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Intrinsic Resistivity of Sintered Nickel Manganite vs. Powder Activation Time and Density

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Abstract:

In this work the DC resistivity of sintered nickel manganite $NiMn_2O_4$ (NTC thermistor material) was studied as a function of additional powder activation time in a planetary ball mill (0, 5, 15, 30, 45 and 60 min). The activated powders and non-activated powder were sintered at different temperatures (900, 1050 and 1200^{0}C) for an hour. Structural changes were analyzed using XRD. Sample density, porosity and DC resistivity were measured on the same sintered samples. Correlations between sample density, porosity, and intrinsic DC resistivity vs. additional powder activation time and the sintering temperature were made. It was noticed that the resistivity falls with the increase of sample density (or increase of the sintering temperature).

Keywords: *Nickel manganite, Resistivity, Mechanical activation.*

1. Introduction

Nickel manganite oxides, consisting of these 3d transition metals are very interesting ceramics widely used for negative temperature coefficient (NTC) thermistors [1-3]. NTC thermistors have been in use for a long time, mainly in electronics as elements for temperature control and compensation, time delay, voltage regulation, fan control etc. [4-6]. Their application is limited by a low Currie point (around 150^{o}C). Much work has been done recently, in order to develop different material contents, for high temperature NTC application [7,8]. In order to achieve better understanding of thermistor behavior (its sensitivity and response depends on physical properties) it is significant to characterize the material and analyze more closely its physico-chemical properties.

It is well known that nickel manganite has an intermediate (partially inverse) cubic spinel structure. Values of the cation inversion parameter were calculated to be between 0.8 and 0.88 [9] and this parameter has a direct influence on all physical properties of this material [10]. The mechanism, responsible for conduction in nickel manganite, is commonly described as phonon-assisted electron jumping (so–called hopping) between Mn^{3+} and Mn^{4+} cations placed in octahedral sites. The resistivity of NTC thermistors decreases exponentially with temperature and can be represented with an Arrhenius equation:

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$$\rho = \rho_0 \exp(\frac{B}{T}) \quad (1)$$

where ρ is the resistivity of the material at infinite temperature, T is the absolute temperature, and B is the temperature coefficient of resistivity, given in Kelvin. Resistivity is strongly influenced by the composition and preparation of transition metal oxides.

Many authors have attempted to define a relation between the structure, microstructure, thermal and electrical properties of the sintered material used as the starting material for the production of sensitive NTC thermistors [11]. In our earlier papers we investigated the influence of the time and temperature of sintering on thermal, optical and some electrical properties of this material [12-14]. Electrical properties were also described in [15, 16, 9]. Recently, the influence of oxygen stoichiometry on the magnetic properties of spinel sublattices has been investigated [17].

The main purpose of this investigation is to show the non-negligible influence of mechanical activation of the starting mixed oxides on electrical properties (direct current (DC) resistivity in our case) of the formed nickel manganite. Mechanical activation has great advantages, producing a more homogeneous material, compared to other processes. This technique increases the number of carriers and intensifies transport processes. Besides the time and temperature of sintering, it is very important to optimize the time of mechanical activation, because short mechanical activation doesn't give enough energy to improve material properties, but a long activation time leads to the formation of microstructure defects influencing the number of carriers, conductivity (resistivity) of materials. A very long activation time finally leads to higher nanoparticle agglomeration that causes higher porosity in the material obtained.

Experimental

Samples of the investigated NTC thermistor material ($NiMn_2O_4$) were obtained following the classical procedure for the preparation of NTC thermistor powder [4]. Mixtures of starting MnO and NiO (containing 0.5 wt % CoO and Fe_2O_3) powders were calcinated for 1h at 1050^0C. After vibratory milling in an ultra-fast ball mill for 2h, an average powder particle size of 0.9 μm was achieved. Mechanical activation was done by grinding in a continual regime in a Fritsch Pulversette 5 planetary ball mill for 5,15,30,45 and 60 minutes. Iron grinding balls was used, and the powder to ball mixture mass ratio was 1:10. The powders obtained were uniaxially pressed with 196 MPa into disc shape pellets 8 mm in diameter, and then sintered at 900, 1050 and 1200°C for 60 minutes.

