistors

Berat YÜKSEL PRICE

İstanbul Üniversitesi Mühendislik Fakültesi Metalurji ve Malzeme Mühendisliği Bölümü
Avcılar, İstanbul, +90 212 4737070
berat@istanbul.edu.tr

Abstract

Negative temperature coefficient (NTC) thermistors are ceramic semiconductors derived from metal oxides such as Mn, Ni, Co, Cu, Cr, Fe etc. The electrical resistance of NTC thermistors decrease with increasing temperature. In industrial applications, the desired material constant (B) of NTC thermistors is in the range of 2000 to 5000 K and the sensitivity coefficient (α) is in the range of (-2.2) to (-5.5) %/K. The electrical properties of NTC thermistors can be changed significantly by the type and molar ratio of metal oxide additions as well as the selected process parameters during manufacturing of samples. In this study, the effect of Cr_2O_3 addition on the electrical properties of Mn-Ni-Co-O NTC thermistors sintered at 1100°C for 5 hours was investigated. The electrical resistance was measured in a temperature programmable furnace between 25 and 85°C in steps of 0.1°C. The material constant "B", the activation energy "E_a" and the sensitivity coefficient "α" values were calculated. The aging behaviour of Mn–Ni–Co–Cr-O NTC ceramics was also investigated by electrical resistivity measurement after aging.

Keywords — Aging, Chromium (III) oxide, electrical properties, NTC thermistor, sintering.

1 Introduction

Thermocouples, thermistors and electrical resistance-temperature detectors (RTD) are used for sensitive and accurate determination of temperature. The advantages of thermistors compared to other sensors are their low cost, small size, fast response time and wide variation of electrical resistance against temperature. Thermistors, manufactured by using various metal oxides at specific ratios, can be classified into two types, (1) increasing resistance with temperature known as Positive Temperature Coefficient (PTC) and (2) decreasing resistance with temperature, Negative Temperature Coefficient (NTC). Some transition metal oxides (derived from Mn, Ni, Co, Fe, etc.) have been widely used as NTC thermistors. The oxides represented by the general formula AB_2O_4 exhibit a spinel- type crystal structure. In this chemical formula, "A" represents one or more divalent metal oxides (NiO, CoO, CuO, FeO etc.) and "B" also represents one or more trivalent metal oxides (Mn_2O_3, Fe_2O_3 etc.) [1].

Electrical conduction in NTC thermistors takes place by an electron hopping mechanism based on the principle that charge carriers jump from one ionic site to another. This mechanism in the spinel structure can only occur between ions of different valence of the same element on the B sites. However, the electron hopping mechanism is not possible on the A sites due to the larger distance between two adjacent ions.

As mentioned in the literature, the electrical characteristics of nickel manganite based NTC thermistors are altered by the addition of additives such as Co_2O_3, Fe_2O_3, Cr_2O_3, CuO [2-6]. Having a single phase structure is an important property for the enhanced electrical properties of thermistors.

It has been reported that the single-phase spinel

structure changed according to the amount of Ni content in NTC thermistors. Jung et al. [2] reported that single-phase cubic spinel formation occurs when the Mn / (Mn+Ni) ratio is 0.82 or less, and tetragonal spinel formation occurs above this ratio. In another study, it is also determined that formation of single-phase cubic spinel occurs when x = 0.8 in $Ni_xMn_{3-x}O_4$ system [3].

Duran et al. [4] studied the sintering behavior of Co-doped nickel manganite in their work. For this purpose, samples were prepared according to the stoichiometry of $Co_xNiMn_{2-x}O_4$ ($0.2 \leq x \leq 1.2$) and sintered at 900-1200°C for 6 hours. According to the XRD analysis results, $Co_{0.2}NiMn_{1.8}O_4$ and $Co_{0.6}NiMn_{1.4}O_4$ samples have cubic spinel structure whereas $Co_{1.2}NiMn_{0.8}O_4$ sample, including the highest amount of cobalt content, has tetragonal structure. It is also reported that the grain size decreases with increasing Co content and bulk density changes with the change of sintering temperature rather than Co content. All samples had maximum density at 1050°C (92-99.9%).

