Crystalline structure and electrical properties of solid solutions $\text{YNi}_x\text{Mn}_{1-x}\text{O}_3$

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Solid solutions belonging to the Mn-rich region of the $\text{YNi}_x\text{Mn}_{1-x}\text{O}_3$ system have been studied. The powders were prepared by solid state reaction between the corresponding oxides. Sintered ceramics were obtained by firing at 1325-1350°C. The incorporation of 20 atomic % Ni^{2+} to the Yttrium manganite induces the formation of a perovskite phase, with orthorhombic symmetry. Increase of the Ni amount leads to an increase of the orthorhombicity factor b/a , up to an amount of 50 atomic % Ni^{2+} . Above this Ni amount, a biphasic system has been observed, with the presence of unreacted Y_2O_3 . DC electrical conductivity measurements have shown semiconducting behaviour for all the solid solutions with perovskite-type structure. The room temperature conductivity increases with Ni until ~33 atomic % Ni, and then decreases. The 50/50 Ni/Mn composition has different values of conductivity and activation energy against those corresponding to samples with lower values of that ionic ratio. Small polaron hopping mechanism controls the conductivity in these ceramics. Results are discussed as a function of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio for each composition

Keywords: Manganites, perovskite solid solutions, electrical properties, ceramics.

Estructura cristalina y propiedades eléctricas de soluciones sólidas $\text{YNi}_x\text{Mn}_{1-x}\text{O}_3$

Se han estudiado las soluciones sólidas correspondientes a la región rica en Mn del sistema $\text{YNi}_x\text{Mn}_{1-x}\text{O}_3$, entre 0 y 50 atomic % Ni. Los compuestos fueron preparados por reacción en estado sólido de los óxidos correspondientes. Se sinterizaron materiales cerámicos a 1325-1350°C. Con cantidades de 20 atomic % Ni se produce la formación de una fase con estructura de perovskita, y simetría ortorrómbica. La distorsión ortorrómbica crece con el contenido de Ni. Por encima de 50 atomic % Ni, aparece Y_2O_3 sin reaccionar. Las soluciones sólidas muestran semiconducción con valores de σ que aumentan con el contenido de Ni hasta ~33 atomic %, para luego decrecer, hasta $x=0.5$. La composición 50/50 Ni/Mn muestra un comportamiento eléctrico algo diferente. Se discuten los resultados en función de la razón $\text{Mn}^{3+}/\text{Mn}^{4+}$ para cada composición.

Palabras clave: Manganitas, Soluciones sólidas, propiedades eléctricas, cerámicas

1. INTRODUCTION

The rare earth (R.E.) manganites have attracted a great interest because of their electrical and magnetic properties such as their semiconducting behaviour and their magnetoresistive features. A big lot of work is being developed about the properties of light RE manganites, particularly on the knowledge of the features of the LaMnO_3 compound, modified by Sr, or Ca substitution (1). Use of these solid solutions as ceramic electrodes for Solid Oxide Fuel Cells (SOFC's) is being studied from several years (2). Lately, the colossal magnetoresistive effect found in both single crystals and bulk ceramic of those solid solutions has been extensively treated by many authors (3).

The light RE manganites crystallise with a perovskite-type structure and space group (S.G.) $\text{Pbm}\bar{n}$, which tends to increase its anisotropy when the atomic weight of the RE increases, and its ionic radius decreases, from rhombohedral, quasi-cubic symmetry for La, to orthorhombic symmetry, for Dy, high b/a ratio manganite. For ions as Er and smaller the RE manganites crystallise with a hexagonal symmetry and S.G. $\text{P6}_3\text{cm}$ (4) despite the corresponding values of the Goldschmidt tolerance factor $t=(r_A+r_O)/(r_B+r_O)^{1/2}$ for structure. The structural change to hexagonal symmetry can be associated not only to the decrease of the tolerance factor but also to the presence of Mn^{3+} cation, which is a Jahn-Teller-type one, on B sites with

octahedral of lower co-ordination. Such a cation promotes a strong anisotropical deformation, which induces the change of symmetry, when the tolerance factor attains a enough small value (5). On the contrary, the heavy RE ferrites, such as the ErFeO_3 with the same tolerance factor, ~0.80, that those of ErMnO_3 , crystallises with an orthorhombic perovskite-type structure.

