Phase transition and electrical conductivity in the system YMnO$_3$-CaMnO$_3$

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Solid solution formation between the ferroelectric hexagonal compound YMnO$_3$ and the semiconducting perovskite compound CaMnO$_3$ has been studied in the Y-rich region of the pseudobinary system. The materials were prepared by reaction of the corresponding oxides and the calcium carbonate for obtaining the corresponding phases and subsequent sintering of the pressed powders in the 1400–1525 °C-temperature range. Their ceramic characteristics were established. Samples with relative density >98% D_{th} were obtained. The hexagonal symmetry of the pure yttrium manganite changes to an orthorhombic one, isostructural with that of the GdMnO$_3$ compound, for ~32 mol % CaMnO$_3$. The incorporation of the Ca cation causes an increasing in the compactness of the lattice cell, promoting a rise in the apparent density, despite of the smaller atomic weight of the Ca cation against that of the Y one, until the transition to the orthorhombic lattice occurs. Subsequent increase in the Ca amount lead to a decrease in the theoretical density.

The electrical conductivity of the solid solutions increases strongly from 100 to the 90/10 Y/Ca composition, and more moderately for higher Ca amounts. Conductivity values as high as 10^{-2} S · cm^{-1} were measured on the denser samples. The activation energy for conduction suffers a corresponding decrease when the Ca amount is increased. © *1999 Kluwer Academic Publishers*

1. Introduction

The rare-earth manganites REMnO$_3$ are a group of semiconducting compounds, which show, at room temperature, two different types of structure, depending on the ionic radius of the lanthanide cation. Thus, the light, high ionic radii, lanthanide manganites, (from La^{3+} to Ho^{3+}) crystallize with a perovskite structure [1], of orthorhombic symmetry, with a space group Pbnm. The orthrhombicity factor b/a raises when the lanthanide ionic radius lowers. The CaMnO$_3$ compound have a perovskite structure, isomorphous of the above mentioned compounds, with a quasi-tetragonal, orthorhombic lattice [2], similar to that of the LaMnO$_3$. The heavy rare-earth manganites, (from Ho^{3+} to Lu^{3+} and yttrium), show a hexagonal structure with a space group P6$_3$cm [3]. In a strength relation with the structural evolution, the electrical conductivity changes from the very high values measured at the lanthanum manganite to that of the semiisolating yttrium compound [4]. Therefore it seems also to exist a correlation between the RE ionic radii and the electrical conductivity.

As was above indicated the YMnO$_3$ compound crystallizes with a hexagonal structure, which changes to an orthorhombic, perovskite-type structure only at high temperatures and/or pressures. It is an antiferromagnetic, ferroelectric material with a Neel temperature below 0 °C, and a Curie ferroelectric point above 600 °C [5]. It is a poor p-type semiconducting material with σ_{20} ~10^{-6} S · cm^{-1}, and an activation energy for electronic conduction of 0.36 eV [6]. The ceramic materials based on this compound have shown an interesting non-ohmic behavior and electronic switching processes under the action of high electrical fields [7]. The incorporation of divalent cations as a solid solution on the lattice sites corresponding to the Y cation, would lead to low substantially the resistivity of the compound, by creating a higher amount of Mn^{4+} cations on sites corresponding to the Mn ones. The mechanism acts in a similar manner as one have been seen in the lanthanum-alkaline-earth manganites [8]. The CaMnO$_3$ compound shows a higher electrical conductivity value than that of the YMnO$_3$ one. The ionic radii of the Y^{3+} and Ca^{2+} are enough similar, and therefore one can predict the formation of solid solutions in a wide range of compositions.

The goal of the present work is to study such a solid solution formation in the Ca-Y manganite system, and to establish the modification in the electrical conductivity of the obtained ceramic materials.

2. Experimental

MnO, Y oxalate and CaCO$_3$ compounds with r.g. purity were used as raw materials. Stoichiometric amounts corresponding to formulations which ranging from pure YMnO$_3$ to 60/40 molecular ratio between YMnO$_3$ and CaMnO$_3$ were weighted and thoroughly wet-mixed using isopropyl alcohol as liquid medium. The mixed

