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E. Jabry, G. Boissier, A. Rousset, R. Carnet, A. Lagrange. PREPARATION OF SEMICONDUCTING CERAMICS (NTC THERMISTORS) BY CHEMICAL METHOD. Journal de Physique Colloques, 1986, 47 (C1), pp.C1-843-C1-847. 10.1051/jphyscol:19861129 . jpa-00225526

HAL Id: jpa-00225526

<https://hal.science/jpa-00225526>

Submitted on 1 Jan 1986

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PREPARATION OF SEMICONDUCTING CERAMICS (NTC THERMISTORS) BY CHEMICAL METHOD

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Résumé - La décomposition en atmosphère contrôlée de précurseurs oxaliques mixtes $(\text{Mn}_{1-y}\text{Ni}_y)\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ permet de préparer directement et à basse température (600-700°C) des poudres de manganites de nickel $\text{Mn}_{3-x}\text{Ni}_x\text{O}_4$ ($0 < x < 1$) présentant une morphologie contrôlable. Ces poudres, frittées à 1160°C seulement, conduisent à des céramiques semi-conductrices très bien densifiées (96 % de la densité théorique) et présentant des résistivités électriques nettement plus faibles que celles observées jusque là pour de tels composés.

Abstract - The decomposition in controlled atmosphere of mixed oxalic precursors $(\text{Mn}_{1-y}\text{Ni}_y)\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ allows at low temperature (600-700°C), direct preparation of powders of nickel manganites $\text{Mn}_{3-x}\text{Ni}_x\text{O}_4$ ($0 < x < 1$) producing a controlled morphology. These powders sintered at only 1160°C lead to highly densified semiconducting ceramics (96 % of the theoretical density) and have electrical resistivities clearly lower than those observed up until now for such compounds.

I - INTRODUCTION

Thermistors with a Negative Temperature Coefficient (N.T.C.) are semiconducting ceramics, most often constituted by transition metals manganites. In these solids the electrical conductivity is due to the phenomenon of transfer of electrons (hopping) between the Mn^{3+} and Mn^{4+} ions in octahedral sites /1/. The resistivity of these phases follows the classical law of semiconductors : $\rho = \rho_0 e^{B/T}$ with $B = \frac{\Delta E}{2K}$, ΔE is the activation energy of the hopping mechanism.

The necessity for improving the electrical properties of these electronic components necessitates the modification of the preparation process notably through the reaching of an optimized microstructure /2//3/. Therefor recent investigations have stressed the importance that must be given to the morphology of the powders submitted to sintering /3//4//5/.

In this study we will reveal the interest of preparing powders of nickel manganites at low temperature which, as a result of this, have a controlled morphology. The sintering operation is then much simplified, it leads to very dense and well optimized ceramics as far as the electrical properties are concerned.

The nickel manganites $\text{Mn}_{3-x}\text{Ni}_x\text{O}_4$ ($0 < x < 1$) are phases with a spinel structure which are very difficult to obtain in the pure state /6//7//8//9/. Rather than using the conventional method of solid-solid reaction between Mn_3O_4 and NiO we have preferred

to use the decomposition of a mixed organic precursor in order to obtain directly powders of nickel manganites. These powders may be sintered at relatively low temperatures which appears as a great advantage as the nickel manganites are unstable at high temperature /10//11/.

From a structural point of view, different distributions have been proposed in particular for the compound NiMn_2O_4 ($x = 1$); we will adopt the model based on the stabilisation energies of the manganese and nickel ions in the crystalline field, namely $\text{Mn}^{2+} | \text{Mn}^{3+}_{2-2x} \text{Mn}^{4+}_x \text{Ni}^{2+}_x | \text{O}_4^{2-}$ ($0 < x < 1$) /12/.

II - PREPARATION OF NICKEL MANGANITES POWDERS

The powders result from the decomposition of oxalic precursors $\text{Mn}_{1-y} \text{Ni}_y (\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ ($0 < y < 1/3$) prepared by coprecipitation in aqueous solution. Different compositions have been studied as shown in table I which also gives the compositions of the corresponding manganites $\text{Mn}_{3-x} \text{Ni}_x \text{O}_4$ with $x = 3y$ and $0 < x < 1$.