Vidales et al. [5] studied the fabrication and characterisation of Mn-Ni-Co-O NTC thermistors. It is stated that most of the NTC thermistors possess the spinel structure and $Ni_xMn_{3-x}O_4$ system shows the best performance. In this study, compositions were prepared according to the stoichiometry of $Mn_{2-x}Ni_1Co_xO_4$ (x= 0.2, 0.6, 1) and $Mn_{1.5}Ni_{0.6}Co_{0.9}O_4$. It is reported that the tetragonal and cubic phases formed when the sintering temperature was between 200-400°C, but the single cubic spinel phase formed with increasing sintering temperature from 500 to 1000°C for the $Mn_{1.5}Ni_{0.6}Co_{0.9}O_4$ samples. The material constant (B) values are found 3068-3804 K in the range between -10 and 200°C.

Varghese et al. [6] investigated the effect of Fe and Cr addition on the electrical characteristics of Ni-Mn-O NTC thermistor ceramics. Samples were prepared by conventional ceramic processing techniques according to the stoichiometry of $Ni_{0.75}Mn_{2.25-x-y}Cr_xFe_yO_4$ ($0 \leq x \leq 0.3$, $0 \leq y \leq 0.3$). XRD analysis showed the formation of cubic spinel structure in the samples sintered at 1150 and 1200°C and no secondary phase was observed. The formation of single phase cubic

spinel is very important for the development of stable and reliable NTC thermistors. The partial decomposition of cubic spinel phase occurs forming rock salt NiO phase when the sintering temperature is increased above 1200°C. The relative density of the samples was found to be in the range of 96-98%. It has been found that resistivity, activation energy and the B value increase with increasing sintering temperature and the amount of Cr_2O_3 content. This increase in resistivity has been explained as a change in cation distribution. It has been reported that Fe^{3+} and Cr^{3+} substitution does not change the valence of Mn^{3+}, it only changes the hopping distance between the charge carriers Mn^{3+} - Mn^{4+}. Consequently, the hopping probability of charge transfer decreases with increase in Cr and Fe content.

Park [7] investigated the effect of Cr addition on the microstructure and electrical properties of Y-Al-Mn-Fe-Ni system. It could be possible to manufacture a thermistor that covers a wide temperature range (from room temperature to 600°C) using a mixture of Y_2O_3 and Al_2O_3 and transition metal oxides (such as MnO, Fe_2O_3, NiO, Cr_2O_3). Such mixtures facilitate an expanded selection of new compositions with the desirable property to measure a wide temperature range. It is reported that the grain size and density of the Cr_2O_3 doped samples are higher than those of the non-doped samples and demonstrated that the Cr_2O_3 could act as a dopant as well as a sintering aid. Increased electrical resistivity and B value with the addition of Cr_2O_3 are also observed.

For Ni-Mn-Co-O, Ni-Mn-Cr-O and Ni-Mn-Co-Cr-O systems, examples of the experimental conditions and the results of studies in the literature are given in Table 1. In this study, the effect of Cr_2O_3 addition on the electrical properties of Ni-Co-Mn-O NTC thermistors was investigated.

2 Material and Method

The conventional ceramic processing technique was used to prepare $Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$ sample. The metal oxide powders were ball-milled for 6 hours with ethanol using ZrO_2 balls. After drying at 110°C, the resulting powders were calcined at 900°C for 2 hours. Powders were mixed with polyvinyl alcohol (PVA) as a binder then pressed into discs at 450 MPa

to prepare samples 12 mm in diameter 3 mm in thickness. The samples were sintered in air at 1100°C for 5 hours employing a 360°C/hour heating rate then cooled naturally in the furnace.

Table 1. A summary of the experimental conditions and results of some studies for the NTC system based on Ni-Mn-O in the literature.

Composition	Sintering Tempera-ture Time	ϱ_{25} (Ω.cm)	$B_{25/85}$ (K)	REF
$Ni_{0.7}Co_{0.5}Mn_{1.8}O_4$	1200-1280°C 3 hours	725	3563	[9]
$Ni_{0.75}Cr_{0.3}Mn_{1.95}O_4$	1150°C 3 hours	3179	3937	[6]
$Mn_{1.1}Ni_{1.4}Co_{0.29}Cr_{0.21}O_4$	1260°C 3 hours	7762	3264	[10]

In order to determine the electrical properties of sintered samples, two opposite sides of samples were coated with silver paste to form electrodes. The electrical resistivity "ρ" (Ω.cm) of the samples were calculated using Equation 2.1;

$$\rho = \frac{R \times A}{l} \quad (2.1)$$

where R (Ω) is the resistance value at room temperature, A is the cross-sectional area and l is the thickness of the sample.