powders were heated at 1100 °C during 1 h. The calcined powders were attrition milled with the same liquid medium. X-ray powder Diffraction technique (XRD) was used on the synthesized powders and on the sintered samples for establishing the crystalline structure and the existence of solid solution for the different compositions. The lattice parameters were measured by using a scan rate of 0.25° 2θ/min. All the existing peaks from 10 to 65° 2θ were scanned. Submicronic pure silicon powder was employed as internal standard. A minimum square adjust program was used to calculate the parameter values from the peaks. These peaks were indexed according to Pbnm space group for perovskite phases and according to P6$_3$cm for the hexagonal ones. On the synthesized powders, DTA and TG analysis were performed to know the oxygen evolution during the sintering. The powders were isostatically pressed at 2000 MPa, and sintered at several temperatures. The apparent density was measured by liquid displacement. The microstructure was observed by Scanning Electron Microscopy (SEM), on polished and chemically etched surfaces. Disc-shaped samples were electroded with Ag paste, the electrodes were fired at 700 °C, and the electrical conductivity was measured between 20 and 250 °C.

3. Results

The samples will be identified as YXC(1 − X), 9 ≥ X ≥ 6, being X the amount of Y cation × 10. Fig. 1 depicts the TG curves corresponding to some synthesized powders. The curves have been taken between 25 and 1500 °C. From these TG curves it can be seen that there are a weight loss processes which start at 1040 °C and end at 1200 °C. The process was less pronounced when the CaO amount was increasing. The weight losses could be associated to a oxygen evolution from the perovskite lattice caused for the high temperature Mn reduction process. Ca presence seems to minimize this reduction, because of the oxidizing nature of that cation. During the cooling, (not represented), weight gain was not observed.
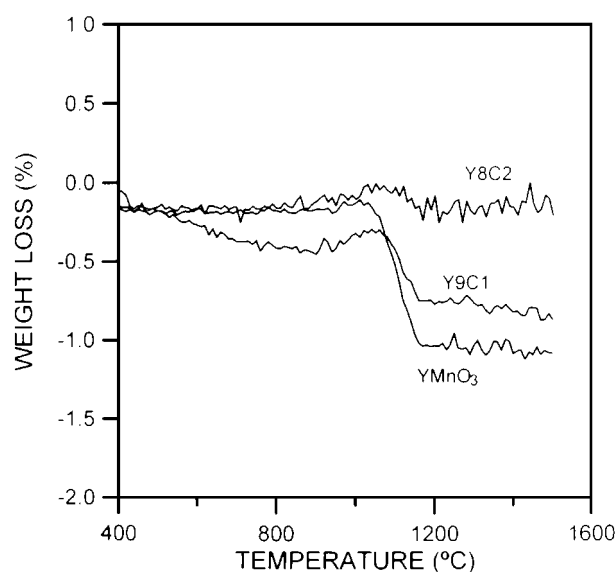

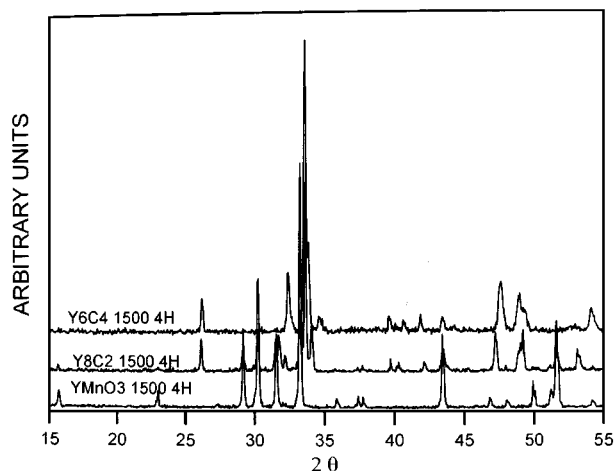*Figure 1* Weight losses of several samples with different Ca amounts.

Figure 2 XRD Patterns corresponding to compositions with 0 mol %, 80 mol %, (both with hexagonal symmetry), and 40 mol % of CaMnO$_3$, (with orthorhombic symmetry).
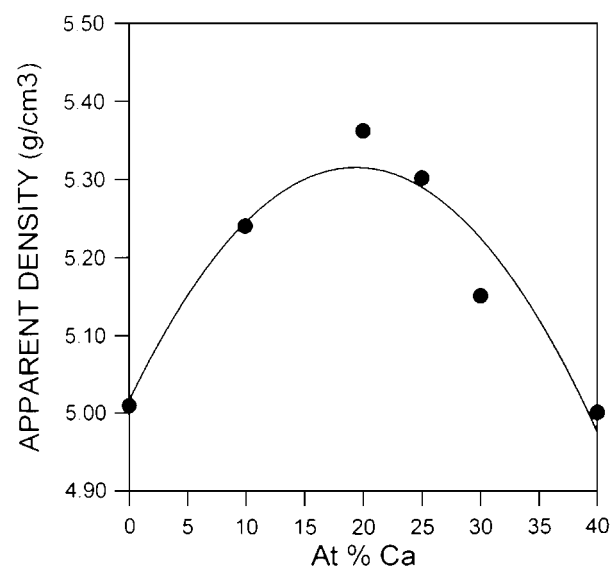

Figure 3 Apparent density as a function of the Ca amount. Samples were sintered at 1500 °C 2 hours.

