

# Recent Progress in the Fabrication of Ceramic Negative Temperature Coefficient Thermistors

A. Rousset, R. Legros

Laboratoire de Chimie des Matériaux Inorganiques, CNRS URA 1311, Université Paul Sabatier 118, route de Narbonne, 31062-Toulouse-Cedex, France

&

A. Lagrange

LCC, THOMSON, Avenue du Colonel Prat, 21850 St Apollinaire, France

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## Abstract

Negative temperature coefficient (NTC) thermistors are ceramics of industrial interest because of the very high dependence of their electrical resistance on temperature. Generally, these materials consist of transition metal (Cu, Co, Ni, etc.) spinel manganites.

This work shows the simultaneous influence of the purity and the morphology of initial powders on the densification. Moreover, correlations between electrical properties, thermal stability and microstructure have been established. Results of a comparative study on ceramics prepared either by conventional or chemical methods are given. Increasing the performance yields thermistors which have great precision and stability.

NTC-Thermistorkeramiken sind aufgrund ihrer sehr großen Temperaturabhängigkeit des elektrischen Widerstandes von industriellem Interesse. Meistens bestehen diese Materialien aus Übergangsmetall- (Cu, Co, Ni, usw.) Manganspinellen.

Die vorliegende Arbeit zeigt den gleichzeitigen Einfluß der Reinheit und der Morphologie der Ausgangsmaterialien auf die Verdichtung. Darüber hinaus werden Zusammenhänge zwischen den elektrischen Eigenschaften, der thermischen Stabilität und der Mikrostruktur untersucht. Es werden vergleichende Ergebnisse dargestellt, wobei die Keramik entweder durch eine konventionelle oder chemische Methode hergestellt wurde. Diese Verbesserungen erlauben es, Thermistoren mit großer Präzision und Stabilität zu erhalten.

Les thermistances à coefficient de température négatif (CTN) sont des céramiques dont l'intérêt industriel

est lié à la très grande sensibilité de la résistance électrique à la température. Généralement, les structures cristallographiques correspondant à ces matériaux sont du type spinelle constitués de manganites de métaux de transition: Ni, Co, Cu, etc.

Des travaux récents ont permis de mettre en évidence l'influence de la pureté et de la morphologie des poudres de départ sur la densification de la céramique. En outre, la corrélation entre propriétés électriques, stabilité en fonction du temps et microstructure a été établie. Les résultats d'une étude comparative des propriétés des céramiques élaborées à partir de poudres obtenues, soit par voie chimique, soit par voie traditionnelle, sont également donnés. L'amélioration des performances obtenues permet de répondre à l'évolution actuelle du marché nécessitant des thermistances de grande précision et stables dans le temps.

## 1 Introduction

The Laboratory of Inorganic Materials Chemistry and the Thomson-LCC Company have been co-operating for several years to improve the performance of negative temperature coefficient (NTC) thermistors. Advances that have been made on these passive components concern the reproducibility of their electrical characteristics in the manufacturing phase, miniaturization, the precision of the electrical characteristics and the stability under thermal stress.<sup>1,2</sup> Progress was made first by undertaking fundamental research of a modelling type, and then transposing this to the industry by attempting to duplicate the laboratory-generated models as closely as possible.

In the present paper, a few particularly significant results of correlations among compositions, structures, microstructures and electrical properties of NTC ceramics are presented. First, however, the main electrical characteristics and a few of the applications of these components will be briefly indicated.

## 2 Electrical Properties and Applications of NTC Thermistors

NTC thermistors are semiconductor ceramics consisting of oxides of transition metals. Their resistivity varies exponentially with temperature, by the classical relation  $\rho = \rho_0 \exp(B/T)$ , in which  $\rho_0$  is the material's resistivity at infinite temperature and  $B$  is thermal sensitivity index, or energy constant.

In fact,  $B = \Delta E/2k$  has the dimensions of temperature and  $\Delta E$  represents the electron transfer activation energy. For a given system of oxides, the value of  $B$  is closely related to the resistivity so the search for different  $(\rho, B)$  pairs requires complete formulation changes. The variation in the resistivity (or of the resistance  $R = \rho L/s$ ) with temperature (Fig. 1) is measured by the temperature coefficient  $\alpha = (1/R)(dR/dT)$ , which is negative here and can reach values of  $-6\%/^{\circ}\text{C}$ , above that of other materials (e.g. metals) in absolute value.

This very high temperature sensitivity of the resistivity will be put to use in many applications, including temperature measurement and regulation, temperature drift compensation, voltage regulation, fluid flow rate measurements, and many others.

Among the principal electrical properties, the stability of the resistivity with time under thermal stress should also be pointed out. This is measured by the variation of  $\Delta R/R$  of an NTC thermistor held at  $125^{\circ}\text{C}$  for 1000 h. Until recent years, it was no

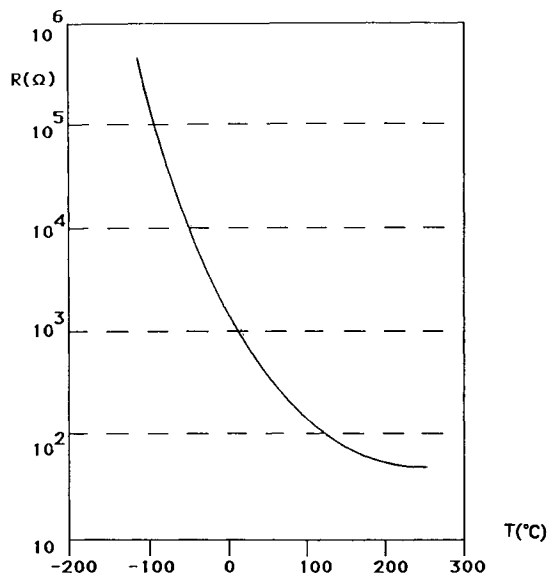


Fig. 1. NTC thermistor resistivity versus temperature.

