A note on the different crystalline features of the EuMnO$_3$-based solid solutions as a function of the modifying cation nature

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The structural properties of solid solutions based on EuMnO$_3$ in which Eu has been substituted by divalent Ca$^{2+}$ and Mn by the divalent cation Ni$^{2+}$ or the variable valence cation Co$^{2+}$-Co$^{3+}$ have been studied by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). These substitutions lead to changes in the lattice parameters and the symmetry of the orthorhombic, O’ perovskite-type of the pristine compound EuMnO$_3$. The structural changes depend on several factors. Solid solutions Eu(Mn,Ni)O$_3$ and Eu(Mn,Co)O$_3$ change from the O’-type to O-type orthorhombic perovskite symmetry when the content of the Mn$^{3+}$ cation decreases due to the progressive substitution by Ni and Co. This change occurs for a percentage of the Ni$^{2+}$ cation of 20 at%, whereas for the Co cation, only 10 at% are needed for such a transition. (Eu,Ca)MnO$_3$ solid solutions showed a different behaviour. Even at an amount as high as 50 at% Ca$^{2+}$ there is no transition from O’ to O-type orthorhombic perovskite symmetry. The tolerance factor, $t$, increases monotonically for both Eu(Mn,Ni)O$_3$ and (Eu,Ca)MnO$_3$, while for Eu(Mn,Co)O$_3$ it first decreases and then increases. The increase is lower for Ni-based and Co-based samples than for the Ca-based ones.

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

Una nota sobre los diferentes comportamientos de las soluciones sólidas basadas en EuMnO$_3$ como una función de la naturaleza del catión modificador

Las propiedades estructurales de las soluciones sólidas basadas en EuMnO$_3$, en donde Eu ha sido sustituido por Ca$^{2+}$ y Mn por Ni$^{2+}$ o por un catión de valencia variable tal como Co, (II ó III) han sido estudiadas por Difracción de Rayos X, (DRX). Estas sustituciones llevan a cambios en los parámetros de red y en la simetría de la perovskita tipo O’ propia del compuesto EuMnO$_3$. Los cambios estructurales dependen de la cantidad y del tipo de catión sustituyente. Ni y Co inducen un cambio desde la estructura tipo O’ a la O para 20 at% Ni y 10 at% Co respectivamente. Por su parte, la incorporación de Ca en lugares A induce este cambio para x(Ca)> 50 at%. El factor de tolerancia de la estructura perovskita también muestra un comportamiento diferente en función del catión modificador.

Palabras clave: Manganitas, soluciones sólidas de perovskitas, estructuras cristalinas, cambios de fase.

1. INTRODUCTION

Rare-Earth manganites REMnO$_3$ have focused a great deal of attention during the last decades due to their interesting properties in several fields of possible applications.

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

1º-Potential use of some manganites, such as $La_xSr_{1-x}MnO_3$-$\delta$ or $Sm_xSr_{1-x}MnO_3$-$\delta$ as cathodes for Solid Oxide Fuel cells, SOFC’s, because of their both electronic and ionic conductivity features.

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

These two issues are due to a mechanism of double-exchange interaction between Mn$^{3+}$ and Mn$^{4+}$, induced by stoichiometric defects and produced by the partial substitution of trivalent cations, RE$^{3+}$ or Mn$^{3+}$ by divalent ones.

3º-Potential multiferroic features, which are bounded to the simultaneous presence of a ferroelectric behaviour and a long-range antiferromagnetic order in some highly-anisotropic crystalline structures, as found in ReMnO$_3$ compounds based on RE cations with the lower ionic radii, such as Y, Lu, Yb, and Er.

The mixed oxides with general formula REMeO$_3$, 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 REMnO$_3$ compounds show the orthorhombic distorted perovskite structure only up to the Tb cation, whereas the compounds corresponding to RE with smaller ionic radii, from Er to Y, crystallize with a hexagonal-type structure and S.G. P6$_3$cm [1].