DC resistivity measurements were performed on a HP 4194A impedance/gain phase analyzer. For these measurements, sample contacts (electrodes) were prepared by spreading a one component epoxy paste with silver filler. After that, the samples were annealed for 15 minutes at 150°C, achieving a homogeneous electrode on the sample surface. The thickness of the electrode was about 100μm. DC measurements were performed on three different temperatures, at room temperature (25°C), 50°C and 80°C. The coefficient of temperature sensitivity $B_{25/80}$ can be calculated using the well known equation which verifies R-T thermistor characteristics:

$$B = \frac{T_1 T_2}{T_1 - T_2} \ln \frac{R_2}{R_1}, \quad (2)$$

where T_1 and T_2 are the room temperature and 80°C respectively, and R_2 and R_1 are the resistivities at those temperatures.

The activation energy (E_a) for electrical conduction can be calculated from the following expression:

$$B = \frac{E_a}{k}$$, where k is the Boltzman constant.

Crystalline structures of the nonactivated and activated samples were recorded using a Philips PW 1050 X-Ray Difractometer, with Cu K_α radiation and scans were taken with a step of 0.05°/s.

Results and Discussion

Figure 1 gives a typical XRD pattern of NiMn2O4, activated for 15 minutes and then sintered at 1200°C for 60 minutes and. For all analyzed samples X-ray analysis showed that a single phase spinel structure was obtained (Tab. I). Very slightly changes in the lattice parameter parameter a, were noticed, for different activation times.

Tab. I Lattice parameter a for different activation times

t (min)	a (Å)
0	8.385
15	8.406
30	8.388
60	8.383

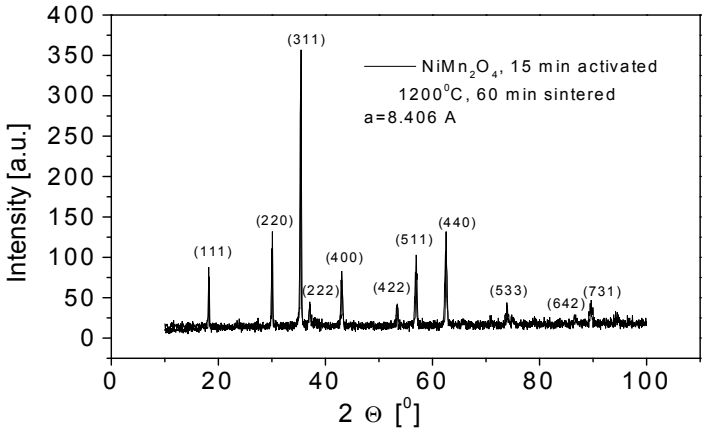

Fig. 1 X-ray diffraction pattern of $NiMn_2O_4$ sintered at 1200°C for one hour, milled for 15 minutes

A relatively dense material was achieved, and Fig. 2 shows the variations in density of the $NiMn_2O_4$ samples with changes of sintering temperature and time of mechanical activation. It is well known that density rises, as the temperature of sintering increases, and that behavior was shown in Fig 2. A high density jump was noticed at 1200°C compared to the values obtained for lower sintering temperatures. For all three sintering temperatures, variations of density with the change of mechanical activation time showed a similar trend. First, the density increases (due to powder attrition) but for longer activation times (45 and 60 minutes) density decreases as a consequence of powder agglomeration.

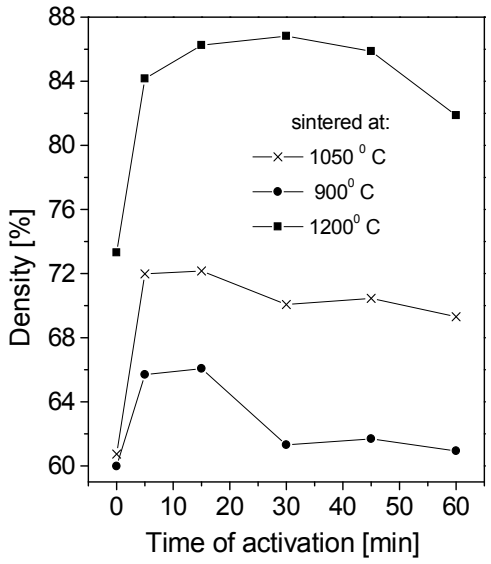

Fig. 2 Variations of density vs. change of activation time and sintering temperature