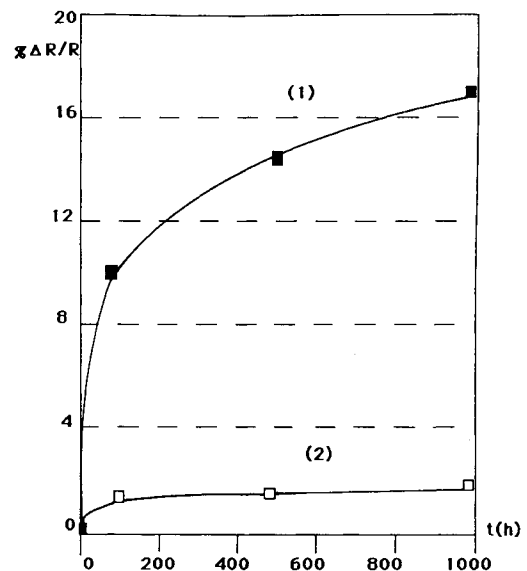


Fig. 2. Comparison of resistance drift between NTC thermistors of the same resistivity: (1) NTC thermistor elaborated prior to this study and (2) stabilized NTC thermistors.

rarity to observe a drift during aging of as much as 15% at 1000 h (Fig. 2, curve 1) for NTC thermistors ( $\rho \leq 100 \Omega\text{cm}$ ).

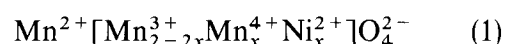
## 3 Results

### 3.1 Simplification of formulations and choice of compositions

Before this work, the formulations were characterized by mixtures of many transition metal oxides—sometimes 5 or 6—to which silica was often added. The primary result of this was a major heterogeneity of the composition on a local scale, with great ensuing difficulties in the reproducibility of the electrical characteristics, and major aging problems. Simplifying the formulations therefore seemed to be a decisive element in gaining control of all the physical and chemical properties. With this in mind, the manganites of transition metals prove themselves to be interesting components, although difficult to prepare in the monophase state and to stabilize with respect to thermal stresses.<sup>3-6</sup>

These spinel-structured compounds derive from  $\text{Mn}_3\text{O}_4$ , an insulator,  $\text{Mn}^{2+}[\text{Mn}_2^{3+}]\text{O}_4^{2-}$ , by substitution of the  $\text{Mn}^{3+}$  ions with divalent or monovalent ions. This substitution produces  $\text{Mn}^{4+}$  ions by the process  $2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{M}^{2+}$ , and therefore donor-acceptor pairs of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  in the octahedral sites. This gives rise to a conduction by electron transfer, and semiconductor properties.<sup>6</sup>

For example, in the case of substitution by the  $\text{Ni}^{2+}$  ( $3d^8$ ) ion, having a high stabilization energy in the octahedral crystal field, the structural formula of the corresponding manganites  $\text{Mn}_{3-x}\text{Ni}_x\text{O}_4$  ( $0 \leq x \leq 1$ ) should be close to the model:



since the  $\text{Mn}^{3+}$  ( $3d^4$ ) and  $\text{Mn}^{4+}$  ( $3d^3$ ) ions, like the  $\text{Ni}^{2+}$  ions, exhibit a strong affinity for the octahedral sites, compared with the  $\text{Mn}^{2+}$  ( $3d^5$ ) ions.<sup>7</sup>

Since the degree of oxidation (+2) of nickel is at the same time invariable in these compounds, it appears that, of all of the manganites of transition metals, the ceramics of nickel manganites are in principle the least complex. For this reason, they are the most likely to serve as a basis for establishing correlations between their composition, their structure, their microstructure and the electrical properties, i.e. to serve as theoretical models.

The above structural formula (1) forecasts a maximum conductivity for  $x = 2/3$ , i.e. when the number of  $\text{Mn}^{3+}$ - $\text{Mn}^{4+}$  pairs is maximum. The curve of resistivity versus nickel content should therefore exhibit a minimum for  $x = 2/3$ . In fact, this minimum is generally observed at somewhat higher nickel contents, most often at about  $x = 0.75$ , and moreover the minimum resistivity fluctuates greatly according to different authors and is dependent on practically all of the ceramic process parameters.<sup>8,9</sup> Thus, to optimize these parameters, the lowest possible resistivity on the  $\rho = f(\text{Ni})$  curve has to be found. Here, a remarkable value close to  $1000 \Omega\text{cm}$  was obtained. The authors were able to extend toward lower resistivities by substituting cobalt or copper ions for the manganese ions in the nickel manganites of minimum resistivity. Then manganites  $\text{Mn}_{3-x-y}\text{Ni}_x\text{Co}_y\text{O}_4$  or  $\text{Mn}_{3-x-y}\text{Ni}_x\text{Cu}_y\text{O}_4$ , with  $0 \leq x + y \leq 1.5$  were mixed. The former group leads to resistivities of  $300 \Omega\text{cm}$  and the latter to the order of  $1 \Omega\text{cm}$ .<sup>10,11</sup>

The copper manganites  $\text{Mn}_{3-x}\text{Cu}_x\text{O}_4$  ( $0 \leq x \leq 1.5$ ) and the combined copper-cobalt manganites  $\text{Mn}_{3-x-y}\text{Cu}_x\text{Co}_y\text{O}_4$  ( $0 \leq x + y \leq 1.5$ ) can also cover a domain of resistivities ranging from the insulator state to  $1 \Omega\text{cm}$ ;<sup>10</sup> but their structure (the position of the ions in the spinel lattice sites and the

degrees of oxidation of the copper and cobalt ions) is more complex and they could not be used to begin with as 'model' materials. Moreover, a vigorous quenching in liquid nitrogen is required to manufacture pure phases, and such conditions are difficult to transfer to the industrial environment.

Finally, nickel manganites and their derivatives appear to be particularly advantageous materials for making NTC thermistors, both from the scientific point of view and from that of the industrial transfer.

### 3.2 Manufacture of reference materials

#### 3.2.1 Nickel manganites

The substitution of  $\text{Mn}^{3+}$  ions in  $\text{Mn}_3\text{O}_4$  by  $\text{Ni}^{2+}$  ions should, for the reason already given, lead to a gradual decrease in the resistivity, with the  $\rho = f(\text{Ni})$  curve passing through a minimum for  $[\text{Mn}^{3+}] = [\text{Mn}^{4+}]$ . The authors consider that the lower this minimum value in the scale of resistivities, the more successful the optimization of all of the physical and chemical properties. So by manufacturing nickel manganite powders by chemical process,<sup>9,12</sup> a minimum resistivity of  $1030 \Omega\text{cm}$  was achieved, a value far below those published previously.<sup>8</sup>

This result was obtained from practically 'ideal' powders in the sense of Yan,<sup>13</sup> i.e. consisting of octahedral grains of very homogeneous shape and size, very well dispersed and having a controllable specific area<sup>14</sup> (Fig. 3 and Table 1). Since these are nickel manganite powders and not mixtures of manganese and nickel oxides, a nonreactive sintering was possible in which the sintering temperature was lowered to  $1160^\circ\text{C}$ . This avoided reducing the  $\text{Mn}^{4+}$  ions, which are unstable above  $1200^\circ\text{C}$ , and thereby the segregation of the spinel phase. High-purity nickel manganite can be prepared in this way, with densifications of 96% of their theoretical density. These ceramics will be considered as