The YMnO_3 is a ferroelectric, antiferromagnetic compound with a very low value of electrical conductivity (6). At high voltages it shows a peculiar non-ohmic behaviour (7). Their solid solutions with the CaMnO_3 perovskite show a transition to this structure for an amount of approximately 22 atomic % of Ca. These solid solutions are semiconducting compounds, and the activation energy for conduction falls out to very low values, with a subsequent rise of the conductivity values when the Ca amount raises (8). This fact makes it possible the use of these solid solutions as ceramic electrode for SOFC's.

On the other hand, there is little work about the modification of the Y manganite by means of the incorporation of appropriate cations on the Mn sublattice. The scope of the present work is to study the effect of the incorporation of Ni^{2+} cations on the structure, symmetry and electrical properties of the YMnO_3 .

2. EXPERIMENTAL METHODS.

$Y(Ni_xMn_{1-x})O_3$ compositions with $x=0.1-0.5$, were prepared by solid state reaction from stoichiometric mixtures of MnO , NiO , and Y_2O_3 r.g. oxides as raw materials, with submicronic particle size. The mixtures were homogenised by wet attrition milling, using isopropanol as liquid medium. The dried mixtures were calcined at $1000^\circ C$, for 2h. The calcined cakes were remilled by the same technique, dried, granulated, uniaxially pressed and sintered at several temperatures and times. Apparent density was measured by water displacement. XRD analysis was performed both on the calcined powder and on the sintered samples using a D-5000 Siemens Diffractometer and the Cu K α radiation. The powder was identified by scanning at a rate of $2^\circ 2\theta/\text{min}$, and the lattice parameters were calculated from the spectra obtained on the sintered samples at

Figure 1.- Relative density of the sintered samples as a function of the temperature at 2h constant time and time at constant temperature of $1325^\circ C$

a scanning rate of $1/2^\circ 2\theta/\text{min}$. Powder of Si was employed as an internal standard. The microstructure of the sintered ceramics was observed by Scanning Electron Microscopy (SEM), on polished and thermally etched surfaces, and on fresh fracture surfaces. Disc-shaped samples were electroded with silver paste, which was sintered at $800^\circ C$, for 1h. Two-points DC conductivity measurements were carried out at different temperatures, between 20 and $300^\circ C$, using a Constant Current DC power supply Tektronix, model PS280 and a HP Multimeter model 44201A, with $1\mu A$ DC current resolution. Activation energy was calculated from the corresponding Arrhenius plots for that temperature interval.

3. RESULTS AND DISCUSSION

The apparent particle size, as measured by laser counting was $1\mu m$, but this size corresponds to the size of the aggregates. The BET measurements indicated a specific surface area values of $4\text{ m}^2/\text{g}$, which correlates well with an average particle size of $\sim 0.2\mu m$.

The pressed, prereacted powders were sintered between 1300 and $1400^\circ C$, 2h, and at $1325^\circ C$, for several times from 1 to 8h. Figure 1 shows the corresponding curves of apparent density vs temperature and vs time. It can be seen that the maximum apparent density values for several compositions were obtained at $1325^\circ C$, for 2h, with values ranging from 94 to 96% D_{th} . Figure 2 depicts the microstructure of a sintered sample. Small grain size is the more characteristic feature of the microstructure of all the studied samples.

The XRD phases analysis of the sintered bodies is shown in the figure 3. As it can be seen from those diagrams, for Ni amounts of 20 atomic %, the phase which is forming seems to be perovskite-type. Above 50 atomic % Ni, a different pattern can be seen, with the appearance of unreacted Y_2O_3 .

Table 1 and Figure 4 resume the measured values of the lattice parameters as a function of the Ni amount. According what it was seen on the prereacted powders, (not shown here), formation of a perovskite-type phase was observed for Ni amounts from 10 to 50 atomic %. For compositions containing