Table I

y	0	0.025	0.100	0.155	0.195	0.220	0.235	0.270	0.285	0.325
x	0	0.07	0.30	0.47	0.58	0.66	0.71	0.81	0.85	0.97

1. Decomposition of the mixed oxalates in air

Thermal decomposition processing is described elsewhere /13/. This process does not lead directly to the required spinel structure. In fact, beyond 420°C, that is to say after the end of the decomposition, XRD analysis reveals a mixture of phases constituted of cubic Mn_2O_3 and of rhomboedric ferromagnetic NiMnO_3 .

Taking into account the high reactivity of the oxides, a thermal treatment of several hours at 800°C allows a simultaneous crystallisation of these oxides in a unique spinel phase according to the reaction

for all values $0.50 < x < 1$.

Thus spinel phase is obtained at 800°C instead of at 1100°C with a conventional processing.

The morphologic analysis of the manganites thus prepared show that the powders are formed of rather strongly conglomerate particles with a large range of sizes shapes and a low surface area ($1-2 \text{ m}^2 \text{ g}^{-1}$). Such characteristics which derived from the thermal treatment done during several hours at 800°C, are not necessarily the best to optimize the microstructure in a further sintering operation. Better controlled properties would be hoped for in the case of these manganites if they were obtained directly at lower temperature. In this way it is essential to avoid the formation of the phase Ni Mn O_3 in lowering the oxygen partial pressure during the precursor decomposition.

2. Decomposition of the mixed oxalates in controlled atmosphere

Due to the conventional atmosphere being too oxidizing, we have worked in mixtures of $\text{N}_2 + \text{O}_2$, poorer in oxygen. After several tests, we have succeeded in obtaining directly and at low temperature (600-700°C) monophasic manganites. The conditions we have used are the following :

- Decomposition of the salt in a mixture of N_2/O_2 whose oxygen partial pressure is $7.5 \cdot 10^{-3}$ Pascal (Pa).
- Heat treatment in neutral atmosphere from 420°C (soaking time : two hours) to 700°C.
- Quenching

Pure phases have been obtained for the compounds $\text{Mn}_{3-x} \text{Ni}_x \text{O}_4$ such that $x > 0.50$ i.e. for all the compounds concerning the N.T.C. thermistors. For high manganese contents

it had been impossible, whatever the operating conditions, to end up with monophasic oxides. These results confirm those of SARKAR /9/ and WALCH /10/ who admit a non miscibility of the oxides Mn_3O_4 and NiO .

Fig. 1

The nickel manganites prepared in this way at relatively low temperature are constituted of very weakly agglomerated particles with a regular size and shape (small octahedra 4-5 μm) (figure n° 1). Their surface area evolves with the heat treatment and can be controlled before sintering.

III - PREPARATION AND CHARACTERISATION OF THE CERAMICS

1. Preparation

The powders formerly obtained from 600 to 800°C, either the ones prepared in air or especially the ones prepared in controlled atmosphere, were put in a matrix after an organic binder had been added, applying a pressure of 4 kb. The resulting discs, with a diameter $\varnothing = 0.5$ cm and thickness $e = 0.1$ cm, were submitted to different heat treatments in air with different profiles (table II).

2. Characterisation

Table II gives XRD analysis and densities.

$Mn_{3-x}Ni_xO_4$ composition x	Sintering at 1160°C, 2hrs, cooling at 30°/hr				Sintering at 1200°C, 2hrs, cooling at 150°C/hr			
	Powder obtained in air 800°C 4hrs		Powder obtained in N_2/O_2 atmosphere 700°C		Powder obtained in air 800°C 4hr		Powder obtained in N_2/O_2 atmosphere 700°C	
	Crystalline phase	Density	Crystalline phase	Density	Crystalline phase	Density	Crystalline phase	Density
0.58	cubic spinel	4.4.	cubic spinel	4.7	cubic spinel	4.1.	cubic spinel	4.7
0.66	cubic spinel	4.4.	cubic spinel	4.8	cubic spinel	4.2	cubic spinel	4.8
0.71	cubic spinel	4.4.	cubic spinel	4.8	cubic spinel	4.2	cubic spinel	4.8
0.81	cubic spinel	4.5	cubic spinel	4.9	cubic spinel	4.4	cubic spinel	4.8
0.85	cubic spinel	4.5	cubic spinel	4.9	cubic spinel	4.4	cubic spinel	4.8
0.97	cubic spinel	4.5	cubic spinel + NiO	4.9	cubic spinel + NiO	4.5	cubic spinel	4.8

Table II

Diffraction analysis revealed the presence of spinel structure and the absence of any other crystalline compounds ($NiO + Mn_3O_4$). The ceramics prepared from powders obtained in controlled atmosphere have a higher density than those treated in air atmosphere (figure 2). High densities are obtained for relatively low sintering temperature (1160°C). The grain size is about 20 μm . Finally, it is necessary to point out that the sintering of the powders Mn_3O_4 and NiO heat treated in the same conditions (1160°C) lead to incomplete solide-solid reactions and that the densities remain low, about 4.2. $g.cm^{-3}$.

