Crystalline structure of the manganites solid solution RE(Me,Mn)O₃⁺
(RE=Gd,Er; Me=Ni,Co)

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The structural properties of the manganites solid solution RE(Me,Mn)O₃⁺, RE=Gd,Er, Me=Ni,Co, have been studied by X-ray diffraction and electric measurements. Powders were prepared by solid state reaction between the component oxides. Incorporation of Ni²⁺ or Co²⁺,³⁺ on the lattice in the Mn sites leads to changes in the parameters and symmetry of the perovskite or hexagonal ErMnO₃ compounds. The phase transitions depend on the amount of substituted Jahn-Teller Mn³⁺ cations, and, therefore, of the cooperative Jahn-Teller interaction weakness. Solid solutions based on GdMnO₃ perovskite compound change from O'-type to O-type orthorhombic perovskite symmetry when the Mn³⁺ cation amount decreases, because of the progressive substitution for Ni, Co. This transition occurs for lower amount of Ni²⁺ than for Co³⁺ cation. The Er-based solid solutions showed a different behaviour. For Ni²⁺ and Co²⁺ incorporation there are changes from hexagonal ErMnO₃-type lattice to perovskite-type symmetry, for 20 at% and 30 at% respectively of substituting cations. The resultant perovskites crystallised directly in the O-type orthorhombic perovskite structure. The steric influence seems to play a secondary role, such as it can be deduced of the small variation of the Goldschmidt tolerance factor, t, for perovskite structure.

Keywords: manganites; perovskite solid solutions; crystalline structure; phase transitions

1. INTRODUCTION

Rare-earth manganites REMnO₃ have focused a great lot of attention during the last decades due to their interesting properties in several fields of possible application.

Three issues are the cause of this interest for studying the manganite perovskites:

1°-Potential use of some manganites, such as LaSrₓMnO₃₋δ as cathodes for Solid Oxide Fuel cells, SOFC’s, because of both electronic and ionic conductivity properties.

2°-Discovery of the colossal magnetic resistance phenomenon in compounds associated to lanthanum manganite.

Both issues are due to the appearance of a mechanism of double-change interaction between Mn³⁺ and Mn⁴⁺ that is induced by stoichiometric defects, vacancies, which are produced by means of partial substitution of trivalent cations, RE⁺ or Mn⁺ by divalent ones.

3°-Potential multiferroic features, which are bounded to the simultaneous appearance of a ferroelectric behaviour and an long-range antiferromagnetic order in some highly-anisotropic crystalline structures corresponding with the lower ionic radius RE cations, such as Y, Lu, Yb, and Er.

All these issues are related to the crystalline structure and the possible symmetries adopted by the rare-earth manganites, which are significatively different to those of other rare-earth REMeO₃ compounds, such as REFeO₃ ones.

The mixed oxides of general formula REMeO₃ where RE is a rare earth ion and Me=Fe, Cr, Ti, V, Rh, belong to the group of orthorhombic distorted perovskites, which crystallize in the space group (S.G.) Pbnm. When Me=Mn, the REMnO₃ compounds show the orthorhombic distorted perovskite structure only up to the Ho cation, whereas the compounds corresponding to RE with smaller ionic radii, from Er to Y, crystallize with a hexagonal-type structure and S.G. P6₃cm (1).
As is well known, the distortion degree of the perovskite structure in ABO₃ compounds depends, between other causes, on steric effects, associated with changes in the ionic radius of the component A and B cations. This contribution is well represented by the Goldschmidt tolerance factor \( t = (r_A + r_O) / (r_B + r_O)^{1/2} \), where \( r_A \) represents the ionic radius of the large A cation (RE in the present case), \( r_B \) represents the ionic radius of the small B cation, (Fe, Cr, Mn, Ti, and others for the above-mentioned compounds), and \( r_O \) is the ionic radius of O²⁻. When the tolerance factor decreases, the distortion degree increases (2). Nevertheless, in the case of the manganite compounds, REMnO₃, another factor must be considered with regard to the structure distortion. Thus, the Jahn-Teller nature of the Mn³⁺ cation induces an additional axial distortion effect, which is cooperative (3). Consequently, a combination of low t values and Jahn-Teller effect leads to a modification of the structure, from perovskite-type to the hexagonal-type structure mentioned above, with a higher grade of distortion with respect to the orthorhombic perovskites. Modifications in the crystalline structure of some manganites by formation of solid solutions (RE,A)MnO₃ in which A is a divalent cation such as Ba²⁺, Sr²⁺ or Ca²⁺, have been studied. The changes are more notorious in hexagonal manganites, which change to perovskite-type ones by adding an adequate amount of A cation, (4-6). Scarcer are works devoted to systematic study of the changes in the crystalline structure for incorporating Me²⁺ cations, such as Ni²⁺, Co²⁺ or Cu²⁺, on Mn sites forming solid solutions (7-9). Magnetic properties of some double perovskites REMnMeO₆ are reported (10-12) but discussion about changes in the symmetry are not well developed.

