Aging Behaviour in $Ni_{0.5}Co_xMn_{2.5-x}O_4$ (x = 0.5, 0.8 and 1.1) Thermistors

Gökhan Hardal and Berat Yüksel Price

Abstract Negative temperature coefficient (NTC) thermistors are required to have good electrical stability for many domestic and industrial applications. The aging phenomenon of NTC thermistors can be described as the change in electrical resistance due to thermal stress with time. In this study, $Ni_{0.5}Co_xMn_{2.5-x}O_4$ (x = 0.5, 0.8 and 1.1) ceramics were fabricated by the conventional solid-state reaction method. The powder mixtures of manganese, cobalt and nickel oxides were ball-milled for 5 h. The powders were calcinated at 900 °C for 2 h. The samples were sintered at 1100 °C for 5 h. To investigate the aging behaviour, the samples were held at 150 °C for 400 h. Aging in the samples were calculated by the following equation; $\Delta R/R_0 = (R - R_0)/R_0$ in which R_0 is the resistance at 25 °C before the aging test, and R is the resistance at 25 °C after the aging test.

Keywords Aging · Electrical properties · NTC thermistors

Introduction

Nickel manganite based materials are used as negative temperature coefficient (NTC) thermistors. They are widely used in air conditioners, refrigerators, medical equipment etc. as temperature sensors due to their interesting electrical properties [1]. Transport phenomena in these materials are frequently explained by phonon-assisted jump of carriers among localized states, this is known as hopping conductivity. Their electrical resistivity (ρ) varies exponentially with temperature (T) by the well-known Arrhenius equation $\rho = \rho_o \exp(B/T)$, where ρ_o is the resistivity of the material at infinite temperature and B is the material constant

G. Hardal (✉) · B.Y. Price
Metallurgical and Materials Engineering Department,
Istanbul University, Istanbul, Turkey
e-mail: gokhan.hardal@ogr.iu.edu.tr

B.Y. Price
e-mail: berat@istanbul.edu.tr

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which is a measure of the sensitivity of the material over a given temperature [2]. The material constant (B) can be calculated by Eq. (1).

$$B_{T1/T2} = \frac{ln\,\rho_1 - ln\,\rho_2}{\frac{1}{T_1} - \frac{1}{T_2}} \tag{1}$$

ρ_1 and ρ_2 being the electrical resistivity at temperature T_1 and T_2, respectively. Nickel manganite based thermistors exhibit the spinel-type crystal structure with the general formula AB_2O_4. In the spinel structure, there are two sites available for the cations; (1) the tetrahedral site is known as A-site and (2) the octahedral site is known as B-site. The distribution of the ions is as follows in nickel manganite: Mn^{3+} will predominantly occupy the B-site, while Mn^{2+} can be found on the A-site and the majority Ni^{2+} can be found on the B-site [3].

The electrical stability of NTC thermistors is very important. However, the drift in resistance ($\Delta R/R$) of a thermistor occurs due to thermal stress with time. The long-term stability of the electrical properties depends on many factors such as the chemical composition, crystal structure (cubic or tetragonal) and the heat treatments applied to NTC thermistors. The chemical composition in thermistor alters its microstructural properties such as crystal structure, density, grain size etc. The atomic diffusion in the spinel lattice can be altered by various heat treatments, the intergranular defects could act as barriers against ion mobility thus explaining the better thermal stability of the thermistors [1].

It is generally considered that the aging is connected with ion exchange between tetrahedral and octahedral sites. The ionic diffusion on octahedral sites may give rise to ionic migration between octahedral and tetrahedral sites. The redistribution of cations occurs owing to cation vacancies and a cationic vacancy migration take places from grain boundary to grains during aging [4].

In this study, we aim to investigate the aging behaviour of $Ni_{0.5}Co_xMn_{2.5-x}O_4$ ($x = 0.5$, 0.8 and 1.1) thermistors.

Experimental Procedures

NiO (99% purity, Alfa Aesar), Co_3O_4 (99.5% purity, Sigma-Aldrich) and Mn_2O_3 (99% purity, Sigma-Aldrich) powders were weighed according to the compositions of $Ni_{0.5}Co_xMn_{2.5-x}O_4$ (where $x = 0.5$, 0.8 and 1.1). The raw powder mixture was ball-milled using ZrO_2 balls as a grinding media with ethyl alcohol in a jar for 5 h. The obtained slurries were dried and powders were calcinated at 900 °C for 2 h. The powders were pressed to form disc shaped specimens and then sintered at 1100 °C for 5 h in air employing a 360 °C/h heating rate then cooled naturally in the furnace.

The phases in the sintered samples were determined by X-ray diffraction (XRD, Rigaku D/Max-2200/PC) analysis using CuK_α radiation at 60 kV/2 kW. The microstructure of samples was observed using a scanning electron microscope (SEM, JEOL, JSM 5600) on fracture surfaces. The sintered samples were coated with silver paste to form electrodes. 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, K), the activation energy (E_a, eV), and the sensitivity coefficient (α, %/K) values were calculated for the NTC thermistors.

The samples were held at 150 °C for 400 h in order to age the samples. The drift in resistance was calculated by equation;

$$\%\Delta R = \frac{R - R_0}{R_0} \times 100 \tag{2}$$

in which "R" is the resistance at 25 °C after aging for 400 h, R_0 is the resistance at 25 °C before aging.

