

Ca_{1-x}Y_xMnO₃ manganites: synthesis and ESR characterization

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Abstract

Ceramic samples of Ca_{1-x}Y_xMnO₃ were synthesized by a liquid-mix method obtaining single phase materials, for 0.1 ≤ x ≤ 1, with orthorhombic structure. The cell volume increases with x indicating that changes in the Mn electronic state overcomes the progressive diminishing of the (Ca, Y) cationic radius, r_{Ca} > r_Y. We observed a continuous broadening of the electronic spin resonance line width with x. This is explained in terms of the increasing orthorhombic distortions. We have measured the DC magnetization for the x = 1 compound YMnO₃. Our results are compatible with a G-type antiferromagnet with T_N = 44 K. © 2002 Elsevier Science B.V. All rights reserved.

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In the perovskite oxides A_{1-x}A'_xMnO₃, with A = divalent alkaline-earth and A' = trivalent rare-earth, the lattice properties greatly influence its magnetotransport properties. We are interested in the properties of the system Ca_{1-x}Y_xMnO₃. Trivalent Y in this kind of compound, is between the ions with lowest radius, r_{A'}, crystallizing in the perovskite structure. Ceramic samples were prepared from solid-state reaction [1] where single orthorhombic phases were not obtained for every Y concentration. Here, we study samples synthesized by a liquid-mix method at T = 800°C for the whole range of x, to determine the existence of the solid solution range and the presence of perovskite-type phase. Magnetic characterization was performed by electron spin resonance (ESR). Because of the non-magnetic character of Y,

ESR is an appropriate technique for this study. When magnetic rare-earth ions occupy A' sites, additional broadening mechanisms are generally present that prevents the observation of the ESR spectrum.

Ceramic samples of Ca_{1-x}Y_xMnO₃ with 0 ≤ x ≤ 1 were synthesized by liquid-mix method starting from stoichiometric proportions of Mn(CH₃CO₂)₂ · 4H₂O, Y₂O₃ and Ca(NO₃)₂ · 4H₂O, all analytical reagents whose purity had been checked previously. Final thermal treatment was done in oxygen (99.999% purity) atmosphere at 800°C during 20 h.

Powder X-ray diffraction patterns were taken at ambient temperature for Rietveld refinement using an X-Pert Philips PW3710 diffractometer with Cu graphite monochromatized radiation, with a 2θ step of 0.02°. Rietveld refinement was performed with the FullProf code [2]. ESR experiments were performed at 9.4 GHz with a Bruker ESP300

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spectrometer operating between 100 and 500 K. Magnetization was measured at $T < 300$ K with a SQUID magnetometer.

1. Results

XRD patterns for $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ show the samples are single phase with orthorhombic Pnma (perovskite-type structure), type O' for $0.2 < x < 1$ and type O for $x = 0.1$ [1] and an extension of the solid solution range is obtained for the liquid-mix method samples.

The behavior of cell parameters with x can be associated with a gradually more distorted lattice, as it is shown in Fig. 1. Important increase of the orthorhombicity $s = 2(a - c)/(a + c)$ is noticeable along the series (see inset Fig. 2). This distortion is compatible with a cooperative Jahn–Teller effect not being clear, for which x concentration starts, though it is clear for the high Y content samples. For the solid-state synthesized samples, where a segregation of phases is observed for $0.2 < x < 0.5$, $x = 0.5$ seems to be the inflection point [1].

For $x = 1$ the pure orthorhombic Y manganite is obtained. For $x = 0$ the sample shows to be a multiphase: CaMnO_3 , $\text{Ca}_2\text{Mn}_3\text{O}_8$, Ca_2MnO_4 , CaMn_3O_7 are present, these synthesis conditions are not adequate for this particular composition and then, this sample will not be further analyzed.

The ESR spectrum consists, in all cases, of a single line with a g -factor close to 2 (see Fig. 2). The resonance field, H_r , is constant with T above ≈ 150 K. This is an indication that all the samples are in the paramagnetic (PM) phase at $T > 150$ K and our analysis will be limited to this range of T .