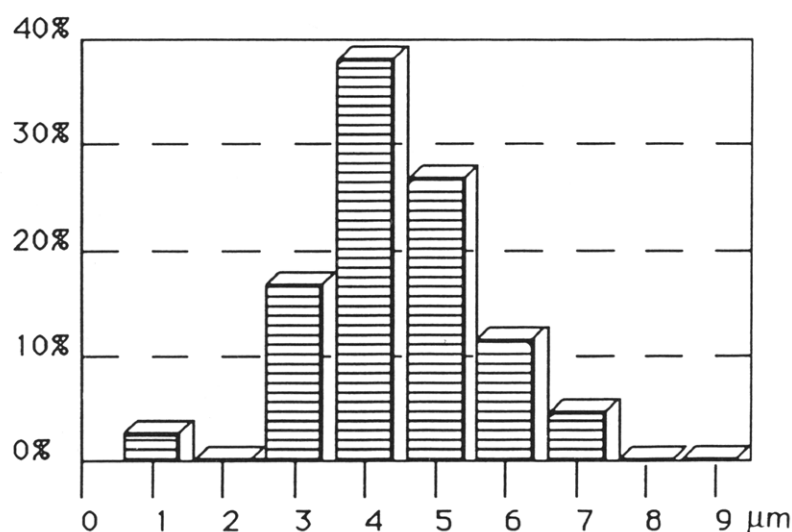


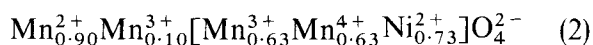
Fig. 3. SEM micrograph and size distribution of nickel manganite powders obtained by the chemical method.

**Table 1.** Comparison of characteristics of ceramics elaborated by the conventional method or by the chemical route (oxalic precursors)

Elaboration process	Nature and purity of oxides	Grain shape	Grain size ( $\mu\text{m}$ )	Particle size distribution $\phi$ medium/ $\phi$ max $\phi$ (diameter)	Specific surface area ( $\text{m}^2/\text{g}$ )	Apparent density ( $\times 10^3 \text{ kg/m}^3$ )	Resistivity ( $\Omega \text{ cm}$ )	B (K)
Chemical route, oxalic precursors Ceramic route sintering 1200°C 2 h <sup>a</sup>	$\text{Mn}_{3-x}\text{Ni}_x\text{O}_4$ , 99.9%	Octahedral	4	2	3	4.9	1030	3855
T <sub>1</sub>	$\text{MnO}_2$ , 91%	Acicular	1–100	5	3	3.7	32 000	4 260
T <sub>2</sub>	$\text{MnO}_2$ , 99.7%	Spherical agglomerate of acicular particle	100	3	0.2	3.6	3 800	3 920
T <sub>3</sub>	$\text{Mn}_2\text{O}_3$ , 99.7%	Polyhedral	1–5	3	3.2	4.2	3 640	3 680

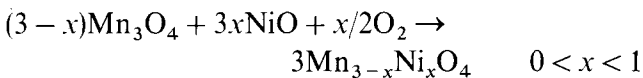
<sup>a</sup>These manganese oxides were mixed and ground with the same nickel oxide NiO (purity = 99.5%, grain size = 5.2  $\mu\text{m}$  and specific surface area = 0.2  $\text{m}^2/\text{g}$ ).

reference materials and will thereafter be of use in calibrating the results obtained by the conventional manufacturing method. Recent work on neutron diffraction and magnetic measurements, as well as thermogravimetric analyses to determine the oxidation of the  $\text{Mn}^{2+}$  ions in these compounds, explains why the resistivity minimum is shifted toward higher nickel contents ( $x > 0.66$ ), and leads to admission of the presence, not of  $\text{Ni}^{2+}$  ions in the tetrahedral sites, but rather 10% of  $\text{Mn}^{3+}$  ions, whence the following model is proposed:<sup>15,16</sup>

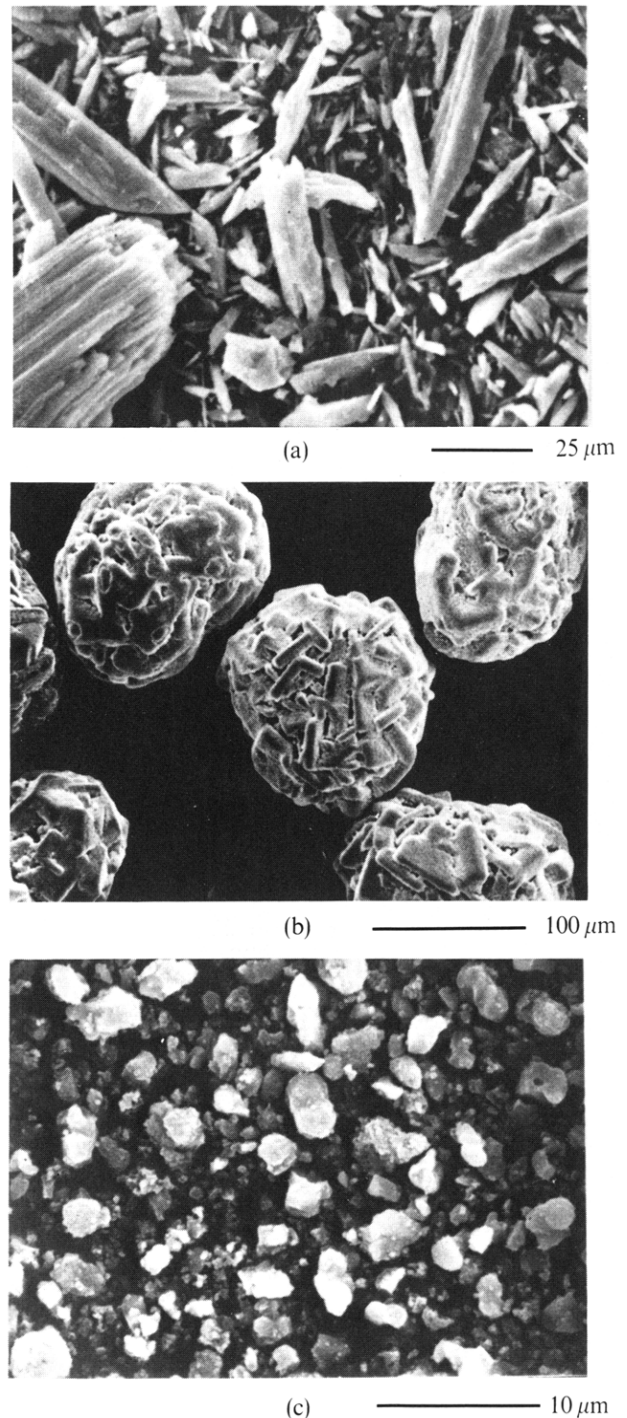


### 3.2.2 Effects of the purity and morphology of the basic materials

The conventional industrial process for manufacturing ceramics uses simple oxide powders that finally react between 1000°C and 1300°C according to:



Economically speaking, it is advantageous to start with very low-cost natural powders of  $\text{MnO}_2$ . However, under the effect of temperature, these oxides gradually decompose into  $\text{Mn}_2\text{O}_3$  and then  $\text{Mn}_3\text{O}_4$ . They are also usually of low-grade purity and very poorly defined morphology (Table 1, Fig. 4). Table 1 gives the characteristics for these powders as well as for synthetic powders, which are purer but of very different morphology. It also lists the apparent specific gravities along with the minimum resistivity that can be obtained for comparable Mn/Ni ratios and shaping and sintering conditions (1200°C, 2 h). In all cases, both densification and resistivity were very far from the results acquired with powders generated by the chemical process. Moreover, for a given densification, purity is essential for obtaining low resistivities (compare T<sub>1</sub> and T<sub>2</sub>). A better morphology (T<sub>3</sub>) leads to an increase (of about 15%) in the densification and a decrease in resistivity. These investigations therefore



**Fig. 4.** SEM micrographs of (a) natural  $\text{MnO}_2$ , (b) synthetic  $\text{MnO}_2$  and (c) synthetic  $\text{Mn}_2\text{O}_3$ .

**Table 2.** Density and electrical properties of ceramics issue from powders T<sub>1</sub> (MnO<sub>2</sub> acicular grains) and T<sub>2</sub> (MnO<sub>2</sub> spherical grains)

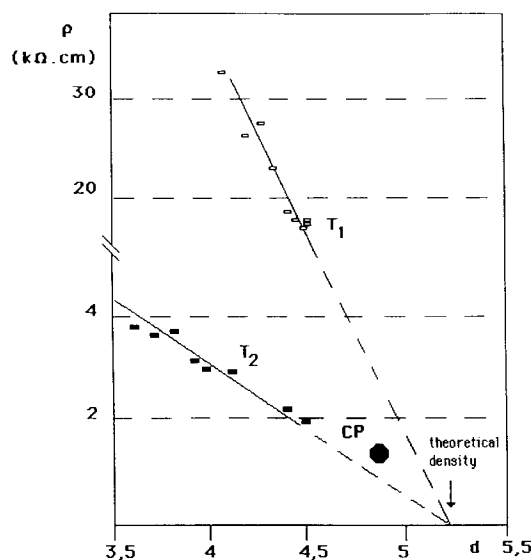
Samples	Density (g/cm <sup>3</sup> )		Resistivity $\rho$ ( $\Omega$ cm)		B (K)	
	Without Grog <sup>a</sup>	With Grog	Without Grog	With Grog	Without	With
					Grog	
T <sub>1</sub>	3.7	4.8	32 000	17 000	4 260	—
T <sub>2</sub>	3.6	4.5	3 880	2 200	3 920	3 850

<sup>a</sup>Grog: the powders are calcined at about 800°C before sintering.

clearly show the decisive role played firstly by the purity of the oxides to start with, and then that of their morphology in achieving optimized electrical characteristics.

### 3.2.3 Improvement of densification: specific gravity/resistivity correlations

The results obtained by the conventional process clearly show, even in the most favorable case of T<sub>3</sub>, a very large densification problem. The density can be improved either by calcining the powders or by increasing the sintering temperature. The latter solution is not very satisfactory, however, because of the instability of the Mn<sup>4+</sup> ions which, as they are reduced to Mn<sup>3+</sup>, precipitate the NiO out of the spinel lattice. Powders T<sub>1</sub> and T<sub>2</sub> underwent the burning treatment at 800°C, 900°C, 1000°C and 1100°C for 2 and 8 h. After these treatments, the powders all underwent the same grinding and were sintered as before at 1200°C. Table 2 gives the results obtained in the most favourable case, which was calcination at 1000°C for 2 h. A large increase appears in the density (+25%), accompanied with a major decrease in the resistivity. The  $\rho = f(\text{density})$  curves obtained for all of the calcining treatments



**Fig. 5.** Resistivity versus density of T<sub>1</sub> (MnO<sub>2</sub>, 91%) and T<sub>2</sub> (MnO<sub>2</sub>, 99%) by the conventional method (1000°C/2 h); CP, chemical process.

are shown in Fig. 5. They reveal a very close correlation between these two characteristics. In fact, for a given density, the observed difference in resistivity essentially reveals the effect of the purity which, as has already been said, plays an essential role.

The burning at 1000°C (2 h) is found to be a very favourable treatment because it initiates the reaction of synthesis between Mn<sub>2</sub>O<sub>3</sub> and NiO and makes the specific areas of the constituents uniform. The later grinding of the powders also renews and increases the reactive surface area, favourably influencing the kinetics in the downstream sintering process.

The ( $\rho, d$ ) pair of values for NTC thermistors obtained by the chemical process (CP) can also be examined in Fig. 5, where it can be seen that this fits quite well into the same type of resistivity–density correlations as observed before.

Finally, for the T<sub>3</sub> samples, the densification was improved by sintering at 1300°C (0.5 h) rather than by prior calcination of the powders (Table 3). Although the specific gravity then reaches 4.8, the resistivity remains high (2810  $\Omega$  cm) considering what it was after sintering at 1200°C (3640  $\Omega$  cm) (Table 1). This anomaly results from a partial decomposition of the manganite which, as has already been pointed out, loses Ni<sup>2+</sup> ions (in the form of NiO) and therefore Mn<sup>4+</sup> ions, so that it is no longer as conductive.

### 3.2.4 Optimization of the structure–resistivity correlations

The sintering test at 1300°C shows the difficulty of obtaining monophasic ceramic because of the reduction of the Mn<sup>4+</sup> ions and the precipitation of NiO out of the spinel lattice. However, this reaction is reversible and single phases can be achieved by very slow cooling (6°C/h). The cooling speed after sintering consequently plays a major role and, the higher the sintering temperature, the slower the cooling rate must be to obtain the lowest resistivity. This observation again points to the interest of the chemical process for which process nonreactive sintering can be carried out below 1200°C (see Table 3). Risks of segregation are therefore decreased and, at equivalent composition and density, lower resistivities are generally obtained than those observed by conventional manufacturing processes. Moreover, these NiO-free samples are the only ones that can be used for establishing strict correlations between the ion distribution in the spinel lattice and the resistivity.