In the present work the crystalline characteristics of solid solutions in four pseudo-binary oxides, based on the REMnO₃, RE=Gd,Er, modified by Ni²⁺ and Co²⁺, are examined as a function of the nature of rare earth and transition metal cation. These compounds represent two different crystalline structural types, one, GdMnO₃ perovskite-type, and the ErMnO₃, hexagonal-type. Relationships between t, Mn³⁺ content, and phase transitions are discussed.

2. EXPERIMENTAL PROCEDURES

The samples have been prepared by solid state synthesis from the corresponding submicronic powder oxides Gd₂O₃, Er₂O₃, MnO₂, NiO and Co₃O₄ that were thoroughly wet mixed and homogenised by means of an attrition mill, with zirconia balls. The dried cake was repeatedly calcined and remilled for three times to assure a total reaction, with a thermal cycle of heating until 1150°C, maintained 6h, and cooling down to room temperature. The heating and cooling rates were 5°C/min and 1°C/min respectively. The reacted products were characterised by X-Ray diffraction technique, and near pure perovskite phase was obtained for each composition. The cakes were remilled in an attrition ball mill. Fine, submicronic powder was uniaxilly pressed and late sintered at several temperatures. The samples were isothermally sintered under O₂ atmosphere, obtaining pure perovskite solid solutions in all the cases. The sintered, powdered samples were X-Ray diffraction, XRD, characterised by the Debye-Scherrer method, using a D-5000 Siemens Diffractometer with CuKα radiation and Ni filter. The phases were identified using a scanning rate of 2° 2θ/min, and the lattice parameters were calculated from the spectra obtained on the sintered, grounded samples using a scanning rate of 1/8° 2θ/min. Si powder was employed as an internal standard. The lattice parameters were calculated using a mean square fits with all the peaks comprising between 2° and 75° 2θ angle range, (16-18 peaks), which have been indexed according to the S.G. Pbnm. Correlation coefficients >0.99 and standard deviation sum <10⁻⁷ have been calculated for all the samples. The Goldschmidt tolerance
factor \( t \) has been calculated using the ionic radii tabulated by Shannon (13), taking into account the oxygen coordination of the involved cations and the existence of different valence states of the Mn and the modifying cations, with different ionic radii, in the solid solutions. The mean ionic radius on \( B \) lattice sites has been used when two or more cations are present in them.

3. RESULTS AND DISCUSSION

Figures 1, 2, 3 and 4 show the XRD patterns of some representative solid solutions of the four systems. All the patterns have been well indexed as Pbnm orthorhombic perovskite-type crystalline structure and no secondary phases have been observed in the range of solid solutions studied for each system. Figures 5, 6, 7 and 8 show the evolution of the lattice parameters of the different solid solutions. In those ones, \( c/\sqrt{2} \) has been represented in place of the \( c \) parameter for obtaining a higher clearness, thus showing the evolution from \( \Omega' \)-type perovskite structure, \( (c/\sqrt{2}a=bc) \) to \( \Omega \)-type one, \( (a=bc) \). Such as was stated for \( Y \)-based manganite solid solutions, (7), the progressive replacement of modifying cation, Ni, Co for Mn leads to a decrease of the lattice volume, which is more pronounced for Co incorporation than for Ni substitution. The decrease is also more pronounced from 50 at% to final of the series for Co replacement. Such as is known, pure ErMnO\(_3\) crystallises with hexagonal-type structure, similar to that of YMnO\(_3\) compound, with a S.G. P\(_6\)cm. Solid solutions with Co, Ni lead to a change of symmetry from hexagonal to orthorhombic perovskite-type structure. It can be seen that the cation amount for which the transition takes place is higher for Co\(^{2+}\) cation than for Ni\(^{2+}\) one. On the other hand, the single-phase solid solution is extended far 50 at% for Co cation whereas with Ni cation, single-phase solid solution only is attained for Ni\(^{2+}\)≤ 50 at%, being biphasic samples those compositions with higher Ni amount. On the other hand, although Gd(Co,Mn)O\(_3\) solid solutions are only represented from 25 to 100 at% Co, it must be say that the solid solution range between GdMnO\(_3\) and GdCoO\(_3\) compounds is total.