As it is well known, the distortion degree of the perovskite structure in ABO$_3$ compounds depends, among 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 $t=\frac{(r_a+r_o)}{(r_a+r_o)^{3/2}}$, 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 \( O^2- \). When the tolerance factor decreases, the distortion degree increases [2]. Besides that, in the case of the manganite compounds, \( \text{REMnO}_3 \) another factor must be considered with regard to the structure distortion, namely the Jahn-Teller nature of the Mn\(^{3+} \) cation, which induces an additional axial distortion effect. This distortion is accomplished by lengthening two of the Mn-O bond trans to each other, which lowers the energy of the occupied 3d\(^{5/2} \) orbitals, with respect to the empty 3d\(^{3/2} \) orbitals. The filled 3d\(^{5/2} \) orbitals form a zigzag pattern in the \( xy \) plane which leads to an expansion of the \( a \) and \( b \) unit cell dimensions, [3,4]. This effect is co-operative and explains, along with the lowering of the tolerance factor, the appearance of hexagonal symmetry for the small rare-earth atom compounds, [5]. A combination of low \( t \) values and Jahn-Teller effect leads to a modification of the structure, which passes from perovskite-type to the hexagonal-type structure mentioned above, with a higher grade of distortion with respect to the orthorhombic perovskites. Even, in the case of manganite perovskites, crystallising with the S.G. Pbnm, presence of Mn\(^{3+} \) causes other modification with regard to other perovskites, such as REFeO\(_3 \) ones, consisting in a deformation in the ab plane, so that the lattice parameter ratios are \( c/\sqrt{2}a=b \) (O'-type orthorhombic structure) for \( \text{REMnO}_3 \) (RE=La,..... Ho), against the ratio \( a= c/\sqrt{2}b \) (O-type orthorhombic structure) corresponding to \( \text{REMeO}_3 \) compounds, (Me=Fe, Cr) in the whole range of rare-earth cations [6]. There is a lot of work about the crystalline behaviour of \( \text{(RE,A}^{2+})\text{MnO}_3 \) solid solutions. As a first statement, several authors conclude that the increase of the tolerance factor by doping with \( A^{2+} \), along with the lowering of the Jahn-Teller cation amount in the lattice by disappearance of Mn\(^{3+} \) for compensating the charge defect of \( A^{2+} \), lead to an increase of the lattice symmetry, i.e. a decrease of the cooperative distortion, [7-9]. Nevertheless there is scarce work about the corresponding behaviour when Mn is substituted by a divalent cation such as Ni, Co, Cu, [10,11], being very interesting to know this behaviour for further elucidation of the electrical and magnetic features.

Figure 1, XRD patterns of the solid solutions \( \text{Eu}_{1-x}\text{Ca}_x\text{MnO}_3 \), \( x=0.10, \ 0.20, \ 0.30, \ 0.40, \ 0.50, \ 0.75, \ 0.90 \), indexed as belonging to S.G. Pbnm.

Figure 2, XRD patterns of the solid solutions \( \text{EuMn}_{1-x}\text{Ni}_x\text{O}_3 \), \( x=0.10, \ 0.25, \ 0.33, \ 0.40, \ 0.50 \), indexed as belonging to S.G. Pbnm.
The aim of the present work is to establish the evolution of the crystalline characteristics of solid solutions based on EuMnO₃ perovskite manganite, in which RE cation is substituted by aliovalent cations, either by Ca²⁺ cation in site A, Eu₁₋ₓCaxMnO₃, or by two small cations, Me= Ni²⁺, Co³⁺ substituting Mn cation in site B, EuMn₁₋ₓMeₓO₃, and relating that crystalline evolution as a function of the substituting cation and the substituted lattice site.

