Synthesis, Microstructure and EPR of CaMnO₃ and EuₓCa₁₋ₓMnO₃ Manganite, Obtained by Coprecipitation

Maribel Santiago-Teodoro,[1]* Leticia Hernández-Cruz,[1] Herlinda Montiel-Sánchez,[2] Guillermo Álvarez-Lucio,[3] Marco Antonio Flores-González,[4] and Felipe Legorreta-García[1]

[1] AACTyM. Universidad Autónoma del Estado de Hidalgo, Carr. Pachuca-Tulancingo km 4.5, C. P. 42074, Pachuca Hgo., México. mar200878@hotmail.com

[2] Departamento de Tecnociencias, Centro de Ciencias Aplicadas y Desarrollo Tecnológico de la Universidad Nacional Autónoma de México, A.P. 70-186, México, D. F., C. P. 04510.

[3] Departamento de Física, Escuela Superior de Física y Matemáticas del Instituto Politécnico Nacional, Adolfo López Mateos, Edificio 9. Av. Instituto Politécnico Nacional s/n, San Pedro Zacatenco, México D. F., C. P. 07738.

[4] Laboratorio de Nanotecnología y Bioelectromagnetismo Aplicado. Universidad Politécnica de Pachuca, Pachuca-Cd. Sahagún, km 20, Ex-Hacienda de Santa Bárbara, 43830, Zempoala Hgo., México.

Abstract. The synthesis of $CaMnO_3$ and $Eu_xCa_{1-x}MnO_3$ obtained by coprecipitation method is showed. The synthesized samples were characterized by X-ray diffraction (XRD) and scanning electronic microscopy (SEM), the powders showed orthorhombic structure and *pnma* space group. When it was doped with Europium, their morphology tendency was spherical. Measurements were carried out on electron paramagnetic resonance (EPR) with constant frequency = 9.4 GHz (band X) and dc magnetic field (Hdc) 0-0.8 T, measurements were at 300 K and 77 K. EPR spectra showed significant differences between both samples, indicating that the substitution of divalent alkaline earth cations by trivalent rare earth ions, allowing the formation of a mixed valence state of manganese, Mn^{3+} and Mn^{4+}. A 77 K, the manganite of concentration $x = 0.30$ had a magnetic ordering, noted by the presence of hysteresis.

Key words: Synthesis, microstructure, manganite, coprecipitation, electronic paramagnetic resonance.

Resumen. Se presenta la síntesis de $CaMnO_3$ y $Eu_xCa_{1-x}MnO_3$, obtenidas por el método de coprecipitación. Las muestras sintetizadas fueron caracterizadas por difracción de rayos X (DRX) y microscopía electrónica de barrido (MEB); presentando los polvos una estructura ortorrómbica con grupo espacial pnma y morfologías con tendencia esférica cuando se dopó a la manganita con Europio. Se llevaron a cabo mediciones por resonancia paramagnética electrónica (RPE) para cada uno de los compuestos a una frecuencia constante de 9.4 GHz (banda X) y campo magnético dc (H_{dc}) de 0-0.8 T; las mediciones fueron a 300 y 77 K. Los espectros de RPE mostraron diferencias importantes entre ambas muestras, indicando que la sustitución de los cationes alcalinotérreos divalentes por iones de tierras raras trivalentes, permiten la formación de un estado de valencia mixta del manganeso, Mn^{3+} y Mn^{4+}. A 77 K la manganita de $x = 0.30$ presentó un ordenamiento magnético el cual fue observado por la presencia de histéresis.

Palabras clave: Síntesis, microestructura, manganita, coprecipitación, resonancia paramagnética electrónica.

Introduction

Synthesis and application of polycrystalline structures based on perovskite manganite has been the subject of intense research during the last decade due to their unique properties that make them attractive, both from the scientific value of understanding their properties, and technological significance of enhancing the performance of the existing materials [1]. In this sense, the manganites with the perovskite structure have the general formula $A_{1-x}B_xMnO_3$, where A is rare-earth element: La, Pr, Ce, Eu; and B is an alkaline earth metal: Ca, Sr, Ba and Pb [2-5], show the unusual property of being paramagnetic insulators at high temperatures and ferromagnetic metals at low temperatures [6, 7]. The substitution of trivalent ions instead of Ca in $CaMnO_3$, allows original magnetic and transport properties. On partial doping of the divalent alkaline earth cation by trivalent rare earth ion, leads to the formation of a mixed valence state of the Manganese, Mn^{3+} and Mn^{4+} to maintain the charge neutrality of the system. The Eu induces mixed valence manganese by means of a double-exchange interaction between ions Mn^{3+} and Mn^{4+} [8-11]. Eu ions enter the crystals being in trivalent

nonmagnetic state. The ionic radius of europium (0.947 Å) [12] is smaller in comparison with Ca ions (1.34 Å), inducing local distortions of Mn–O–Mn bonds in the system that cause random distribution of magnetic exchange interactions in magnitude and, probably, in sign. The double exchange process is the transfer of an electron from the Mn^{3+} to Mn^{4+}, through the intermediate oxygen. This is possible when the spins of both Mn ferromagnetic coupling [13].