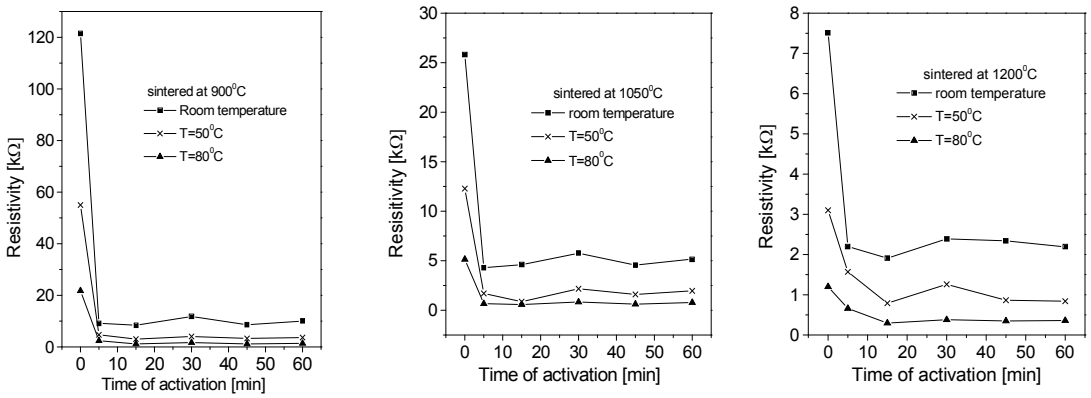

Fig. 3 Intrinsic resistivity vs. change of mechanical activation on different ambient temperatures

The activation energy (shown in Tab.II) is the energy of conduction, and represents the energy for the hopping process from Mn^{3+} to Mn^{4+} situated on the octahedral sites, and thus the mobility of small polarons.

It is obvious, from Tab. II, that the electrical properties for thermistors differ, (the smallest *B* value and thus E_a was obtained for the sample sintered at 1200°C for one hour and activated 5 min) and can be controlled by changing the conditions of sintering and the time of mechanical activation.

Tab. II Resistivity values at 25°C and 80°C, *B* constant and activation energy E_a for $NiMn_2O_4$ samples sintered at different temperatures and with different mechanical activation times of the starting powder

Samples (Sintering conditions)	R_1 (25°C) [Ω]	R_2 (80°C) [Ω]	Coefficient of temperature sensitivity $B_{25/80}$ [K]	Activation energy E_a[eV]
1200°C, 60 min				
Nonactivated	7520	1200	3510	0,302
5 min	2200	662	2297	0,197
15	2200	296	3566	0,307
30	1910	380	3517	0,303
45	2340	350	3633	0,313
60	2190	360	3454	0,297
1050°C, 60 min				
Nonactivated	25800	5140	3085	0,275
5 min	4300	662	3578	0,308
15 min	4600	578	3967	0,342
30 min	5760	837	3689	0,318
45 min	4560	620	3816	0,329
60 min	5160	780	3613	0,311
900°C, 60 min				
Nonactivated	121500	21780	3287	0,283
5 min	9180	2407	2560	0,220
15 min	8400	1184	2830	0,244
30 min	11800	1700	3705	0,319
45 min	8600	1194	3776	0,325
60 min	10000	1390	3774	0,325

It can be noted (Fig. 3.) that the intrinsic resistivity falls with the increase of the sintering and environment temperature, as a consequence of carrier number growth, which provides a higher conductivity and hence decrease of resistivity. Mechanical activation for shorter times produces a reduced grain size and porosity, an increase of sample density, leading to a reduction in electrical resistivity. For longer activation times, it leads to an increase of porosity and thus, decrease of sample density. That is in accordance with the resistivity rising.

Conclusion

DC resisitivity of sintered $NiMn_2O_4$ was studied as a function of mechanical activation of the starting powder. The activation energy (energy of conduction) and the coefficient of temperature sensitivity $B_{25/80}$, were also calculated.

It is very well known that electrical properties of ceramics are strongly influenced by the material composition, sintering conditions and the time of mechanical activation. It was shown that electrical properties of a thermistor material sintered and mechanically activated for different times differ and can be controlled by variation of these parameters. That way broad application of these thermistors can be achieved.

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***Садржај**: У овом раду мерена је и анализирана DC отпорност синтерованог $NiMn_2O_4$ (NTC термисторског материјала) у функцији од времена механичке активације која је вршена у планетарном млину 5, 15, 30, 45 и 60 минута. Неактивирани и механички активирани прах је синтерован 1h на различитим температурама од 900^0C, 1050^0C и 1200^0C. Структурне промене су праћене помоћу рефлексионе дифракције X зрака. Мерене су густина, порозност и DC отпорност узорака. Извршена је корелација између густине, порозности и DC отпорности у функцији од механичке активације и температуре синтеровања датих узорака. Примећено је да DC отпорност опада са порастом густине узорака (и временом механичке активације) као и да расте са повећањем температуре синтеровања.*

***Кључне речи:** Никл манганит, отпорност, механичка активација.*