The CaMnO$_3$ and YMnO$_3$ compounds form a continuous series of solid solutions in the studied range, as can be inferred from the XRD patterns obtained on the sintered samples (Fig. 2). The XRD patterns showed the existence of a single phase for all the characterized samples. One of the most striking features is that the incorporation of a lighter cation such as the Ca cation, produces an increase of the apparent density of samples. This increase is caused by the strong reduction in the lattice parameters of the hexagonal phase, despite the higher ionic radius of the Ca cation against that of the Y one (Fig. 3). From 25 to 30 at % Ca there is a change in the structure and symmetry of the solid solution, which passes from hexagonal P6$_3$cm to a perovskite-type structure, with orthorhombic symmetry Pbnm, isomorphous to the CaMnO$_3$ one, with a higher orthorhombicity factor, which is decreasing when the Ca amount is raised. As it can be seen in the Fig. 4, the hexagonal c_0 parameter shows a strong decrease when the Ca amount increases whereas the a_0 parameter grows until the hexagonal-orthorhombic transition region is
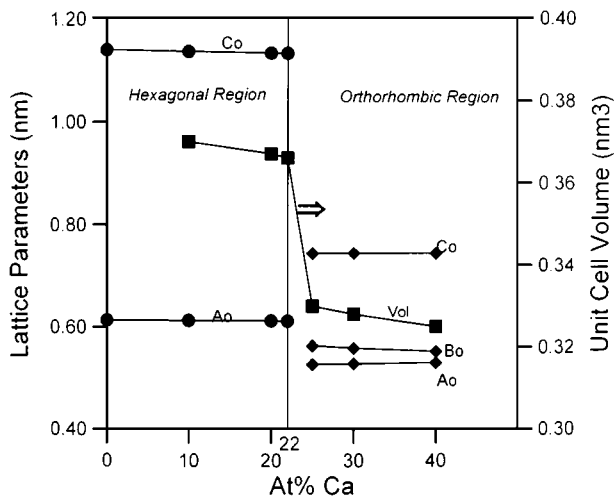
Figure 4 Variation of the lattice parameters and unit cell volume of the solid solutions between YMnO$_3$ and CaMnO$_3$.

attained. The lattice volume is lowering with the Ca amount increase. From the boundary composition, and through the orthorhombic phase region, the c_0 lattice parameter remains almost unaltered. Meanwhile, the b_0 parameter decreases markedly and the a_0 parameter grows less pronouncedly than that. The lattice volume suffers also a monotone decrease as a consequence of such modifications of lattice parameters in this phase domain. On the other hand, if a normalized orthorhombic volume V_N (hexagonal) $= 3/2 \cdot V$ (orthorhombic) is considered, taking into account that the Z value of the orthorhombic lattice is $Z = 4$, and that of the hexagonal one is $Z = 6$, it is possible to see in the Fig. 4 that there is a sharp lowering of the lattice volume through the phase transition. This lowering agrees with the maximum density seen in the samples corresponding to the transition zone. As the lowering of the lattice volume in the orthorhombic region is less pronounced, and the effect of the CaO incorporation on the molar weight is more important, the density will fall out as a function of the CaO amount in solid solutions of the orthorhombic phase region. Those effects are reflected in the Fig. 3.

As was indicated above, the rare-earth manganites show a change of their crystalline structure when the ionic radius of the lanthanide cation is decreasing. The lower value of ionic radius for which the perovskite structure is still keeping is $r_0 = 1.17$ Å. The mean radius of the A site of the Perovskite structure, corresponding to the 72/22 Y/Ca composition is 1.174 Å. This result seems to be in good agreement with that minimum for crystallizing as orthorhombic perovskite. Nevertheless, further work will allow to establish with higher precision the boundary value.