The properties of materials depend strongly of composition, particularly, the effect of doping ion concentration, i.e. the rare earths content (Eu, Tb, Gd), so likewise depends greatly on the material preparation method, as these properties are directly related to the synthetic routes employed. For example, the structural defects often control many of the physical and chemical properties of solids, type and concentration of these defects can be determined by the synthetic routes used for their preparation [14, 15]. In this work, the synthesis is carried out by coprecipitation. This method is attractive due that is used extensively in powder preparation to improve the compositional homogeneity and, as a result, the microstructural homogeneity of the fired product. Coprecipitation is also more efficient

than a conventional solid-state reaction for the preparation of ceramic powders [16].

In this work, we present the synthesis, microstructure and EPR study of $CaMnO_3$ and $Eu_xCa_{1-x}MnO_3$ manganite obtained by coprecipitation. The magnetic interactions were carried out by EPR technique. This technique provides important information about the behavior of paramagnetic substances subject to an external magnetic field and they are made to influence electromagnetic radiation of appropriate frequency [17, 18]. The interaction that occurs between the magnetic field of radiation and magnetic moments of the chemical species in the presence of external magnetic field leads to transitions between different magnetic levels of the electrons.

Results and discussion

Figure 1 shows the powder X-ray diffraction patterns for $CaMnO_3$ and $Eu_xCa_{1-x}MnO_3$ (where x = 0.05 and 0.30). The powder X-ray diffraction patterns revealed that the samples show a main phase with orthorhombic perovskite structure (PDF-01-
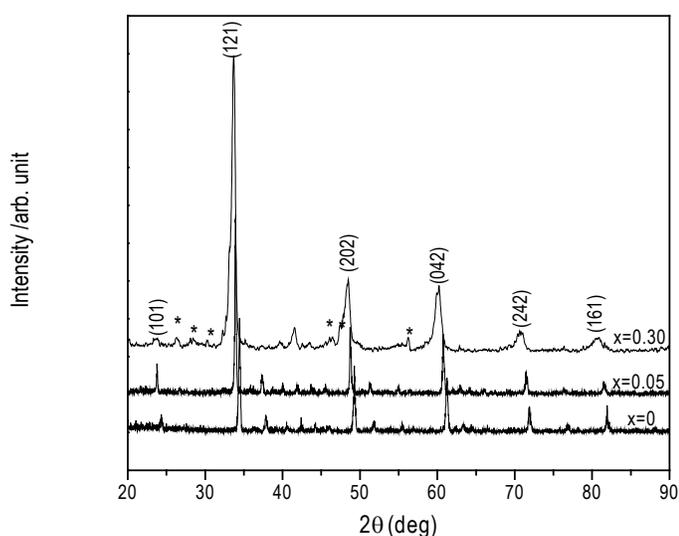
Table 1. Unit cell parameters and unit cell volume of $Eu_xCa_{1-x}MnO_3$ manganite.

Compound	a (Å)	b (Å)	c (Å)	V (Å^3)
$CaMnO_3$	5.2819	7.4547	5.2658	207.6635
$Eu_{0.05}Ca_{0.95}MnO_3$	5.2942	7.4676	5.2882	209.0747
$Eu_{0.30}Ca_{0.70}MnO_3$	5.3992	7.4991	5.3213	215.4605

089-0666) and a little of Mn_3O_4 (PDF-01-086-2337) as a low impurity. The Rietveld refinement XRD patters of all samples were carried out considering an orthorhombic structure (*Pnma* space group). Peaks are slightly displaced to the left with respect to $CaMnO_3$ peaks, which was attributed to substitution of Eu ions instead of Ca ions. However, this shift in the peaks is not only related to the substitution of Ca^{2+} ions for Eu^{3+} ions, but also due to the conversion of Mn^{4+} by Mn^{3+}. The evolution of the cell volume confirms that the doping elements have entered into the perovskite matrix and show that the volume increases with x concentration. In table 1 is showed that the lattice parameters increase with Eu substitution instead of Ca and the unit cell volume also shows a progressive expansion. This effect is easily understood since the Ca^{2+} substitution by Eu^{3+} leads to an increased concentration of Mn^{3+} (0.645 Å) in the structure, which is larger than Mn^{4+} (0.530) [12]. The introduction of Eu^{3+} atoms leads to the replacement of Mn^{4+} by Mn^{3+}. In fact, the Mn-O-Mn bond length an angle dominates the lattice parameters. Moreover, they are also strongly affected by the Eu doping level, thus resulting in different local lattice distortion.