In this respect, the curve of Fig. 6 showing the variation of resistivity with the nickel content is quite in agreement with the distribution already given. A regular decrease in the resistivity is

**Table 3.** Comparison of density and electrical properties of ceramics elaborated by conventional method ( $T_3$ ,  $Mn_2O_3$  polyhedral) or by the chemical route

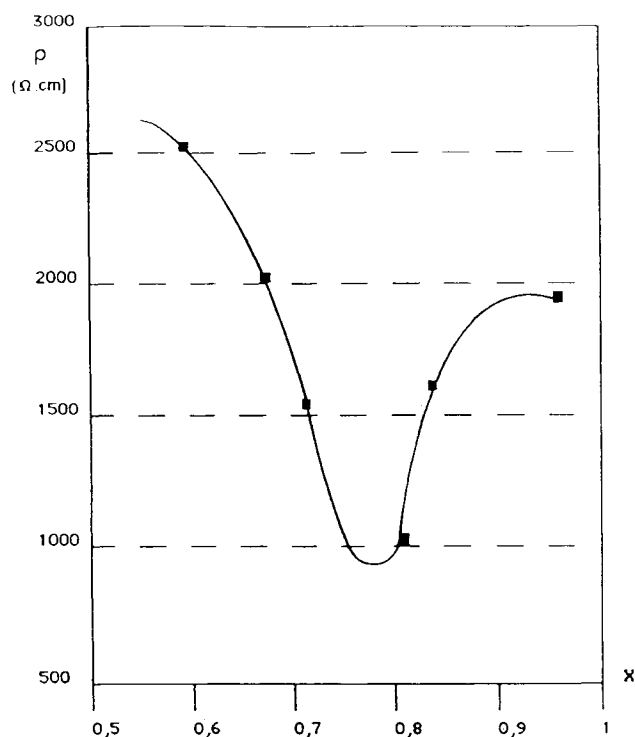
Ratio $Ni/Mn = 0.32$	Sintering temperature ( $^{\circ}C$ )	Phases	Density ( $g/cm^3$ )	Resistivity $\rho$ ( $\Omega cm$ )	$\Delta R/R$ after 1000 h
$T_3$	1300	Spinel + NiO	4.8	2810	0.7%
Chemical route	1200	Spinel	4.9	1030	3%

observed with an increase in the number of  $Mn^{3+}-Mn^{4+}$  pairs and with the decrease in the crystalline parameter  $a$ , and therefore in the  $Mn^{3+}-Mn^{4+}$  distances. The theoretical minimum predicted for  $x = 0.66$  is shifted toward  $x = 0.75$  due to the presence of a low proportion (10%) of  $Mn^{3+}$  ions in tetrahedral sites, as revealed by neutron diffraction (formula (2)). Moreover, this distribution seems to be fairly insensitive to the cooling rate, as the authors were able to verify on samples that were cooled at very different rates ( $30^{\circ}C/h$  and  $300^{\circ}C/h$ ).<sup>14</sup>

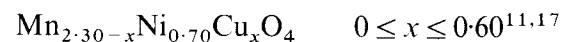
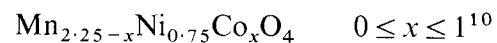
### 3.3 Low-resistivity NTC thermistors

These investigations show that resistivities of less than  $1000 \Omega cm$  cannot be obtained from nickel manganites when they are prepared by a chemical process, or less than  $2000 \Omega cm$  in the best cases, when manufactured by the conventional process. For applications requiring lesser resistivities, mixed nickel and cobalt manganites,  $Mn_{3-x-y}Ni_xCo_yO_4$  or mixed nickel and copper manganites,  $Mn_{3-x-y}Ni_xCu_yO_4$  are used.

Considering all the previous results, it was reasonable to choose a nickel content for the

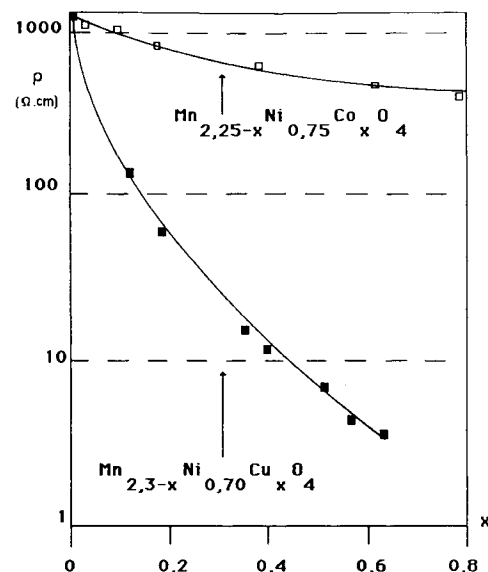
**Fig. 6.** Resistivity versus Ni content ( $x$ ) in  $Mn_{3-x}Ni_xO_4$  prepared by the chemical method.

composition of these oxides that would be close to the one yielding the minimum resistivity, i.e.  $x = 0.73$ . So the authors proceeded with systematic studies of the solid solutions:

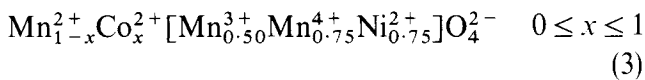


The former solution results in minimum resistivities of  $300 \Omega cm$ , and the latter in resistivities of the order of  $1 \Omega cm$  (Fig. 7). Generally speaking, the same approach was followed as for the nickel manganites; monophase ceramics were first manufactured and characterized, from powders of controlled morphology synthesized directly in the form of mixed oxides by a chemical process.<sup>18</sup> These 'model' materials serve to establish correlations between the composition, structure, microstructure and resistivity. Then electrical performance of the same order was sought by a conventional manufacturing process, in consideration of the essential requirements defined before as concerns the purity and morphology of the raw materials, the sintering temperatures, cooling rates and densification.

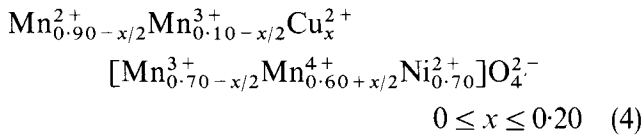
In these ternary oxides, the distributions become very complex because the copper and cobalt can exist in several degrees of oxidation. The best correlations able to be made at the present time between the variations of the crystalline parameters, the evolution of the electrical properties, the

**Fig. 7.** Resistivity versus Co or Cu content ( $x$ ), in  $Mn_{2.25-x}Ni_{0.75}Co_xO_4$  and  $Mn_{2.30-x}Ni_{0.70}Cu_xO_4$  respectively.

