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Electrical properties comparison of NTC thermistors prepared from nanopowders and mixed-oxide process

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Abstract: We have synthesized and studied the effects of cobalt doping on the electrical properties of NTC thermistors with composition of $NiMn_{2-x}Co_xO_4$ (x= 0.0, 0.4, 0.8, 1.2, 1.6). The electrical properties of NTC thermistors prepared from nanopowders by gel auto-combustion and mixed-oxide process have been compared. The measured results indicated that the fluctuation of B values for samples made from nanopowders is less than that for the samples prepared from mixed oxide method. As the electrical properties of these ceramics are depend too much on grain size. The samples made from nanopowders have smaller grain size since the sintering time was chosen to be the same for both samples.

Keywords: NTC thermistors; nanopowders; material constants.

Introduction

NTC thermistors elements, which exhibit a decrease in electrical resistance with increasing temperature, are widely used in manufacturing temperature sensors with negative temperature coefficient.

Most ceramic compositions, which used in NTC thermistors, have spinel structure with general formula AB_2O_4. This structure is based on the oxygen atoms arranged in an fcc structure containing tetrahedral A and octahedral B lattice sites. The electrical conductivity of materials having spinel structure has been explained via hopping process [1]. The electrical charge transport occurs by the hopping of electrons between the B^{+3} and B^{+4} ions present at the octahedral sites in the lattice. The electrical conductivity of Mn_3O_4 and similar spinel structures, with Mn^{+2} on tetrahedral sites and Mn^{+3} on octahedral sites, is not very significant. This structure does not contain ions of the same element with different charges on similar sites, as required for electron hopping. However, the substitution of Ni for Mn increases the conductivity. Ni^{+2} occupy octahedral sites and the charge balance is maintained by the conversion of Mn^{+3} to Mn^{+4}, thus providing a basis for hopping process [2].

Nanosized NTC precursor powder fabrication is of a special interest to sinter fine-grained ceramics. Chemical methods such as coprecipitation and polymerized complex process [3, 4, 5] are employing nowadays to synthesis the NTC nanopowders.

In this work, we have synthesized NTC nanopowders with compositions of $NiMn_{2-x}Co_xO_4$ (x=0.0, 0.4, 0.8, 1.2, 1.6) by gel auto-combustion method. We also employed mixed oxide process in order to compare the performance of these samples. The dependence of resistivity, material constant (B) and temperature coefficient (α) have been measured. The electrical properties of the samples prepared by gel auto-combustion and solid solution methods have been studied and compared to each other.

Despite the number of papers already published on the synthesis of NTC powders and electrical properties of thermistors. The comparison of electrical properties obtained by these methods has rarely been studied. However, to our knowledge no previous experimental results for these compositions have been seen to compare with the results of this paper.

Experimental

(A) Samples from nanopowders

NTC nanopowders were synthesized by gel auto-combustion method. Nickel nitrate [$Ni(NO_3)_2.6H_2O$], cobalt nitrate [$Co(NO_3)_2.6H_2O$], manganese nitrate [$Mn(NO_3)_2.4H_2O$] (Merck, Germany), citric acid and nitric acid (scharlau) were used as starting materials. According to the composition of $NiMn_{2-x}Co_xO_4$, the appropriate amount of nitrates, citric acid and nitric acid were dissolved into deionized water to form the mixed solutions. Sol of NTC was maintained at pH of 7 by adding ammonium hydroxide (Fluka). The gel was prepared by heating the sol at temperature of about 75°C.

Finally, the nanopowders of NTC were obtained by adding nitric acid to the gel in order to ignite it. The resultant nanopowders were calcinated at 800°C to obtain the desired single phase nanopowders. The calcinated powder was granulated using PVA as a binder, and pressed to form a disk shape specimens. The specimens were sintered at 1200°C for 6h in air. For measuring the electrical properties, the disk obtained from nanopowders are named sample A.

(B) Samples from traditional solid solution

Manganese, cobalt and nickel oxide with high purity (Merck, Germany) were weighed and mixed according to the composition of $NiMn_{2-x}Co_xO_4$ (x=0.0, 0.4, 0.8, 1.2, 1.6). The mixed oxide powder was calcinated at 900°C. The calcinated powders were granulated using PVA as a binder, and pressed to form a disk shape specimens. The samples were sintered at 1250°C for 6h in air. For measuring the electrical properties, the specimens made by this method were named sample B.

The electrical resistance was measured at constant d.c voltage with a high resolution digital voltmeter, model Hioki-3200 and the temperature was measured using a high resolution (0.1°C) microprocessor-based digital thermometer, model Fluke-51.

Results and Discussion

Fig. 1 shows the resistivity-temperature response of gel auto-combustion samples between 308 and 473°K. The resistivity at 308°K vary from 59877.41Ω-cm for sample A1 (without cobalt) and to 665.091Ω-cm for sample A3 (with 0.8 mol. of cobalt). It decreases to 1255.43Ω-cm for sample A1 and to 19.64 Ω-cm for sample A3 at temperature of 473°K.