Fig. 5 shows the microstructure developed by the sintered bodies. Samples corresponding to pure YMnO$_3$, Y8C2, which is a hexagonal phase near of the transition, and a perovskite-type, Y6C4 sample are represented. There are not appreciable changes in the microstructure when the symmetry changes. The grain shape is irregular and size distribution is heterogeneous, as corresponding to ceramics processed by a solid state way. Intragranular porosity can be seen. The spherical shape
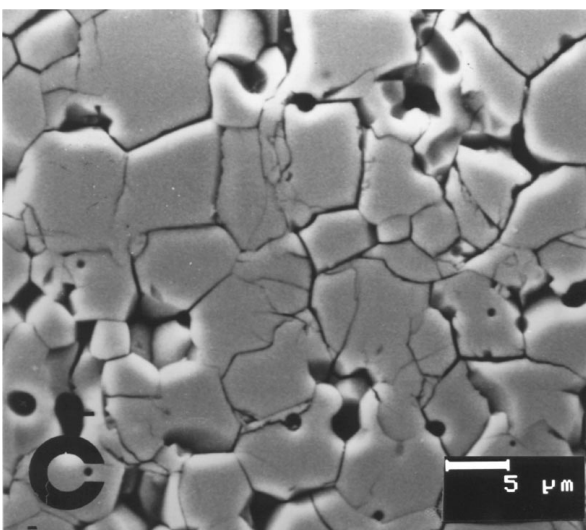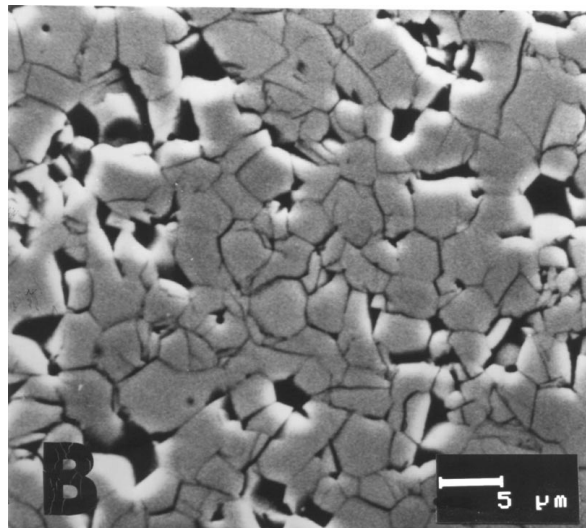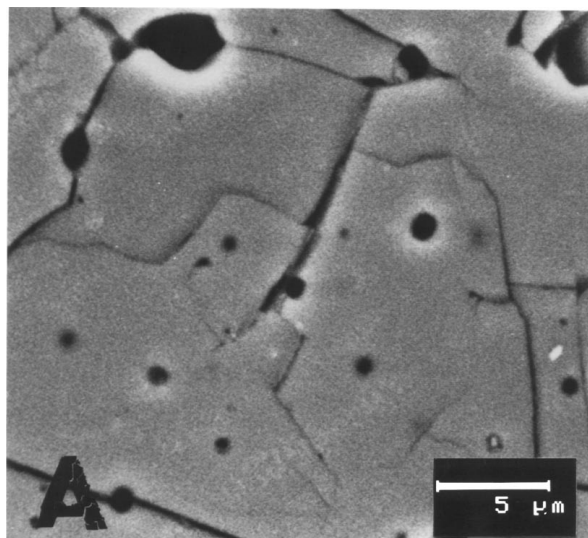

Figure 5 SEM micrographs corresponding to the samples: (A), Pure YMnO$_3$, (B) Y$_{0.8}$Ca$_{0.2}$MnO$_3$, (C) Y$_{0.6}$Ca$_{0.4}$MnO$_3$, all the samples sintered at 1500 °C, for 2 h.

of a number of pores could be indicating that this porosity is created by oxygen evolution during the ultimate sintering step, at very high temperatures, which, as been seen by TG essays correlates with a weight loss.

Table I summarizes the most relevant electrical parameters of the ceramics as a function of the Ca amount.