2. EXPERIMENTAL PROCEDURES

The samples have been prepared by solid state synthesis from the corresponding submicronic powder oxides and carbonates, Eu₂O₃, MnO, NiO, Co₃O₄ and CaCO₃, thoroughly wet mixed and homogenised by means of an attrition mill with zirconia balls. The dried cake was repeatedly calcined and re-milled three times to assure a total reaction, with a thermal heating cycle until 1150ºC, maintained 6h, and cooled down to room temperature. The heating and cooling rates were 5ºC/min and 1ºC/min respectively. The reacted products were characterised by X-Ray Diffraction, XRD, showing that almost pure perovskite phases were obtained for each composition after first thermal cycle. The cakes were re-milled in an attrition ball mill. Fine, submicronic powder was uniaxially 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 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 fit with all the peaks comprising between 20° and 65° 2θ angle range, (16-18 peaks), which have been indexed according to the S.G. Pbnm. Correlation coefficients >0.999 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 [12], 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 of the B-lattice sites has been used when two or more cations were present in them. Although the possibility to get oxygen vacancies cannot be neglected, firing and cooling in O₂ atmosphere is expected to minimize its formation. X-ray Absorption Spectroscopy (XAS) measurements at the Mn K-edge and Eu L₃ edge were performed at room temperature in transmission mode at the BM25 Spanish CRG Beamline (SpLine) of the European Synchrotron Radiation Facility (ESRF). Two gas ionization chambers, filled with nitrogen and argon, were used to measure the incident and the transmitted beam, respectively. Samples for analysis were in powdered form and placed onto a kapton tape located in the beam path at room temperature. The powder amount to be mounted was calculated so as to achieve similar signal intensity for all the samples. Several scans were taken to improve the signal-to-noise ratio. Data were normalized applying the same normalization parameters for all of the spectra by means of in-house software (Athena).
3. RESULTS AND DISCUSSION.

Figures 1, 2, 3 show the XRD patterns of the compositions corresponding to the three solid solutions, \((Eu, Ca)MnO_3\), \((Eu(Mn, Ni))O_3\) and \((Eu(Mn, Co))O_3\) respectively. All the systems showed complete solid solution in the prepared ranges of compositions, obtaining single phase samples. All patterns were indexed as perovskites with a S.G. Pbnm.

Figures 4, 5, 6 show the evolution of the lattice parameters of the different solid solutions \((Eu, Ca)MnO_3\), \((Eu(Mn, Ni))O_3\) and \((Eu(Mn, Co))O_3\) respectively. In all figures, \(c/\sqrt{2}\) has been represented instead of the \(c\) parameter for obtaining a better clarity of the representation, and also show the evolution from \(O'\)-type perovskite structure, \((c/\sqrt{2} < a \leq b)\) to \(O\)-type one, \((a \leq c/\sqrt{2} < b)\) for each compositional system.

As it is possible to observe there are some differences in the crystalline behaviour among the different compositions. First of all, it must be said that, under the experimental conditions proposed in this work, it was impossible to obtain a single phase perovskite in the \((Eu(Mn_{1-x}Ni_x))O_3\) system for \(x > 0.50\), being relatively hard to prepare single phase samples for \(x = 0.50\). This fact was already pointed out in other manganite compounds, such as \((GdMn_{1-x}Ni_x)O_3\), \((ErMn_{1-x}Ni_x)O_3\), and \((YMn_{1-x}Ni_x)O_3\) [10, 11]. This behaviour was attributed to the high stability of the valence (II) of the \(Ni\) cation, which makes difficult to maintain valence equilibrium in compositions with an excess of divalent cations on the sites \(B\), which can lead to the developed formula \(Eu[Mn^{4+}_{1-x}Ni^{2+}_x]O_3-\delta\) for \(x > 0.50\).