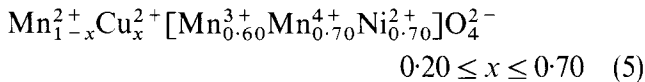
oxidation–reduction properties of these phases lead to distributions close to



for nickel–cobalt manganites, and



and



for nickel–copper manganites.

Structural analyses are in progress, by neutron diffraction and magnetic measurements, to complement these investigations and further clarify these distributions. Whether the manganese ions are substituted by cobalt or nickel ions, the crystalline parameters are greatly decreased in both cases, bringing the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions closer together in the octahedral sites, thereby promoting hopping and at least partly explaining the decrease in resistivity (Fig. 8).

The fastest and largest decrease in resistivity observed for the combined nickel–copper manganites is interpreted by considering first a faster drop in the crystalline parameter than what is measured on the nickel–cobalt manganites, and then an increase in the number of  $\text{Mn}^{3+}$ – $\text{Mn}^{4+}$  pairs in octahedral sites up to  $x = 0.20$ , which is not the case with cobalt. Finally, although it seems normal to find cobalt in its more stable divalent form, it could have turned out otherwise for the copper ions, especially considering that in the copper manganites,  $\text{Mn}_{3-x}\text{Cu}_x\text{O}_4$  ( $0 \leq x \leq 1$ ), the authors' work showed that the copper was essentially in the state of  $\text{Cu}^+$

ions in tetrahedral sites.<sup>19</sup> It should be nonetheless emphasized that the distributions proposed should be seen as approximations and that the presence of  $\text{Cu}^+$ – $\text{Cu}^{2+}$  pairs cannot be totally excluded as long as the values observed with the combined nickel–copper manganites are low (of the order of  $1 \Omega\text{cm}$ ).

Nearly identical results were obtained for the same phases manufactured by the conventional process, while respecting the constraints of purity, morphology, sintering temperature, cooling rate and density resulting from the study of the nickel manganites. As before, the resistivity minima are generally higher than those observed with the chemical process:  $18 \Omega\text{cm}$  instead of  $3 \Omega\text{cm}$ , for example, for  $\text{Mn}_{1.70}\text{Ni}_{0.70}\text{Cu}_{0.60}\text{O}_4$ . However, the entire range of resistivities of interest for the applications are finally covered with only three elements, i.e. manganese, nickel and copper. The Mn–Ni–Co system is also suitable between  $2000 \Omega\text{cm}$  and  $300 \Omega\text{cm}$ .

### 3.4 Time stabilization of electrical properties under thermal stress

As was pointed out initially, one of the important characteristics of NTC thermistors is their time stability under thermal stress. This stability is measured by the relative variation (drift)  $\Delta R/R$  of an NTC thermistor held at  $125^\circ\text{C}$  for 1000 h. Among all the systems studied until now, Mn–Ni, Mn–Ni–Co and Mn–Ni–Cu, it is the last of these that exhibits the largest drifts, sometimes exceeding 20%. It is the copper ions that cause this phenomenon, as the drifts can exceed 100% in the Mn–Cu system.

Many hypotheses have been put forward to explain the origin of this 'aging'; although no experiments have yet confirmed them, even if much progress has been made in reducing it, as shall be seen. One basic and systematically verified observation in the authors' work is that, regardless of the composition of the NTC, thermistor polyphase ceramics have better stability than monophase ones.

These polyphase ceramics generally appear in sintering treatments carried out at too high a temperature, followed by too fast a cooling. For the  $T_3$  samples (see Table 1) sintered at  $1300^\circ\text{C}$  and cooled at  $150^\circ\text{C}/\text{h}$ , containing an NiO phase next to the spinel phase, stabilization appears to be very high compared with results obtained on monophase ceramic sintered at  $1200^\circ\text{C}$  and of an equivalent or even greater density (Table 3).

Precipitating NiO out of the spinel lattice does not allow lower resistivities for a given composition, but does improve the stability so much that the advantage of polyphase ceramics has come to be seen as decisive in the search for high stabilities. This principle, applied to the very unstable Mn–Ni–Cu

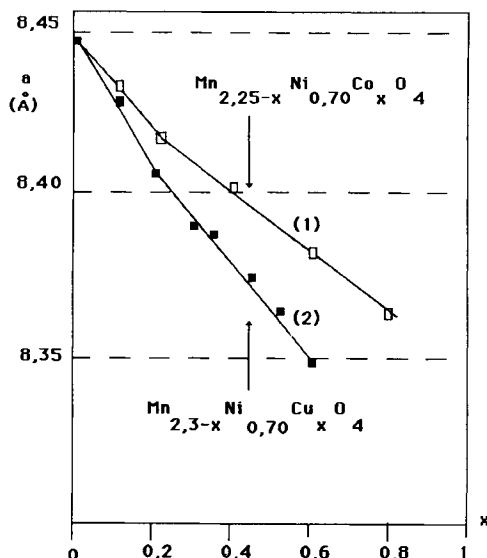


Fig. 8. Lattice parameter versus (1) Co or (2) Cu content ( $x$ ), in  $\text{Mn}_{2.25-x}\text{Ni}_{0.70}\text{Co}_x\text{O}_4$  and  $\text{Mn}_{2.30-x}\text{Ni}_{0.70}\text{Cu}_x\text{O}_4$  respectively.