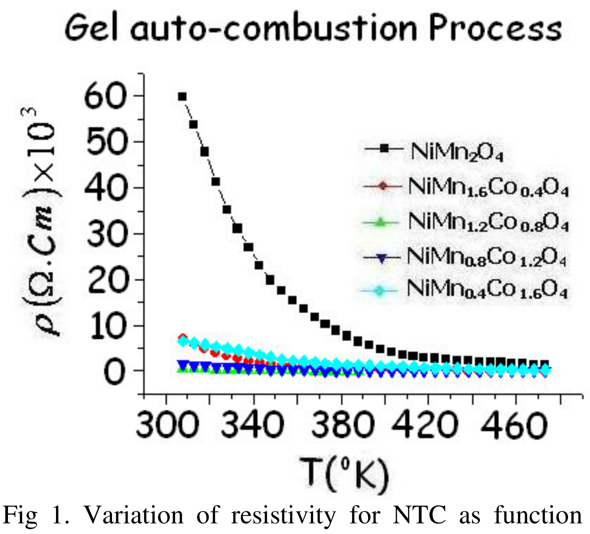


Fig 1. Variation of resistivity for NTC as function of temperatures for the samples prepared by gel auto-combustion process.

Fig. 2 shows the resistivity-temperature response of traditional solid solution (mixed oxide) samples between 308 and 473°K. The resistivity at 308°K vary from 313.57Ω-cm for sample B2 (with 0.4 mol. of cobalt) and to 59.51Ω-cm for sample B4 (with 1.2 mol. of cobalt). It decreases to 2.4Ω-cm for sample B2 and to 0.3Ω-cm for sample B4 at 473°K.

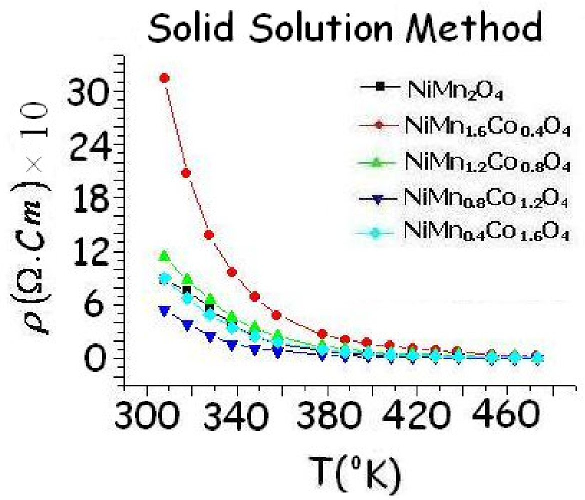


Fig 2. Variation of resistivity of NTC as function of temperatures for the samples prepared by mixed oxide method.

Fig. 3 shows the values of the d.c resistivity of the samples as function of cobalt content. The specific resistance, ρ, was determined from R=ρd/S by measuring the resistance (R) and thickness/area (d/S) of the samples. Fig. 3 indicates that the resistivity of the samples, prepared by gel auto-combustion process, for x=0 is highest and decreases with increasing the cobalt content. For x=0.8 the resistivity is minimum and increases by increasing the amount of cobalt in the samples.

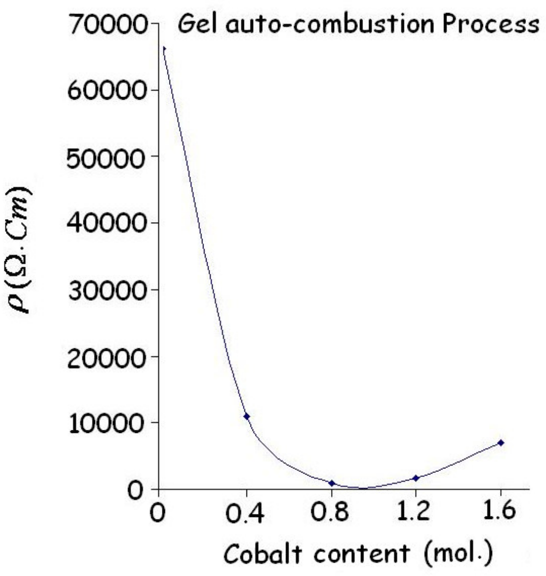


Fig 3. Variation of d.c resistivity of the samples perpetrated from nanopowders as function of cobalt content.

Fig. 4 shows the resistivity with the cobalt content, for samples made by mixed oxide method. As it can seen in the Fig, the resistivity for x=0 is rather low and that increases and reaches a maximum for x=0.4, then decreases and reaches a minimum for x=1.2. After that increases gradually for the sample with higher cobalt content.

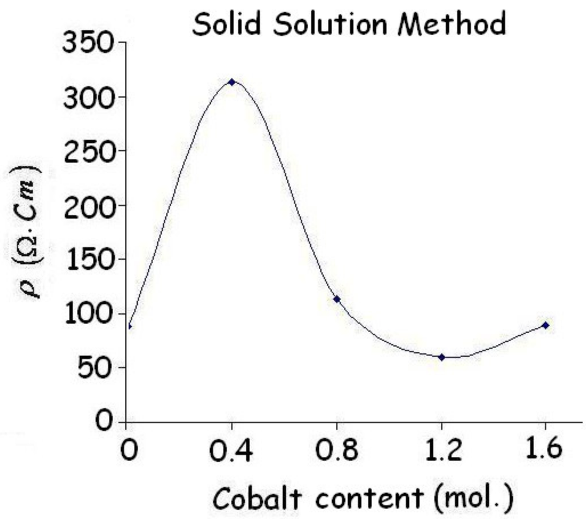


Fig 4. Variation of d.c resistivity of samples perpetrated by mixed oxide method as function of cobalt content.