An important parameter in ESR experiments is the line width. We have measured the peak-to-peak line width, ΔH_{pp} , for the derivative spectrum as a function of T and x . Fig. 2 shows the evolution of ΔH_{pp} with the Y concentration, x . We plotted the limit value, $\Delta H_{pp}(T \rightarrow \infty)$, of $\Delta H_{pp}(T)$ that is expected to be constant for T well above crystalline and magnetic transitions. We found a continuous increase of ΔH_{pp} with x . For $x > 0.8$ the spectrum is no longer observed. The ESR line intensity can be approached by $I \approx (\Delta H_{pp})^2 h_{pp}$, where h_{pp} is the peak-to-peak amplitude. Therefore, for similar values of I , small h_{pp} would be expected for broad lines as observed for high x values (see Fig. 2) and could prevent the spectrum observation for $x > 0.8$. Instead, for high x values DC magnetization was measured.

In Fig. 3 we plot the DC susceptibility, $\chi(T)$, for YMnO_3 that shows a typical antiferromagnetic (AF) behavior. A well-defined peak is found at $T_N = 44$ K. As is shown in the inset, the susceptibility can be described by a Curie–Weiss law $\chi(T) = C/(T - \theta)$ where the Curie–Weiss temperature $\theta = -48$ K $\approx -T_N$ and the

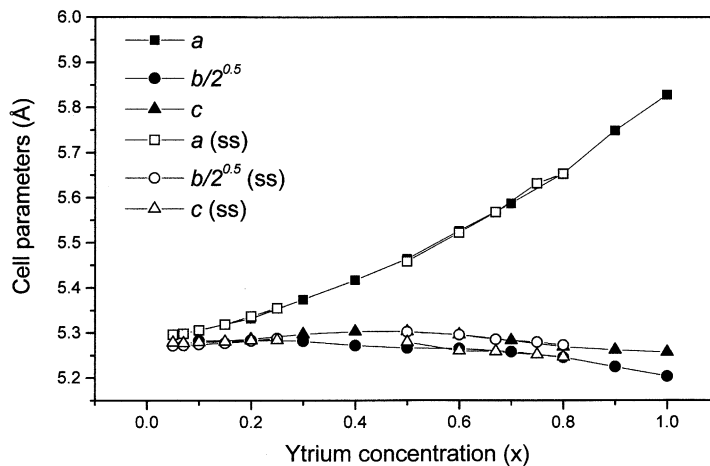


Fig. 1. Cell parameters as function of Y concentration x . Open symbols: solid state, solid symbols: liquid-mix samples.

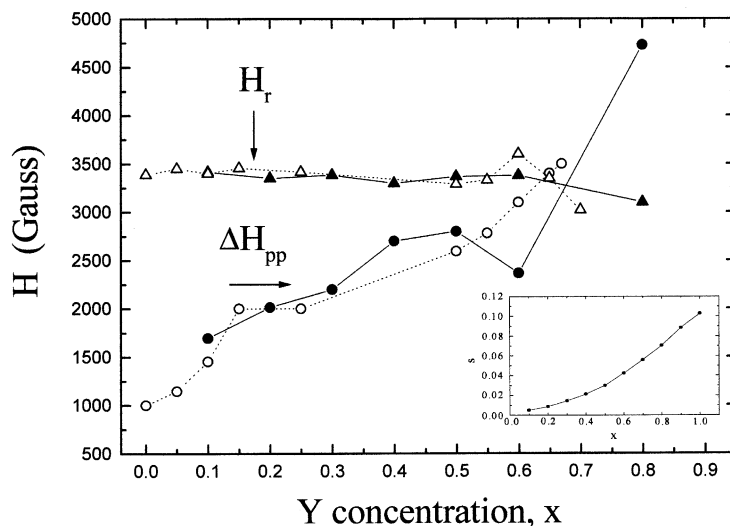


Fig. 2. ESR line width, ΔH_{pp} (circles) and resonance field, H_r (triangles) vs. Y concentration, x . Solid symbols, liquid-mix and open symbols, solid-state samples. Inset orthorhombicity s vs. x .