The electrical resistance was measured in a temperature programmable furnace between 25 and 85 °C. The material constant B (K) was calculated using Equation 2.2. In this equation, ρ_{25} (Ω.cm) and ρ_{85} (Ω.cm) being the resistivity at temperature T_{25} (°C) and T_{85} (°C), respectively. The sensitivity coefficient at 25°C of samples α_{25} (-%/K) calculated using Equation 2.3.

$$B_{25/85} = \frac{\ln \rho_{25} - \ln \rho_{85}}{\dfrac{1}{T_{25}} - \dfrac{1}{T_{85}}} \quad (2.2)$$

$$\alpha = \frac{B}{T^2} \quad (2.3)$$

The activation energy E_a (eV) of samples was found by the Equation 2.4, where k_B is the Boltzmann constant, 8.617 x 10⁻⁵ eV.

$$E_a = Bk_b \quad (2.4)$$

The samples were held at 150°C for 100 hours in or-der to determine the aging behavior of $Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$ sample. The change in resistance after aging was found using Equation 2.5.

$$\% \Delta R = \frac{(R - R_0)}{R_0} \times 100 \quad (2.5)$$

3 Results and Discussion

The electrical properties (such as electrical resistance, resistivity, material constant, activation energy, sensitivity coefficient) of $Ni_{0.5}Co_{0.5}Mn_2O_4$ sample was reported in our previous study [8]. In this study, the influence of Cr_2O_3 addition on the electrical properties of Ni-Co-Mn-O NTC system was investigated and compared to the result of our previous work [8]. The comparison of the results obtained in our two studies is shown in Table 2. A linear dependence of log ρ versus 1000/T for $Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$ sample is shown in Figure 1.
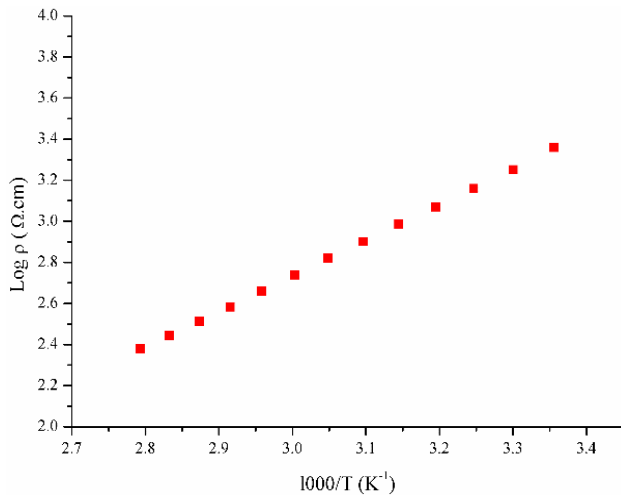
The electrical resistance and resistivity of $Ni_{0.5}Co_{0.5}Mn_2O_4$ sample are found as 266 Ω and 1330 Ω.cm, respectively [8]. With the addition of Cr_2O_3, these values increased to 405 Ω and 2290 Ω.cm for $Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$ sample.

The material constant of $Ni_{0.5}Co_{0.5}Mn_2O_4$ sample was obtained as 3797 K [8], it increased to 4019 K with the addition of Cr_2O_3.

The activation energy of $Ni_{0.5}Co_{0.5}Mn_2O_4$ sample was found as 0.327 eV [8] and the value of 0.346 eV was obtained for $Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$ sample. Similarly, the sensitivity coefficient increased from 4.275 -%/K to 4.525 -%/K with addition of Cr_2O_3.

Table 2. The electrical properties of NTC samples sintered at 1100°C for 5 hours.

Composi-tion	$Ni_{0.5}Co_{0.5}Mn_2O_4$ [8]	$Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$
R_{25} (Ω)	266	405
ρ_{25} (Ω.cm)	1330	2290
$B_{25/85}$ (K)	3797	4019
E_a (eV)	0.327	0.346
α_{25} (-%/K)	4.275	4.525

Figure 1. Relationship between log ρ and reciprocal of the absolute temperature (1000/T) for $Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$ sample.

A comparison with the results of previous studies doped with Cr_2O_3 are summarized in Table 1., $Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$ sample has lower electrical resistivity and higher B value. This result is desirable for NTC thermistors.

It is also important to note that the properties of NTC thermistors are very sensitive to selected raw materials, experimental conditions and composition ratios.