Results

Figure 1a shows the variation of electrical resistance with Co content at 25 °C before and after the aging process. The resistance of samples decreased with the increasing Co content. For the $Ni_{0.5}Co_{0.5}Mn_2O_4$ (A05) sample, the resistance was found as 298 Ω, it decreased to 136 Ω for the $Ni_{0.5}Co_{0.8}Mn_{1.7}O_4$ (A08) sample. A further decrease in resistance to 88 Ω was observed for the $Ni_{0.5}Co_{0.8}Mn_{1.7}O_4$ (A11) sample. In our previous work, the resistivity, $B_{25/85}$ constant and activation energy of samples decreased when Co content increased from 0.5 to 1.1 [5]. This can be explained by the increase in Co^{2+} and Co^{3+} ions, which are responsible for the hopping mechanism on octahedral sites, due to increased Co content.

Muralidharan et al. [6] reported that the resistivity, B constant, the activation energy and temperature coefficient of resistance decreased with the increasing Co content for $Ni_{0.7}Mn_{2.3-x}Co_xO_4$ ($0 \leq x \leq 0.7$) NTC thermistors. This observation was explained by the Co^{2+} and Co^{3+} ions also occupying the octahedral sites and contribute to the electrical conductivity along with Mn^{3+}/Mn^{4+} ion pairs in the octahedral sites.

Park et al. [7] reported that the resistivity of samples increased with the addition of Cr_2O_3 in $Mn_{1.1}Ni_{1.4}Co_{0.5-x}Cr_xO_4$ ($0 \leq x \leq 0.35$) NTC thermistors. They reported the resistivity of the thermistors increased as the Cr content increased. There are two possible reasons for the increase in the resistivity with increasing Cr content. (1) Both the grain size and density of the as-sintered samples decreased with an increase in Cr content, decreasing the time between electron scattering events of charge carriers and thus increasing the resistivity. (2) The amount of Co_3O_4 for the thermistors decreases with increasing Cr content, decreasing Co^{2+}/Co^{3+} ions on octahedral sites. As a result, the number of Mn^{3+}/Mn^{4+} ions on octahedral sites decreases to preserve the overall electrical neutrality of the system.

Fig. 1 **a** Variation of electrical resistance at 25 °C **b** Variation of $\Delta R/R_0$ as a function of Co content (x)

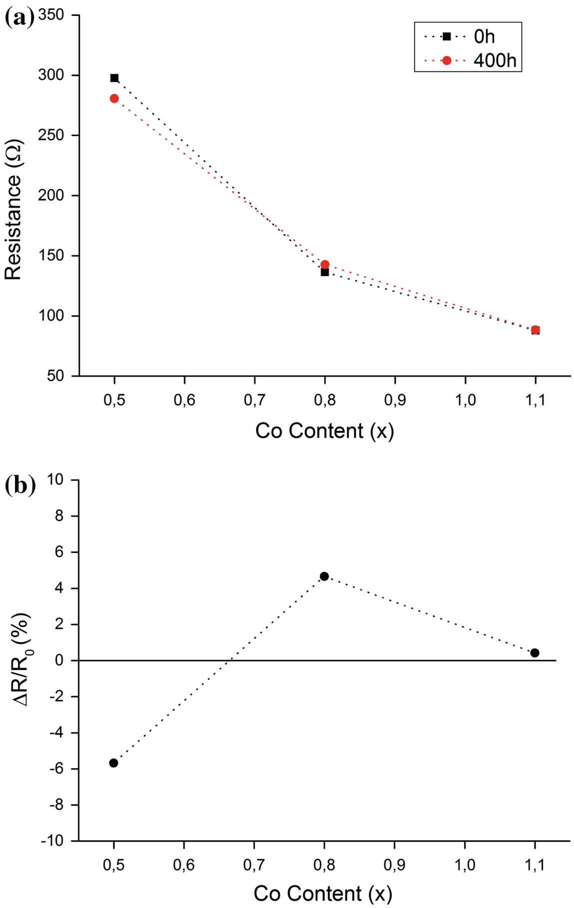

Figure 1b shows the variation of $\Delta R/R_0$ as a function of Co content for $Ni_{0.5}Co_xMn_{2.5-x}O_4$ (where x = 0.5, 0.8 and 1.1) ceramic system. The A05 sample aged negatively, but A08 and A11 samples behaved unlike A05 sample. The drift in resistance of A05 sample was calculated as ≈−6%. For A08 sample, the aging value was a positive change in resistance of ≈5%. Then, it decreased sharply to +0.4% with increasing Co content from 0.8 to 1.1.

Conclusion

Aging phenomenon of nickel manganite based NTC thermistors thermally stressed at 150 °C for 400 h was investigated. The drift in resistance ($\Delta R/R$) of $Ni_{0.5}Co_xMn_{2.5-x}O_4$ (where x = 0.5, 0.8 and 1.1) thermistors varied in the range from −5.7% to +0.4%. The drift in resistance decreased with increasing Co content from 0.8 to 1.1. In this study, the best electrical stability was observed for the $Ni_{0.5}Co_{1.1}Mn_{1.4}O_4$ thermistor with a positive change in resistance of 0.4%.

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