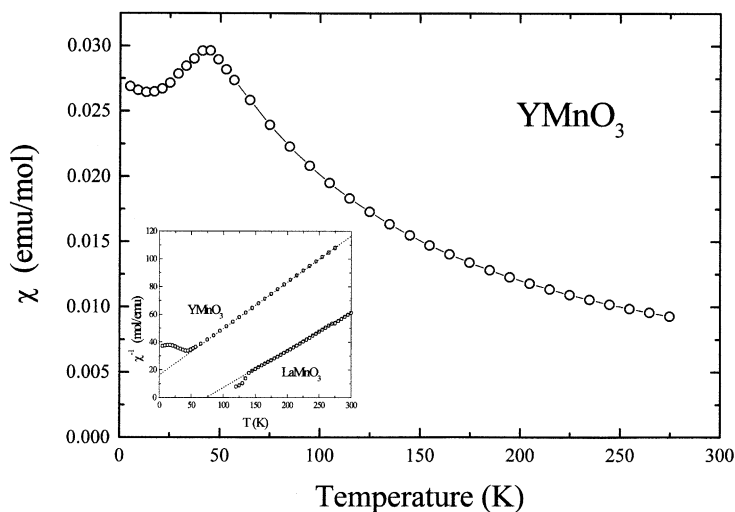


Fig. 3. T dependence of the DC susceptibility, $\chi(T)$ for orthorhombic $YMnO_3$. In the inset we plot the $\chi^{-1}(T)$ vs. T for $YMnO_3$ and $LaMnO_3$ (from Ref. [5]).

Curie-constant $C = 3.0 \text{ emu K/mol}$. This value of C corresponds to an effective magnetic moment, in the paramagnetic regime, $\mu_{\text{eff}} = 4.9\mu_B$ coincident with the expected value for Mn^{3+} (spin $S = 2$). The measured Θ and C parameters are in reasonable agreement with the findings in early experiments [3] indicating $\approx 100\%$ of orthorhombic phase.

2. Discussion

The x dependence of the cell parameters resembles that of the series $Ca_{1-x}Tb_xMnO_3$ [4], where the ionic radius r_{Tb} of the magnetic Tb^{3+} ion is slightly larger than that of the Y^{3+} , r_Y . In both the cases, the cell volume increases with x .

This shows that the differences in the Mn electronic state overcomes the difference between r_{Ca} and $r_{\text{Y}}, r_{\text{Tb}}$ ($r_{\text{Ca}} > r_{\text{Y}}, r_{\text{Tb}}$).

The line width increases with increasing x can be understood in terms of the progressive distortion of the crystalline structure. In a previous report [5] a relationship between ESR line width and orthorhombicity, s , was proposed for the LaMnO_{3-d} series. In the inset of Fig. 2 we show the dependence s vs. x for our samples. Comparison of the line width results for LaMnO_{3-d} and $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ indicate a proportionality between ΔH_{pp} and s . Notice, for example, that for $s \approx 0.03$ we have measured $\Delta H_{\text{pp}} \approx 3000$ G for LaMnO_3 . An equivalent distortion is obtained in $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ for $x = 0.5$ where $\Delta H_{\text{pp}} \approx 2800$ G.

In the inset of Fig. 3 we have compared susceptibility measurements for YMnO_3 with that of [5] for LaMnO_3 , both compounds with 100% of Mn^{3+} . LaMnO_3 is an antiferromagnet with competing FM and AF interactions that results in A-type (FM planes ordered AF) ordering at $T_{\text{N}} = 140$ K and a characteristic PM susceptibility which gives a positive $\theta < T_{\text{N}}$. For YMnO_3 we have not found evidences of A-type AF in accordance with [3] where G-type AF ordering was proposed for the orthorhombic species. Ordering of the Mn ions was observed [4] in TbMnO_3 , by neutron diffraction experiments below $T_{\text{N}} = 45$ K, also well below the ordering temperature of LaMnO_3 . An incommensurate magnetic phase develops at $T < T_{\text{N}}$ in TbMnO_3 . The influence of the magnetic character of Tb on the Mn magnetic ordering was not discussed.

In summary, despite of the low ionic radius of Y^{3+} and the important $\text{Y}^{3+}-\text{Ca}^{2+}$ mismatch, we have synthesized single phase samples of $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ for $0.1 \leq x \leq 1$.

For YMnO_3 , by the usual solid-state reaction method, the hexagonal phase is obtained [1]. The reported studies on orthorhombic YMnO_3 were performed on samples obtained by transformation of the normal hexagonal phase heated at 1000°C under 35–40 kbar. The liquid-mix method seems to be a very useful and simple alternative for this material that does not require special equipment.

The same ΔH_{pp} vs. x dependence was found for liquid-mix and solid-state samples. The ESR line width seems to be a physical parameter that closely follows the cell distortion in manganites. In this sense, our present results confirm the relationship ESR-line width/cell-distortion that was previously [5] found in the LaMnO_{3-d} series.

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