Figure 2.- Micrograph of polished surface of a sintered sample corresponding to the composition with 33 atomic % Ni, sintered at $1325^\circ C$, 2h

an amount lower than 20 atomic % Ni, biphasic samples were obtained. In those samples a main phase with hexagonal, YMnO_3 -type structure was observed, along with small amounts of a perovskite-type phase which is growing with the Ni amount. For samples containing from 20 to 50 atomic % Ni, a single phase was identified. This phase was indexed as an orthorhombic perovskite-type compound, isomorphous to the GdMnO_3 compound and a S.G. Pbnm. As it can be seen in the table 1, the orthorhombicity of the perovskite phases increases with the Ni amount. Above 50 atomic % Ni, the samples have shown a new biphasic structure, coexisting the perovskite phase with unreacted Y_2O_3 and NiO compounds. The lattice parameters of the perovskite corresponding to the composition with 55 atomic % Ni are the same of that corresponding to the 50/50 composition. These results are indicating that the Ni^{2+} cannot take a valence state of $3+$, and therefore, it seems to be non-feasible to form a perovskite structure with the following ion distribution: $\text{Y}[\text{Ni}^{2+}_{0.45}\text{Mn}^{4+}_{0.45}\text{Ni}^{3+}_{0.10}]\text{O}_3$, being the 50/50 composition the boundary between a monophasic field and a new biphasic field.

The crystal-chemical behaviour of the samples containing ≤ 50 atomic % Ni is very similar to that observed in another parent systems, such as $(\text{Y,Ca})\text{MnO}_3$, $(\text{Er,Ca})\text{MnO}_3$ and $(\text{Gd,Ca})\text{MnO}_3$ ones (9)

The progressive disappearance of the Jahn-Teller cations, Mn^{3+} , which are passing to the $4+$ valence state, caused by the incorporation of lower-valence state cations such as the Ni^{2+} , decreases the high anisotropy of the crystalline lattice, and promotes the appearance of a perovskite-type phase. When it is compared the orthorhombicity of these solid solutions, (Table 1), with that of the GdMnO_3 compound (9) it is possible to appreciate that the b/a ratio of all those solid solutions is always lower than that of the pure Gd perovskite. Nevertheless, the tolerance factor of these structures is lower than that of the mentioned Gd perovskite. For the $(\text{Y,Ca})\text{MnO}_3$ solid solutions, the tolerance factor increases with the Ca amount, due to the higher ionic radius of this cation against that of the Y, which leads to an increase of the mean ionic radius on the A sites. On the contrary, in the solid solutions of

TABLE 1. LATTICE PARAMETERS OF THE SOLID SOLUTIONS $\text{Y}(\text{Ni}_x\text{Mn}_{1-x})\text{O}_3$

Atomic % Ni	a (nm)	b (nm)	c (nm)	b/a	V (nm ³)	D _{th} (g/cm ³)
0	0.6136*	—	1.1400*	—	0.37170*	5.15
20	0.5243	0.5651	0.7460	1.078	0.22107	5.76
30	0.5241	0.5638	0.7452	1.076	0.22020	5.82
33	0.5239	0.5641	0.7449	1.077	0.22018	5.83
40	0.5229	0.5656	0.7427	1.082	0.21965	5.85
45	0.5223	0.5666	0.7414	1.085	0.21942	5.86
50	0.5221	0.5667	0.7412	1.086	0.21930	5.87

*Hexagonal Lattice, Z=6

the present case, the tolerance factor remains practically unchanged. Whereas the ionic radius of the Ni^{2+} is slightly higher than that of the Mn^{3+} , and therefore it could cause a decrease of the t value, this decrease can be compensated, if it is supposed that a part of Mn cations are changing to Mn^{4+} valence state, with a lower ionic radius. Therefore the reason of the change to perovskite-type structure can only be attributed to the progressive disappearance of the Jahn-Teller cations, and not to a modification of the tolerance factor. The maintenance of the t value can be the cause of the behaviour of the b/a ratio, with a small decrease for values between 20 and 30 atomic % and a subsequent increase from 33 to 50 atomic %. The low t values favour the high grade of asymmetry of the lattice. The compactness grade of the perovskite lattice rises and the XR density do it when the Ni^{2+} content increases.

If the data obtained in this system are compared with those existing in the literature, such as the above cited: $(\text{Y,Ca})\text{MnO}_3$ and $(\text{Er,Ca})\text{MnO}_3$ (9) systems, it can be stated that the change from hexagonal to perovskite structure occurs at practically the same amount of the modifier cation, i.e. when the Mn^{3+} amount falls out below a critical value which is around 80 atomic % of the Mn^{3+} original amount, independently of the value of the corresponding tolerance factor for stabilising the perovskite lattice

Figure 3.- XRD patterns of the solid solutions corresponding to samples with 0.2, 0.3 and 0.55 atomic % Ni