On the other hand, the morphology and particle size result is important for studying the properties, due to the surface/volume ratio for small sizes and homogeneous surfaces. Manganite microstructures are shown in figure 2, where it can be seen the morphology of the samples which is a little different. When x = 0.05 a significant increase in particle size is observed, however, in x = 0.30 this morphology change, the particles are smaller compared with the other two samples and also homogeneity is better. This microstructure corresponds with the results of XRD for this sample, shown in figure 2c, which shows that the width of the pick is higher when x = 0.30, indicating that the particle size is smaller.

Figure 1. Powder X-ray diffraction pattern for $Eu_xCa_{1-x}MnO_3$ (where x = 0, 0.05, 0.30). PDF-01-089-0666. (*) Mn_3O_4-PDF-01-086-2337.

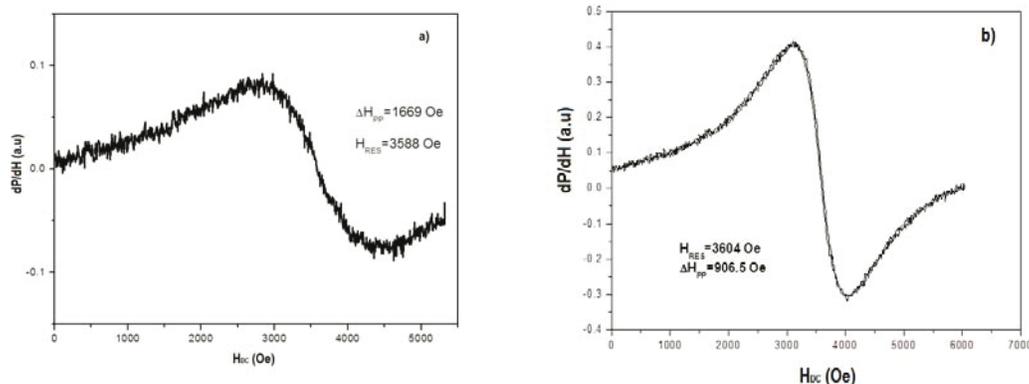**Figure 2.** Scanning electron micrographs of $Eu_xCa_{1-x}MnO_3$ manganite: a) x = 0, b) x = 0.05, c) x = 0.30.

Figure 3. EPR signals at 300 K, a) $CaMnO_3$, b) $Eu_{0.05}Ca_{0.95}MnO_3$ manganite.

Figure 3a shows the magnetic behavior of $CaMnO_3$ at 300 K. We observed a single broad symmetric Lorentzian line, corresponding to a paramagnetic absorption, due to strong dipolar interaction of manganese ions. Shows a linewidth of ΔH_{pp} = 1669 Oe, due to the high concentration of Mn^{4+} ions. When different cations are added to the structure, in this case europium atoms which replace the calcium, we can see that the line width is smaller as shown in figure 3b, corresponding to spectra of $Eu_{0.05}Ca_{0.95}MnO_3$ manganite. The substitution of trivalent ions instead of Ca leads the formation of a mixed valence state, Mn^{4+} and Mn^{3+}, inducing a double exchange (DE) interaction. However, the double exchange interaction is still small to cause a magnetic order at 300 K.

In order to observe the magnetic behavior at low temperature, the manganites were studied by EPR at 77 K. Figure 4 shows the comparison of $CaMnO_3$ and $Eu_{0.30}Ca_{0.70}MnO_3$ manganite at 300 K and 77 K, observing that the $CaMnO_3$ compound have a magnetic behavior of type paramagnetic in both temperatures (figure 4a), however, when europium is added at x = 0.30, at 300 K shows a paramagnetic absorption, but at 77 K, changes this resonance field, noting a hysteresis effect, probably due to a magnetic ordering due the presence of magnetization in material (Figure 4b).