![Figure 3. XRD patterns of Er(Co,Mn)O\(_3\) solid solutions, for 40 and 60 at% Co](image3)

![Figure 4. XRD patterns of RE(Ni,Mn)O\(_3\) solid solutions, for 33 and 40 at% Ni](image4)

![Figure 5. Lattice parameters vs at% Co for Gd(Co,Mn)O\(_3\) solid solutions](image5)

![Figure 6. Lattice parameters vs at% Ni for Gd(Ni,Mn)O\(_3\) solid solutions](image6)
between the two extremes. With Ni cation, the solid solution range only is attained for Ni\textsuperscript{2+} ≤ 50 at%.

There are some differences between the solid solutions corresponding to the different rare-earth cations. Thus, the Gd-based solid solutions with Ni and Co cations always showed perovskite-type structure, parent of pure GdMnO\textsubscript{3} until 50 at% Ni-containing samples and until 100 at% Co, (GdCoO\textsubscript{3} crystallises with perovskite-type structure), such as corresponds to the stability of the Gd manganese perovskite structure. At the contrary of that reported by Farhoudi and Wang\textsuperscript{(9)} lattice parameters a and b decrease when Co rises from 50 to 90 at%, in a good correlation with the decrease of the B mean radius, such as is represented in figure 9. On the other hand, Er-based solid solutions showed the perovskite-type structure only from Ni or Co amounts above 20 or 30 at%, respectively, being biphasic samples those with lower doping contents, in which perovskite- and hexagonal-type coexist. Another difference is that the Er-based solid solutions as well with Ni as with Co have orthorhombic O-type structure in all the existing perovskite solid solution range, see figures 7 and 8, whereas those Gd-based solid solutions show a transition from O'-type to O-type for an amount of modifying cation, which is higher for the Co cation than for the Ni cation, see figures 5-6. Finally, it is necessary to say as a last difference of Er-based solid solutions, with regard to Gd system, which was impossible to obtain pure perovskite-type samples for the Er(Co,Mn)O\textsubscript{3} solid solutions with Co amounts above 70 at%. Pure ErCoO\textsubscript{3} compound was not synthesised in the experimental conditions used in this work. Samples with Co≥70at% showed a biphasic nature, with free Er\textsubscript{2}O\textsubscript{3} and some traces of Co\textsubscript{3}O\textsubscript{4}, along with perovskite solid solutions with lattice parameters corresponding to Co amounts ≥70at%.

The reason for the different cation amount limit, which has been observed for Ni\textsuperscript{2+}-doping and Co\textsuperscript{2+}-doping, 20 and 30 at% respectively, which is needed for obtain perovskite-type samples from hexagonal ErMnO\textsubscript{3} can be attributed to the higher stability of the 2+ valence of Ni against Co, which could be in some extension in the form of Co\textsuperscript{4+}. Such as was stated elsewhere\textsuperscript{(7)}, transition of hexagonal to perovskite-type structure is mainly due to progressive lowering of the Mn\textsuperscript{3+} amount in the lattice, and in a minor extension, to modification in the t tolerance factor, such as further will be discussed in this paper. Thus, if it is supposed that a small amount of Co\textsuperscript{3+} is formed, an equivalent part of Mn remains, as Mn\textsuperscript{4+} and, therefore, more amount of Co will be needed for causing the change from hexagonal to orthorhombic crystalline phase.

The observed decreasing of lattice parameters, Figures 7-8, when the doping cation amount rises, which are produced despite of the increase of the mean cationic radius by adding Co\textsuperscript{2+} and Ni\textsuperscript{2+}, with higher ionic radii than Mn\textsuperscript{3+}, (figure 10 and 11), and even taking into account that the incorporation of divalent cations leads to the appearance of equivalent amounts of Mn\textsuperscript{4+}, with lower ionic radius, only can be explained by the progressive disappearance of Jahn-Teller Mn\textsuperscript{3+} cations, and, therefore, of the cooperative distortion effect caused by the anisotropic structure of the external orbital\textsuperscript{(7)}.

The hypothesis that is established about the valence state of the doping cations is the following: for Co amounts ≤50 at% the valence state seems to be Co\textsuperscript{2+}, leading to the corresponding formation of an equivalent amount of Mn\textsuperscript{4+} to preserve the electroneutrality of the lattice. The B cation mean ionic radius must shows an increase. Effectively, the lattice volume grows but not in a significant mode. This is so probably due to the progressive disappearance of the Mn\textsuperscript{3+} cations, which are the responsible of the strong lattice deformation that leads to an O'-type perovskite structure. It can be seen that for these Co amounts the tolerance factor decreases but the lattice symmetry slightly increases, see figure 5 and 7, c/\sqrt{2} curve, which is then associated to that disappearance. Nevertheless, the symmetry of the solid solution is even orthorhombic O'-type. If the Co should be in the 3+ state, the B mean ionic radius must lower strongly because the ionic radius of LS Co\textsuperscript{3+} is lower than Mn\textsuperscript{3+}, and the Vegards'law would be accomplished.