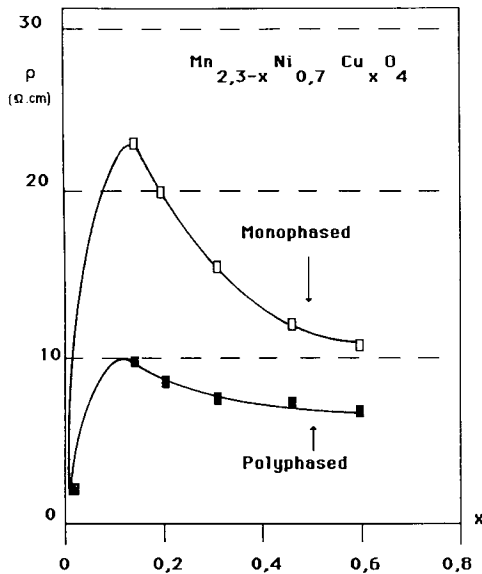


Fig. 9. Influence of Cu content ( $x$ ) on resistance drift after 1000 h at 125°C on mono- and polyphased NTC thermistors with formula  $\text{Mn}_{2.3-x}\text{Ni}_{0.7}\text{Cu}_x\text{O}_4$ , in function of Cu content.

systems, reduces the drifts by a factor of two (Fig. 9). As the drifts are still large, however, it was by doping the ceramics with  $\text{Ba}^{2+}$  ions—whose radius is too large ( $1.35 \text{ \AA}$ ) to enter into the spinel lattice—that the precipitation of  $\text{BaMnO}_3$  was caused, to get much lower values of drift  $\Delta R/R$ .<sup>17</sup> Finally, by combining doping and quenching to make the  $\text{BaMnO}_3$ ,  $\text{NiO}$  and  $\text{CuMnO}_2$  phases appear next to the spinel phase in the ceramic, the authors were able to obtain very low drifts of 1% to 2% (Fig. 10), although with an increase of resistivity.<sup>11,17</sup> This disadvantage was eliminated by replacing the barium doping of the combined copper–nickel manganites with an increase in the nickel content which, beyond a certain concentration, no longer enters the spinel lattice and appears in the form of  $\text{NiO}$ .<sup>20</sup> Ceramics formulated this way can be cooled slowly. But they are still polyphase ceramics and offer very high stabilities for resistivities of less than  $10 \Omega \text{ cm}$  (Fig. 2, curve 2).

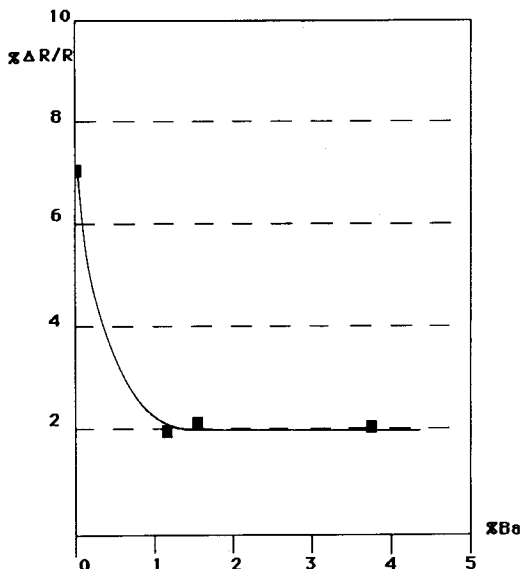
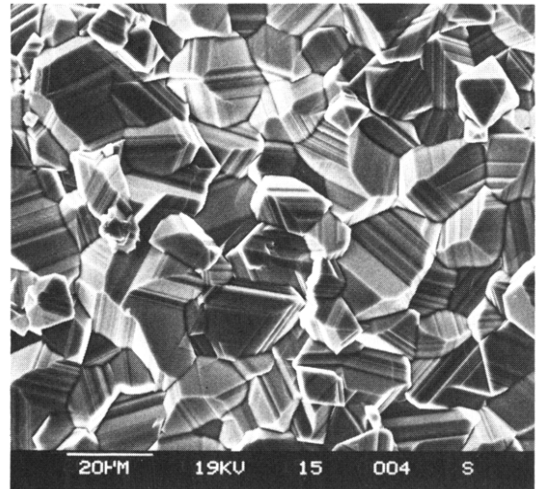
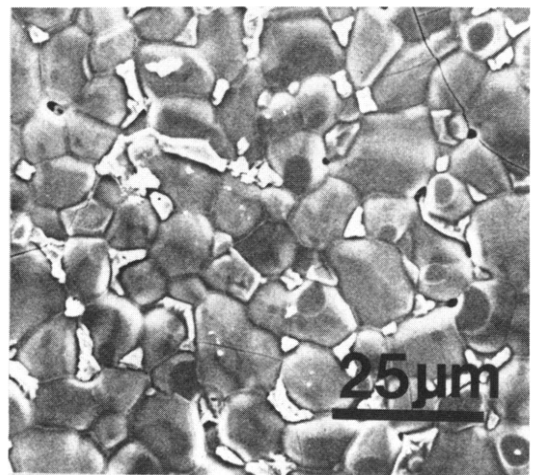


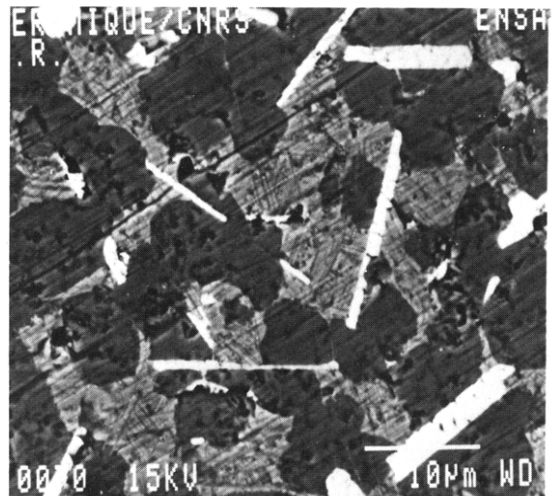
Fig. 10. Influence of Ba content on resistance drift after 1000 h at 125°C; in  $\text{Mn}_{2.3-x}\text{Ni}_{0.7}\text{Cu}_x\text{O}_4$  in function of Ba content.



(a)



(b)



(c)

Fig. 11. Microstructures of (a) undoped and (b) and (c)  $\text{Ba}^{2+}$ -doped NTC thermistors obtained by the chemical process.

The presence of several phases in the ceramic leads to very complex microstructures (Fig. 11), chiefly with the presence of interphases that are currently being analysed in depth by electron microscopy.<sup>21</sup> How do these  $\text{NiO}$ ,  $\text{CuMnO}_2$  and  $\text{BaMnO}_3$  phases surrounding the spinel phase improve the stability of the resistivity and modify the conduction mechanisms? The work currently under way is attempting



to answer these important questions both on a fundamental and application level.

#### 4 Transfer of Results to Industrial Scale

For economic reasons, these results were transferred for industrial use in the conventional manufacturing process. By their very nature, industrial constraints are more numerous and more important, even on the technical level alone, than those encountered in the laboratory or in predevelopment. In spite of everything, the results already described nearly all found their way into the industrial manufacturing process.<sup>22</sup>

The Mn–Ni system was in fact chosen as the reference for the new generation of NTC thermistors. By substituting copper or cobalt in this nickel manganite based matrix, very low resistivities were achieved. Most of the industrial products are now manufactured with only three elements, which simplifies the manufacturing process, increases productivity, avoids having to manage a stock of many different raw materials, and limits the risk of irregularities in the quality of the supply. To achieve a high level of local homogeneity in the composition of the spinel lattice, great attention has been paid to the purity and morphology of the basic oxides. These parameters are decisive for obtaining well-defined, reproducible electrical characteristics.