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TABLE I Electrical conductivity at 20 °C, activation energy and NTC parameter as a function of the Ca amount

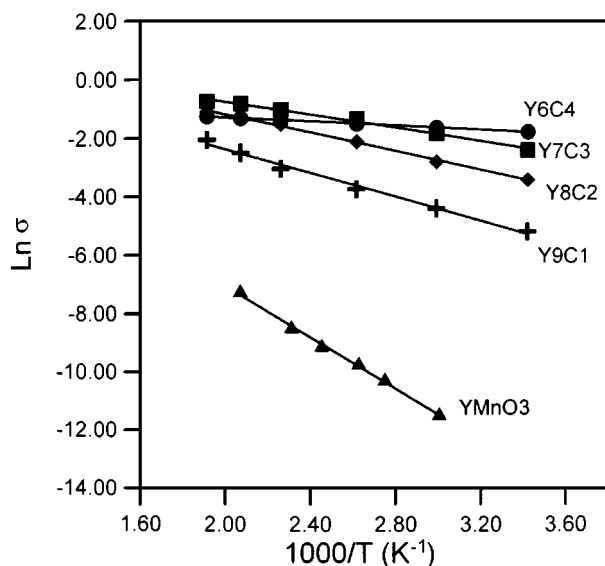| at % Ca	0	10	20	30	40
$\sigma_{20\,°C}$ (S·cm^{-1})	$9.47 \cdot 10^{-6}$	$5.53 \cdot 10^{-3}$	$3.23 \cdot 10^{-2}$	$8.36 \cdot 10^{-2}$	$1.63 \cdot 10^{-1}$
E_a (eV)	0.38	0.18	0.14	0.105	0.03
B	4411	2051	1590	1140	366

Figure 6 Conductivity vs. temperature curves for samples sintered at 1500 °C, 2 h.

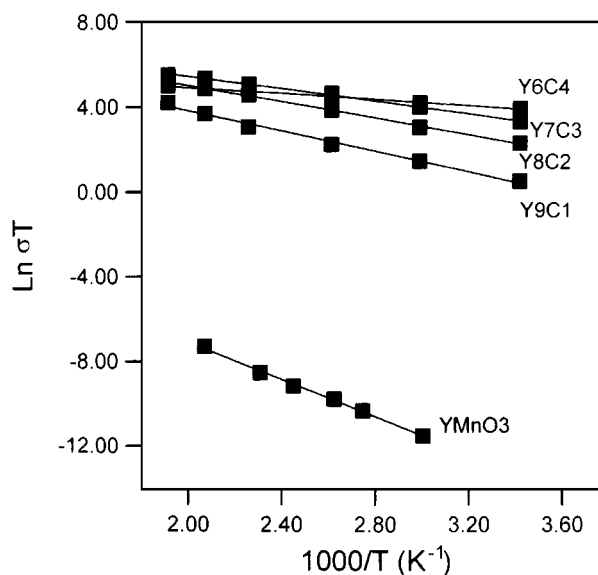*Figure 7* σT vs. $1/T$ curves for samples sintered at 1500, 2 h.

One has also shown the value $B = \Delta\rho/\Delta T$, which represents the NTC parameter of the materials.

Fig. 6 depicts the Arrhenius curves $\ln \sigma$ vs. $1/T$ corresponding to the different compositions. All the measured compositions showed semiconducting behavior in the temperature range essayed. It can be seen the strong increasing of the conductivity value when 10 at % is incorporated, and how successive increases cause lower relative raising of that parameter. The sample Y6C4, with perovskite structure, shows a high conductivity value, and a very low activation energy for conductivity. These values are comparable with those of the most known compounds (La, Sr)MnO$_3$ [9]. Therefore they are good candidates for its possible use as ceramic electrodes.

Fig. 7 shows the curves $\ln(\sigma T)$ vs. $1/T$. It can be seen that these curves are straight lines for all the compositions. According to these results it is possible to state that the conductivity mechanism is by thermally activated hopping of small polarons between localized states corresponding to Mn sites of different valence value, Mn^{3+}-Mn^{4+} such a statement as supported by the conduction mechanism for REMnO$_3$ compounds reported by Rao *et al.* [4]. The increase of the conductivity with the Ca amount is consequence of the increment of Mn^{4+} sites which is induced for compensating the lower valence of Ca^{2+} against Y^{3+}.

4. Conclusions

1. The Y and Ca manganites form a complete solid solution for the composition range 0 to 40 mol % CaMnO$_3$.

2. At ≈ 22 mol % CaMnO$_3$ there is phase transition from hexagonal to orthorhombic symmetry. The incorporation as solid solution of Ca cations causes an increment in the compactness of the crystalline lattice, so of the hexagonal phase as the orthorhombic one.

3. The incorporation of Ca^{2+} to the YMnO$_3$ provokes a strong increase of the electronic conductivity, higher than four magnitude orders.

4. The mechanism of conduction is that of the mixed valence semiconductor, for thermally activated small polaron hopping.

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