Conclusions

Rare earth manganites $Eu_xCa_{1-x}MnO_3$ (x = 0, 0.05, 0.30) were synthesized by coprecipitation method using ethanol as reaction medium. Structural characterization showed samples with orthorhombic structure and *pnma* space group. Scanning electron microscopy results showed spherical morphology; however, when x = 0.30, particles size was smaller and more homogeneous than the other two samples. The $Eu_{0.05}Ca_{0.95}MnO_3$ and $Eu_{0.30}Ca_{0.70}MnO_3$ compounds had paramagnetic behavior to 300 K. EPR analysis showed that it is possible to substitute europium instead of the alkaline earth metal, inducing a double exchange interaction, observed by the decrease in line width of spectrum. A lower temperature, 77 K, the manganite of concentration x = 0.30 had a magnetic ordering, noted by the presence of hysteresis.

Experimental

$CaMnO_3$ and $Eu_xCa_{1-x}MnO_3$ powders were prepared by coprecipitation method reported previously for other kind of systems [19-22]. $Ca(NO_3)_2 \cdot 4H_2O$ (99%, Aldrich), $Mn(NO_3)_2 \cdot 6H_2O$

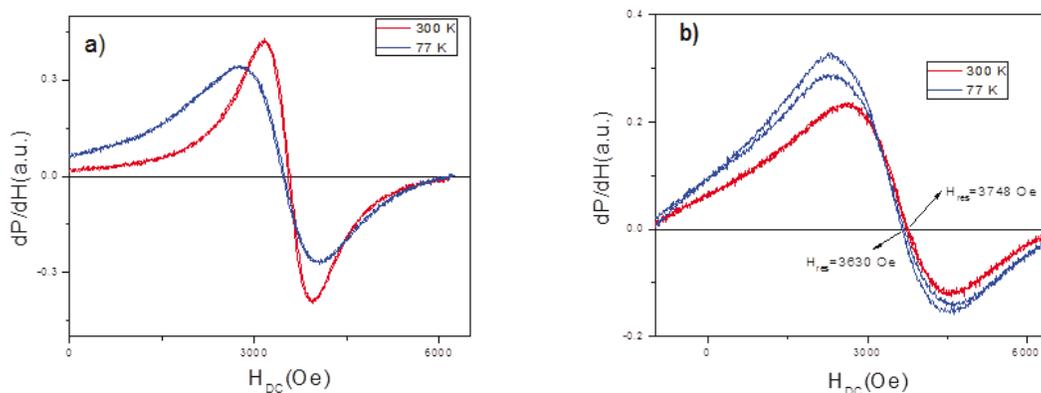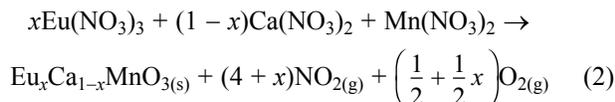**Figure 4.** EPR spectra of a) $CaMnO_3$ and b) $Eu_{0.30}Ca_{0.70}MnO_3$ manganite at 300 and 77 K.

(98%, Aldrich) and $Eu(NO_3)_3 \cdot 6H_2O$ (99%, Aldrich), were used as starting materials according to the following reactions:

For $CaMnO_3$;

$$Ca(NO_3)_2 + Mn(NO_3)_2 \rightarrow CaMnO_{3(s)} + 4NO_{2(g)} + 2O_{2(g)} \quad (1)$$

And for $Eu_xCa_{1-x}MnO_3$ (x = 0.05, 0.30);

$$x Eu(NO_3)_3 + (1 - x)Ca(NO_3)_2 + Mn(NO_3)_2 \rightarrow$$

$$Eu_xCa_{1-x}MnO_{3(s)} + (4 + x)NO_{2(g)} + \left(\frac{1}{2} + \frac{1}{2}x \right)O_{2(g)} \quad (2)$$

Precipitation was performed on a hot plate equipped with a temperature controller and a magnetic stirrer. Stoichiometric amounts of $Ca(NO_3)_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$ and $Eu(NO_3)_3 \cdot 6H_2O$ were separately dissolved in ethanol (99.9%, J. T. Baker) at 330 K with continuous stirring. After this, solutions were mixed. Then sodium hydroxide (97+%, Sigma-Aldrich) was added with constant stirring to the above solution mixture until pH >10 to ensure complete precipitation. After filtration, the precipitate was washed several times with ethanol and dried in an oven at 373 K. The oven dried-precursor was calcined at 973 K to get phase pure sample. The experiment was repeated several times to test reproducibility.

The phase purity and crystallinity of the powders were obtained by X-ray diffraction (XRD) on a SIEMENS X-Ray diffractometer model D5000 using Cu Kα radiation. The size, shape and distribution of the grains were examined using JE-OL-JSM 6300 scanning electron microscopy (SEM). To study the magnetic behavior was used X-band (9.4 GHz) with a dc magnetic fielding up to 6000 Gauss, at 300 K.

Acknowledgements

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