The figures n° 3 and 4 allows us to define the differences of microstructure observed. Figure n° 4 shows a more heterogeneous grains size and an important porosity.

Fig. 2: Change of density with the nickel content
Sintering at 1160°C, 2 H, cooling at 30°C/h

— starting powders obtained at 700°C
in controlled atmosphere, $7,5 \cdot 10^3$
Pascal (Pa).
--- starting powders obtained at 800°C
4 H in air
-.-.- ceramics obtained by conventional
method
(sintering at 1200°C, 2 H)

Fig. 3 $\longrightarrow$ 50 μ m

Fig. 4 $\longrightarrow$ 10 μ m

IV - ELECTRICAL PROPERTIES OF THE N.T.C. THERMISTORS

To determine the electric characteristics, the samples were electroded with silver print and fired at 800°C. The resistivity is determined by resistance measurements at $25 \pm 0.05^\circ\text{C}$ and using the relationship $\rho = \frac{RS}{e}$ (R = resistance in ohms, S = surface in cm^2 , e = thickness in cm). A second measurement done at $85 \pm 0.05^\circ\text{C}$ allows deduction of the thermal sensitivity coefficient B /1/. The results obtained are shown in figure 5.

Fig. 5 : Change of resistivity with the nickel content.

Sintering at 1160°C, 2 H cooling at 30°C/h

— starting powders obtained at
700°C in controlled atmosphere,
 $7,5 \cdot 10^3$ (Pascal) Pa.
--- starting powders obtained at
800°C, 4 H in air
-.-.- ceramics obtained by conventional
method
(sintering at 1200°C, 2 H)

For similar sintering and composition, we can observe sensible divergences of resistivity which can be attributed to the differences of microstructure. Ceramics with the higher densities exhibit lower resistivities. The minimum resistivity (1030 $\Omega \cdot \text{cm}$) is the lowest of all the ones we have found in the bibliography concerning the nickel manganites. It means that the electrical properties of these compounds were not optimized and that it is probably still possible to obtain inferior values by increasing the densification.

The sintering temperatures above 1160°C did not allow improvement in the electrical performances from the powders produced by chemical methods.

On the other hand, for the ceramics prepared from solid-solid reactions between Mn_3O_4 and NiO , the best results are observed at a sintering temperature of 1300°C, which allows a minimum of resistivity at 2200 $\Omega \cdot \text{cm}$ only.

Figure 2 shows the resistivity versus nickel content. For the ceramics obtained by conventional method and sintered at 1200°C, i.e. in conditions rather close to those prepared by chemical method, we observe high values of resistivity as well as very irregular variations with the nickel content, which shows little coherence with the model proposed. Such characteristics can be explained by considering that the substitution of nickel in the spinel lattice is not controlled as confirmed by the XRD studies.

On the other hand, whatever the sintering temperature, the ceramics prepared by chemical method show a minimum of resistivity. This appears for a nickel content of $x = 0.80$ whereas theoretically this minimum was expected for $x = 0.66$. This divergence can be the result of a distribution slightly different from the one proposed initially, taking into account the presence of Ni^{2+} ions in the tetrahedral sites for example and in the case of the compound NiMn_2O_4 it has already been proposed [11]/[14].

V - CONCLUSION

The preparation by chemical process at relatively low temperature of pure powders of nickel manganites with a controlled morphology has a beneficial effect on the density of N.T.C. ceramics. Besides lower sintering temperature, clearly lower resistivities can be obtained and a better correlation of the electrical properties with the nickel content can be observed. In contrast to the conventional process based on the reaction at high temperature of mixture of manganese and nickel oxides, this method allows us to break away from the problems of purity but also from problems of morphology of raw materials, which through the microstructure largely influences the electrical properties. In this way using chemical process makes the optimisation of electrical properties of nickel based manganites easier.

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