Figure 4.- Variation of lattice parameters against the Ni amount

Table 2 shows the room temperature conductivity values, and the activation energy for electrical conduction of the single phase samples. The figure 5 depicts the conductivity vs temperature curves for the same compositions, and the figure 6 shows the σT vs T curves. From the figure 5 two features are noticeable:

The conductivity increases from 20 to 33 atomic % Ni, and lately, falls out for 40 and 45 atomic % Ni. The reason of this behaviour could be attributed to the nature of the substituting cations. The Ni^{2+} seems no contribute to the controlled valence conduction mechanism, because of the lack of another valence state of Ni in the nearest neighbour sites. Therefore, the only pairs contributing to the conduction mechanism are the Mn^{3+} - Mn^{4+} ones. It is easy to see that these possible pairs are increasing until an amount of 33 atomic % Ni, - 67 atomic % Mn; a subsequent rise in the Ni percentage leads to a decrease of the possible forming pairs, (it is possible to form 0.33 pairs per formula unity in the 33/67 compositions, whereas it is possible to form only 0.2 in the 40/60 composition, and 0.1 in the 45/55 one). This variation in the relative percentage between the two Mn cations explains the existence of a maximum in the conductivity values for an intermediate Ni percentage.

According to the results shown in the figure 6, in which a linear relation between $\log(\sigma T)$ vs $1/T$ is observed, it can be established that the conductivity mechanism for these solid solutions is a thermally activated small polaron hopping, in a similar manner that other controlled-valence ceramic semiconductors.(10)

The strong increase of the conductivity of the 50/50 sample and the consequent decrease in the activation energy is a fact which needs a different explanation. In a similar manner to that occurring in the $\text{La}(\text{Ni},\text{Mn})\text{O}_3$ perovskite, the $\text{Y}(\text{Ni}_{0.50}\text{Mn}_{0.50})\text{O}_3$ could be an ordered perovskite. If this is the case, a strong ferromagnetic interaction between the Ni^{2+} and the Mn^{4+} cations should appear, because of the orthogonality of the d electron orbitals of both cations. These interactions could induce overlapping of the conduction band and therefore could cause an increment of the electronic conductivity via delocalised states, such as it has been established for the lant-

TABLE 2. ELECTRICAL CONDUCTIVITY AT 20°C AND ACTIVATION ENERGY FOR THE PEROVSKITE SOLID SOLUTIONS AS A FUNCTION OF THE Ni AMOUNT

% Ni	20	30	33	40	45	50
σ (Sm^{-1})	$3.05 \cdot 10^{-2}$	$1.04 \cdot 10^{-1}$	$5.79 \cdot 10^{-1}$	$2.01 \cdot 10^{-3}$	$1.37 \cdot 10^{-4}$	$1.56 \cdot 10^{-1}$
E_a (eV)	0.30	0.24	0.28	0.32	0.50	0.13

hanum-nickel manganite (11). Nevertheless, further work is needed to prove if this hypothesis is valid.

The composition 40/60 Ni/Mn shows a good Negative Temperature Coefficient (NTC) behaviour. It has a 300K-resistivity value of $500 \Omega \cdot \text{m}$, a B coefficient, calculated from the $\ln \rho$ vs $1/T$ curve (not represented here), of 3700 K and a TRC value α_R of $-4 \text{ \%} \cdot \text{K}^{-1}$ at 300K, which is comparable to that of some commercial thermistors.

4. CONCLUSIONS

The substitution of Ni^{2+} for Mn^{3+} in the hexagonal YMnO_3 compound leads to a phase transition from hexagonal phase to an orthorhombic, perovskite-type phase for Ni amounts below 20 atomic %, in a similar manner to that reported for the $(\text{Y,Ca})\text{MnO}_3$ solid solutions. The cause for this transition must be related to the decrease of the Mn^{3+} Jahn-Teller cations in the lattice.

Above 50 atomic % Ni a two-phase region has been observed. Unreacted Y_2O_3 is detected. In this system the nickel cation seems to be unable to adopt a three-valence state for incorporating to the perovskite structure in the B lattice sites.

The perovskite-type solid solutions are semiconductor materials. They show good electrical conductivity values, promising NTC features, and could be used as ceramic electrodes for SOFC's because of its probable compatibility with ceria and zirconia solid electrolytes.

Figure 5.- Conductivity vs Temperature of the different solid solutions.

Figure 6.- σT vs T for the different solid solutions.

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