On the contrary, complete solid solutions in the whole compositional range, \(0.00 < x < 1.00\) were easily obtained for the other two systems. In the \((Eu_{1-x}Ca_x)MnO_3\) system, in the range \(0.00 < x < 0.50\), the perovskite maintains the orthorhombic \(O'\)-type symmetry, despite the lattice volume shrinkage and the lowering of the distortion factor \(D = \sum|a_i - \bar{a}|/3\bar{a}\) (where \(a_1 = a_2\); \(a_3 = c/\sqrt{2}\), and \(a = (a_1 a_2 a_3)/(a_1 a_2 c/\sqrt{2})^{1/3}\)) [13], see figure 7. Only at very high values of \(x\), higher than 0.60, the \(O\)-type structure is formed. It is interesting to point out that despite the higher volume of the \(Ca\) cation with regard to that of \(Eu\), the lattice volume decreases monotonically, contrary to that predicted by Vegard’s law.

The system \((Eu_{1-x}Ni_x)O_3\) shows a change in the perovskite type, from \(O'\) to \(O\) for \(x \approx 0.20\). Differently to the case of the \((Eu_{1-x}Ca_x)MnO_3\) system, the \(a\) parameter slightly decreases in the \((Eu_{1-x}Ni_x)O_3\) system when increasing \(x\). On the other hand, a common feature to both systems is the fact that the lattice volume also decreases along with the \(b\) parameter, although the lattice distortion factor \(D\) shows a slightly higher variation in the case of the \((Eu_{1-x}Ca_x)MnO_3\) (figure 7).

A more striking behaviour was observed in the \((Eu_{1-x}Co_x)O_3\) system. The \(b\) lattice parameter first decreases until \(x = 0.10\) and then increases up to \(x = 0.75\), followed by a new decrease. The increase, which occurs in the medium compositional range is also observed in the lattice volume, up to \(x = 0.50\). At the same time, the parameter \(c/\sqrt{2}\) increases at \(x = 0.10\) and then smoothly decreases while the relation \(a < c/\sqrt{2} < b\) holds from \(x = 0.10\) to 1.00. In other words, there is a change from \(O'\)- to \(O\)-type perovskite symmetry at a value of \(x\) as low as 0.10, which has not been observed for any other Co-modified manganites. A possible explanation of this behaviour could be related, well to the relative stability of the two possible valence states of \(Eu\) cation, which in some
conditions, such as the presence of the Co cation, can also adopt the two valence states (II) and (III), favourably stabilised in the lattice, well to a change in the O\textsuperscript{2-}-co-ordination sphere of Eu\textsuperscript{3+} caused by presence of Co\textsuperscript{3+}. XAS analysis was made to elucidate in a first approaching what is the mechanism that drives the observed behaviour.

Figure 8 represents the tolerance factor calculated for the stoichiometric formula, supposing that there are no oxygen vacancies in any samples, and that, for a sake of mutual comparison, Eu is in the valence state (III), according to the observed in the XAS essay. Low-spin state has been taken as corresponding to the different paramagnetic cations, Mn, Ni and Co. For Eu(Mn\textsubscript{1-x}Co\textsubscript{x})O\textsubscript{3} compositions, the following theoretical formulae Eu\textsuperscript{3+}[Mn\textsuperscript{3+}\textsubscript{1-x}Mn\textsuperscript{4+}\textsubscript{x}Co\textsuperscript{2+}\textsubscript{x}]O\textsubscript{3}, for x\leq0.50, or Eu\textsuperscript{3+}[Co\textsuperscript{3+}\textsubscript{2x-1}Mn\textsuperscript{4+}\textsubscript{1-x}Co\textsuperscript{2+}\textsubscript{x}]O\textsubscript{3}, for x\geq0.50, have been used, which seem to be the most favourable for valence equilibrium.