The material constant, B, and the temperature coefficient, α, have been evaluated as follows [6]:

$$B = \ln \frac{(\rho_1 / \rho_2)}{(1/T_1 - 1/T_2)} \qquad (1)$$

$$\alpha = (-B)/T^2 \qquad (2)$$

where ρ_1 and ρ_2 are the nominal values of resistivity at T_1 and T_2 respectively. The measured values of B and α for both methods are summarized in Table 1.

Table 1. Electrical parameters of NTC prepared with different methods.

(a). Gel auto-combustion process

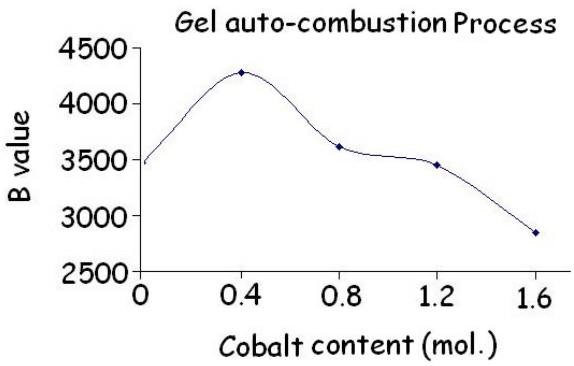
Samples	Composition	B(K)	α [25°C](K^{-1})
A1	$NiMn_2O_4$	3476.8	-3.92
A2	$NiMn_{1.6}Co_{0.4}O_4$	4283.45	-4.82
A3	$NiMn_{1.2}Co_{0.8}O_4$	3620.18	-4.07
A4	$NiMn_{0.8}Co_{1.2}O_4$	3455.59	-3.89
A5	$NiMn_{0.4}Co_{1.6}O_4$	2851.87	-3.22

(b). Mixed oxide method.

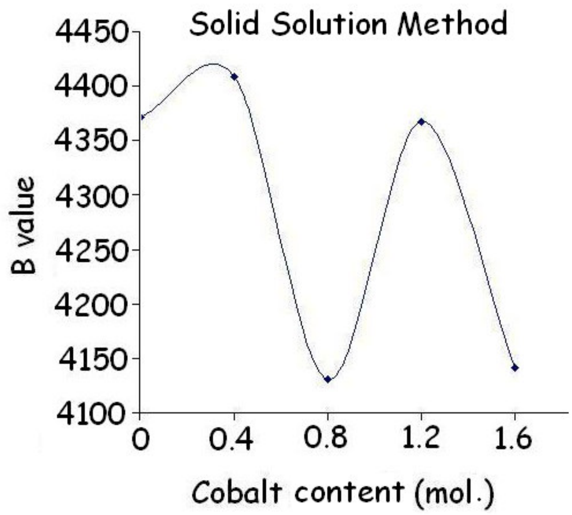
Samples	Composition	B(K)	α [25°C](K^{-1})
B1	$NiMn_2O_4$	4371.59	-4.92
B2	$NiMn_{1.6}Co_{0.4}O_4$	4408.85	-4.97
B3	$NiMn_{1.2}Co_{0.8}O_4$	4130.97	-4.65
B4	$NiMn_{0.8}Co_{1.2}O_4$	4367.51	-4.92
B5	$NiMn_{0.4}Co_{1.6}O_4$	4141.15	-4.66

The effects of cobalt content on constant B for the samples are shown in Figs. 5a and 5b. The results indicate that in both methods the maximum value of B occurs when the content of cobalt is about x=0.4.

The fluctuation of B values for the samples made from nanopowders is less than for the samples prepared from mixed oxide process. Since it is found that the electrical properties of these ceramics depends strongly on the grain size [7]. Therefore, one expects that the samples made from nanopowders have smaller grain size and hence smaller value of B as the sintering time was chosen the same in both methods.



(a)



(b)

Fig 5. The material constant B for NTC as function of cobalt content mol. (a) gel auto-combustion process. (b) mixed oxide method.

Conclusion

We have synthesized NTC nanopowders with compositions of $NiMn_{2-x}Co_xO_4$ (x=0.0, 0.4, 0.8, 1.2, 1.6) by gel auto-combustion process. We employed also the mixed oxide process in order to compare the behavior of these samples. The dependence of resistivity, material constants (B) and temperature coefficient (α) have been measured and the results for the different samples were compared. The fluctuation of B values for samples made from nanopowders is less than that samples prepared from mixed oxide method. Since, the electrical properties of these ceramics are depending too much on grain sizes. The samples made from nanopowders have smaller grain sizes and hence smaller value of B and α in comparison with mixed oxide samples.

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