Park and Han [10] investigated the effect of Cr_2O_3 addition on the microstructure and electrical properties of Mn-Ni-Co-O NTC thermistors. Samples were prepared according to the stoichiometry of $Mn_{1.1}Ni_{1.4}Co_{0.5-x}Cr_xO_4$ (0.07 ≤ x ≤ 0.35) and sintered at $1260°C$ for 3 hours. As a result of electrical measurements of the samples; it was found that resistivity (4753 - 15849 Ω.cm) and B (2386 - 4492 K) values were increased with increasing Cr content. The electrical resistivity at room temperature of $Mn_{1.1}Ni_{1.4}Co_{0.5}O_4$ sample was found 4753 Ω.cm and this value increased to 7762 Ω.cm for $Mn_{1.1}Ni_{1.4}Co_{0.29}Cr_{0.21}O_4$ sample. The amount of Co_3O_4 decreased with increasing Cr content, thus Co^{2+}/Co^{3+} ions at octahedral sites decreased. As a result, in order to provide electrical neutrality, the number of Mn^{3+}/Mn^{4+} ions at octahedral sites decreased and so resistivity of Cr doped samples increased [10].

In order to understand the electrical stability, $Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$ sample was held at $150°C$ for 100 hours. Using Equation 5, the change in electrical resistance of $Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$ sample after 100 hours aging test was found to be – 7 %.

4 Conclusion

The addition of Cr_2O_3 to Ni-Mn-Co-O NTC thermistor gave rise to increase in electrical resistivity, material constant, activation energy and sensitivity coefficient. In comparison with literature [9,10], lower electrical resistivity with higher B value for $Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$ sample was obtained. Furthermore, the change in electrical resistance of the $Ni_{0.5}Co_{0.3}Cr_{0.2}Mn_2O_4$ thermistor after aging was found to be – 7 %.

5 Acknowledgment

6 References

[1] Macklen, E.D. Thermistors; Electrochemical Publications Limited: Scotland, 1979; pp 4-10.

[2] Jung, J.; Töpfer, J.; Mürbe, J.; Feltz, A. Microstructure and Phase Development in $NiMn_2O_4$ Spinel Ceramics During Isothermal Sintering. Journal of the European Ceramic Society, 1990; 6, 351-359.

[3] Fritsch, S.; Sarrias, J.; Brieu, M.; Couderc, J. J.; Baudour, J. L.; Snoeck, E.; Rousset A. Correlation between the structure, the microstructure and the electrical properties of nickel manganite negative temperature coefficient (NTC) thermistors. Solid State Ionics, 1998; 109, 229–237.

[4] Duran, P.; Tartaj, J.; Rubio, F.; Moure, C.; Pena, O. Synthesis and sintering behaviour of spinel-type $Co_xNiMn_{2-x}O_4$ (0.2 ≤ x ≤ 1.2) prepared by the ethylene glycol–metal nitrate polymerized complex process. Ceramic International 2005; 31, 599-610.

[5] Vidales, J. L. M. D.; Chain, P. G.; Rojas, R. M.; Vila, E.; Martinez, O. G. Preparation and characterization of spinel-type Mn–Ni–Co–O negative temperature coefficient ceramic thermistors. Journal of Materials Science 1998; 33, 1491–1496.

[6] Varghese, J. M.; Seema, A.; Dayas, K. R. Ni-Mn-Fe-Cr-O negative temperature coefficient thermistor compositions: Correlation between processing conditions and electrical characteristics. Journal of Electroceramics 2009; 22, 436-441.

[7] J. Park; Microstructural and electrical properties of $Y_{0.2}Al_{0.1}Mn_{0.27-x}Fe_{0.16}Ni_{0.27-x}(Cr_{2x})O_y$ for NTC thermistors. Ceramic International 2015; 41, 6386-6390.

[8] Yüksel Price, B.; Hardal, G. Influence of B_2O_3 addition on the electrical and microstructure properties of $Ni_{0.5}Co_{0.5}Cu_xMn_{2-x}O_4$ ($0 \leq x \leq 0.3$) NTC thermistors without

calcination. Journal of Materials Science: Materials in Electronics 2016; 27, 9226–9232.

[9] Muralidharan, M. N.; Rohini, P. R.; Sunny, E. K.; Dayas, K. R.; Seema, A. Effect of Cu and Fe addition on electrical properties of Ni–Mn–Co–O NTC thermistor compositions. Ceramic International 2012; 38, 6481-6486.

[10] Park, K.; Han, I. H. Effect of Cr_2O_3 addition on the microstructure and electrical properties of Mn-Ni-Co oxides NTC thermistors. Journal of Electroceramics 2006; 17, 1069-1073.