As it can be seen in figure 8, the tolerance factor t grows steeply with the Ca percentage, but the perovskite symmetry type remains unchanged as O\textsuperscript{-}-type up to x(Ca)=0.50, typical of the buckling structures with Jahn-Teller distortion. For the Ni modification, t decreases in the whole studied range of compositions. In the case of Co there is a peculiar behaviour, with a decrease of the factor t and a later increase although lower than the corresponding increase of the Ca solid solutions. Nevertheless, the symmetry suffers a change to less buckling crystalline structure, being noticeable that the change occurs at a value as low as x(Co)=0.10 for this solid solution. Thus, steric influence seems to play a secondary role on the lattice distortion of manganites against the progressive decrease of the Mn\textsuperscript{3+} Jahn-Teller cation; it seems that the nature of the modifying cation in sites B plays also an important role on structural changes.

X-ray absorption spectra were measured at the Co (7708 eV) and Mn K-edge (6537 eV) and Eu L3 edge (6980 eV) in order to investigate dependence of the cation oxidising state environment on the sample composition. Figure 9a shows the X-ray Absorption Near Edge Spectra (XANES) at the Eu L3-edge. The edge position at 6980 eV corresponds to Eu\textsuperscript{3+} without clear differences between the investigated samples. The results allows to discard the presence of a significant amount of Eu\textsuperscript{2+} since divalent Eu that would arise a clearly resolved peak shifted 10 eV toward lower energies. The differences in the white line intensity among the investigated samples are indicative of changes in the Eu 5d states localization in agreement with the changes observed in the lattice parameters and Jahn-Teller deformation.

Figure 9b shows the k\textsuperscript{2}-weighted radial distribution function obtained from the Extended X-ray Absorption Fine Spectra (EXAFS) at the Eu L3 edge. The band corresponding to the Europium first coordination shell appears to be composed, pointing out the existence of two environments with different bond distances. Moreover, we found changes in the relative weight of both environments with the sample composition. This behaviour could be attributed to a change in the coordination sphere of Eu, changing from an EuO\textsubscript{6} polyhedron such as is typical of a Pbnm orthorhombic structure to an EuO\textsubscript{12} polyhedron, typical of a less distorted structure, such as LaFeO\textsubscript{3}. The increase of large bond distances with increasing Co content is also consistent with the increase of volume and lattice parameters inferred from observed from XRD (figure 6).

XANES spectra recorded at Mn K-edge have been represented in the figure 10. As the Mn content decreases,
which passes from eight-fold to twelve-fold O$_2^-$ configuration could promote the change of the nearer neighbours of Eu$^{3+}$, in site B. Presence of Co, which can adopt two valence states structure-forming solid solutions: Ca in site A and Ni and Co valence. Three different cations have been taken to modify the O’-type perovskite, in which both Eu and Mn have variable oxidising state in the samples varies between 2+ and 3+ and increases also with Co content.

the edge shifts toward higher energies. These spectra indicate that the Mn shows an intermediate oxidising state between 3+ and 4+, that increases with the Co content. Similarly, XANES spectra recorded at Co K-edge (not shown) revealed that Co oxidising state in the samples varies between 2+ and 3+ and increases also with Co content.

4. CONCLUSIONS

Mechanisms establishing the structural changes in manganite perovskites have been studied, taking as an example for the first time the changes occurring in EuMnO$_3$, O’-type perovskite, in which both Eu and Mn have variable valence. Three different cations have been taken to modify the structure-forming solid solutions: Ca in site A and Ni and Co in site B. Presence of Co, which can adopt two valence states could promote the change of the nearer neighbours of Eu$^{3+}$, which passes from eight-fold to twelve-fold O$^-$ configuration in the perovskite structure, leading to an increase in the lattice volume besides a change from O$^-$ to O-type for a value as low as 10 at% Co with respect to the total number of B sites. On the other hand, a cation with very stable valence state, such as Ni$^{2+}$, allows only solid solutions until 50 at%, with a structural change at about 20 at%. Finally, Ca cation forms solid solutions in the whole range of compositions, with structural change at about 60 at%. The structural changes seem to be associated to the lowering of Mn$^{3+}$ percentage in the lattice, and less to the tolerance factor variation.

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