Another critical parameter, densification, can, as has already been seen, be obtained by calcination at 1000°C, followed by sintering at 1200°C, or by sintering directly at 1300°C as long as the powders have sufficient specific area and a narrow domain of grain size distribution. This solution leads to polyphase ceramics (spinel + NiO), with the advantages that it brings to stability. The presence of NiO in the ceramics leads to an increase in resistivity over what it would be in a monophase ceramic of the same composition. However, as the cooling rates of industrial furnaces are not very high, the quantities of NiO precipitated may be small (a few percent).

For the base composition  $\text{Mn}_{2.30}\text{Ni}_{0.70}\text{O}_4$ , close to the minimum resistivity in the Mn–Ni system, it is therefore possible to lower the resistivity to 2100  $\Omega\text{cm}$  in spite of everything, and with a very high reproducibility and stability ( $\Delta R/R < 2\%$ ). Finally, the last consequence of the presence of precipitated phases between the spinel grains concerns the decrease in the slopes of the  $\rho = f$  (composition) curves and the possibility in certain cases of obtaining practically zero slopes when the spinel phase composition does not vary, despite global variations in the composition (Figs 12 and 13). These resistivity steps are very interesting, because they offer a high level of formulation safety

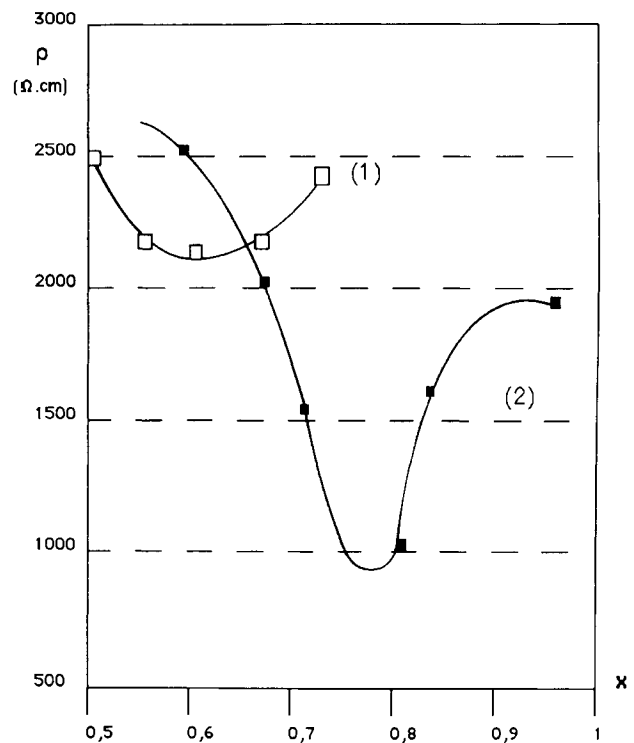


Fig. 12. Resistivity versus Ni content ( $x$ ) for NTC thermistor with formula  $\text{Mn}_{3-x}\text{Ni}_x\text{O}_4$  prepared by (1) the conventional method or (2) the chemical process.

for obtaining reproducible characteristics, and are therefore sought systematically. Generally speaking, by adjusting the compositions, the doping (Ba) and the cooling rates, steps can be obtained in the entire range of resistivities used.

These observations clearly show that the industrial constraints, just like the optimization of all the application properties, can result in the manufacturing of a material with one of its properties blunted—here the resistivity minimum—with respect to the laboratory model, but offering sufficient

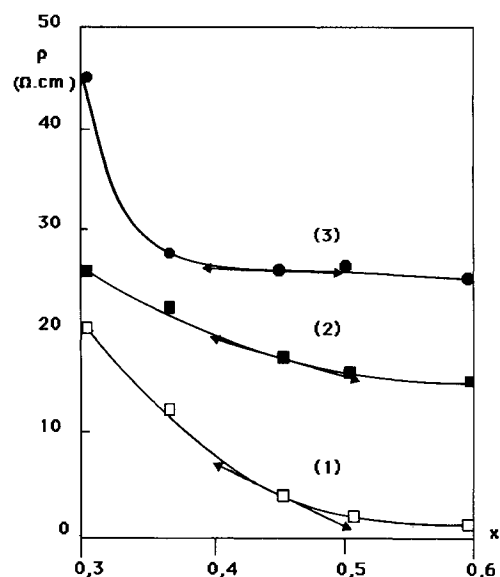


Fig. 13. Influence of precipitated phases on the slope of resistivity versus Cu content. (1)  $\Delta R/R = 12\%$ ; only cubic spinel; (2)  $\Delta R/R = 7\%$ ; polyphased system, CS + NiO +  $\text{CuMnO}_2$ ; (3)  $\Delta R/R = 2\%$ ; polyphased system; CS + NiO +  $\text{CuMnO}_2$  +  $\text{BaMnO}_3$  in  $\text{Mn}_{2.3-x}\text{Ni}_{0.7}\text{Cu}_x\text{O}_4$  doped with barium.

economic and technical advantages overall for it to perform well on the market. This is a question of trade-off among scientific, technical, economic and strategic considerations. And it is not rare either for controlled impurities in a material to endow it with additional properties of interest, making it more attractive than a high-purity material.

## 5 Conclusions

The results obtained over the last few years have led to much progress in the development of high-performance NTC thermistors.<sup>20,23</sup> progress not only as far as their electrical properties (low resistivities, stability, close tolerances, miniaturization, etc) are concerned, but also in the manufacturing process, where simplification and reproducibility have brought high productivity in their wake.

The approach, which consisted in optimizing all the manufacturing and electrical parameters by a chemical process, and then approaching the performance initially achieved in a conventional process, turned out to be very fruitful, making it possible to establish correlations between composition structure, microstructure and electrical properties, and thereby to understand and rationalize the conventional process.

Finally, this research has contributed to the fundamental understanding of the manganites of transition metals, and in particular of the solid solutions which, in contrast to the definite compounds  $M Mn_2O_4$ , have been studied very little. The progress made in this field should help the explanation of the origin of the aging of NTC devices and to come up shortly with ways to achieve components that are perfectly stable under thermal stress.

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