In the Gd(Mn,Co)O\textsubscript{3} system for Co amounts ≥50 at% there is a strong decrease of the a and b lattice parameters and of lattice volume, thus indicating that Co\textsuperscript{3+} increases, lowering the B ionic mean radius and increasing the tolerance factor, with an appreciable rise of the lattice symmetry, represented by the c/\sqrt{2} curve. The observed lattice parameters decreasing is indicating that the possible Co\textsuperscript{3+} cations are in the LS,

![Figure 7. Lattice parameters vs at % Co for Er(Co,Mn)O\textsubscript{3} solid solutions](image)

![Figure 8. Lattice parameters vs at % Ni for Er(Ni,Mn)O\textsubscript{3} solid solutions](image)
(low spin) state, for which the ionic radius is lower than the corresponding to the HS, (high spin) state. In this range is more difficult to establish what is the valence state of the Co cation, if is 3+ in whole, or if is partially 2+ and 3+. On the other hand, it can be seen that there is a transition from O’ to O-type orthorhombic symmetry, i.e. the Mn is in whole in the 4+ valence state, such as is observed in the Er(Ni, Mn)O3, in which Mn is in that 4+ valence state. This LS behaviour is seen as well in the Eu-based solid solutions as in the Gd-based ones.

The strong increase of the lattice parameters and volume that can be seen for pure GdCoO3 is owing to the transition from LS to HS state of the Co3+ cation in this compound, such as was established by magnetic essays, (14).

Figures 9, 10, 11 are very illustrative of the change of symmetry. In the range of existing solid solution, mean B ionic radius grows, and, therefore t decreases. Nevertheless, the orthorhombic symmetry is maintained and c/√2 rises, (figure8), whereas the lattice volume lowers indicating a major lattice compaction and a minor deformation. This can be observed in both Er- and Gd-based solid solutions, see figures 6, and 8. In these figures it can be seen that the tolerance factor decreases when the cation increases, up to 50 at% of doping cation. Above this boundary value, for which it can be expected that all the Mn is in the form of Mn4+ the tolerance factor increases. Despite of the decrease in the t value, in the first region of the curve, the perovskite structures are fully formed and them trends towards a more symmetrical form. The presence or absence of Mn3+ Jahn-Teller cations plays, therefore, a fundamental role for determining the perovskite symmetry, whereas the steric factor represented by the tolerance factor plays a secondary rol. If are compared the values of t corresponding to the Er-based solid solutions with Ni and Co, one can be seen that, despite of the lower t value for Ni-containing compounds, formation of pure perovskite structure is attained at lower amounts of Ni, (20 at%), than that needed for stabilising the perovskite phase in the Co-containing system.

Table 1 resumes some results of conductivity measurements, performed at room temperature for Co amounts ≥ 50 at% in the Gd(Mn,Co)O3 system. As it can be seen, conductivity increases with the Co content, indicating that there exist at least two valence states for Co, 2+ and 3+. If all the Co would be as 3+, and therefore, the Mn as 3+, the Jahn-Teller still should have some influence, and conductivity should be stable or decreasing. Increase of Co leads to an increase of the pairs Co3+-Co2+ and the corresponding charge carriers.

The exposed model can be applied to the other solid solutions. Wider studies published elsewhere, (15) corroborate the model for Er-based solid solutions.

4. CONCLUSIONS.

The incorporation in solid solution of small divalent cations, Ni and Co, substituting for Mn in the hexagonal ErMnO3 compound and in the perovskite-type GdMnO3 compound, leads to a phase transitions in which a perovskite-type structure is formed from the hexagonal phase, or to a change from O’-type to O-type perovskite structure from the GdMnO3 compound. The amount of substituting cation necessary for such transitions depends on the cation nature and less on the ionic radius. Cation with very stable (II)
valence state, such as Ni\(^{2+}\) shows an upper limit to solid solution formation, which has been established at 50 at \%. For variable-valence Co\(^{2+}\) Co\(^{3+}\) the solid solution limits is extended up to 70 at\% for Er-based compounds and for the whole range, 100 at\% for Gd-based compounds. The phase transition depends strongly on the progressive substitution of the Jahn-Teller Mn\(^{3+}\) cation, and therefore of the cooperative interaction weakness. The steric influence, represented by the tolerance factor, \(t\), plays a secondary role, as is shown by the very slow variation of the tolerance factor, \(t\), as a function of the cation content.

Electrical measurements have been carried out for corroborating the valence balance of the different cations involved in the solid solution formation. Gd(Co,Mn)O\(_3\) solid solution shows electrical conductivity, which rises with the Co amount.

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