Study of the parameters that influence the synthesis of $Tb_x Ca_{1-x}MnO_3$ manganites by the chemical coprecipitation method

Dieuvins Valentin[1], Leticia E. Hernández Cruz[1], Herlinda Montiel Sanchez.[2], Guillermo Alvarez Lucio[3], Felipe Legorreta García [1]

[1] Área Académica de Ciencias de la Tierra y Materiales, Universidad Autónoma del Estado de Hidalgo, Carr. Pachuca - Tulancingo Km. 4.5. Mineral de la Reforma, Hgo., México. C.P. 42184, correo e: dieuvinsdcm@gmail.com.

[2] Dep. Tecnociencias, Centro de Ciencias Aplicadas y Desarrollo Tecnológico de la UNAM, Apartado Postal 70-186, México, D. F., C. P. 04510.

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

Abstract. This paper presents the effect of different parameters that affect the preparation of calcium and terbium manganite ($Tb_xCa_{1-x}MnO_3$) through the chemical coprecipitation method. The parameters studied were: the temperature of the heat treatment, the working pH and the dopant´s concentration values. Samples powders were characterized with X-ray diffraction (XRD). Then electron paramagnetic resonance (EPR) was performed. The results of XRD patterns revealed that the single purity phase was obtained at pH 10 with a concentration range from 0.35 to 0.45 at 1000º C. Finally, by EPR we were able to determine the change of the electronic environment of manganese due to the presence of terbium.

Keywords: manganites; perovskite; chemical coprecipitation method.

Introduction

In recent years, the substituted perovskite-type manganites have attracted the scientific community's attention (Tokura et al., 1996; Moritomo et al., 1996). These substitutions have opened doors to new technological advances such as magnetic recording media, credit cards, sensors, abrasives, permanent magnet and case for silicon chips. The manganites, discovered by Jonner and Van santen, are known to have manganese as the principal element, their chemical composition is: $A_x B_{1-x}MnO_3$, where usually A = Tb, La, Pr and B = Sr, Ca (Varshney & Kaurav, 2004). Interesting features of manganites are phase transformations caused by orbital and charge states determining a type of magnetic ordering. For example, charge-ordered compounds are antiferromagnetic insulators whereas charge disordered compounds are ferromagnetic metals (Tokura et al, 1999; Coey et al, 1999). An external magnetic field induces a transition from antiferromagnetic state to ferromagnetic one with the resistivity change by some orders of value (Tomioka et al, Tokura, 1995; Tokunaga et al, 1998). The double exchange interactions involving Mn^{3+} and Mn^{4+} ions give rise to ferromagnetism in the substituted manganites. The changes in the Mn-O-Mn bond angle, from structural distortion, are very crucial in determining the strength of the ferromagnetic interactions. Unlike other rare earth cations, Tb^{3+} ion being magnetically active is expected to cause an impact on the magnetization of $Tb_xCa_{1-x}MnO_3$. Terbium is one of the heavy rare earth elements that are paramagnetic at room temperature and above. At low temperatures its magnetic behavior is complex and becomes ferromagnetic. The ferromagnetic rare earth has magnetic moments per atom exceeding that of iron. Terbium is a very useful material, although an expensive one (Tahmineh et al, 2013).

It is worth nothing that the desired property of the material depends on its composition and the synthesis method used. Because of that there are several synthetic routes to achieve the production of these materials, such as thermal decomposition, hydrothermal, mechanosynthesis (Ivanov et al, 2000; Suryanarayana et al, 2001; Krivoroutchko et al, 2002), solid-state reaction (Chezhina et al, 2007; Arnache et al, 2008; Gutiérrez, 2005), vapor phase (Richerson, 1992), sol gel (Chezhina et al, 2006; Paucar & Gaviria, 1998; Malavasi et al, 1999), combustion and chemical coprecipitation (Komarneni, 2003; Cerón, 2011; Bolarín et al, 2007; Wang et al, 2006). Most of them show advantages and disadvantages, but the coprecipitation method due to its advantages as a fast, simple and most of all low cost process was chosen for this study which aims to identify the different parameters that are crucial for obtaining the pure single phase of $Tb_xCa_{1-x}MnO_3$, such as heat treatment temperature, the suitable work pH and finally the ideal value of x of calcium and terbium manganite concentration. Besides, according to the literature reviewed, there is no study concerning the calcium and terbium manganites by the chemical coprecipitation method whose achievement in a near future could allow the development of magnetic sensors.

Methodology or experimental section

The following commercial precursors with high purity were used for the synthesis, $Tb(NO_3)_3.5H_2O$ (99.9%), $Ca(NO_3)_3.4H_2O$ (99%), $Mn(NO_3)_2.H_2O$ (98%). All of them are of Aldrich brand. The polycrystalline ($Tb_xCa_{1-x}MnO_3$) composition was synthesized by the coprecitation chemistry method by mixing the nitrates in the required stoichiometry (x = 0.35, 0.40, 0.45, 0.65, 0.66) with the following equation after their precipitation.

$$xTb(NO_3)_3 + (1-x)Ca(NO_3)_2\, Mn(NO_3)_2 \rightarrow Tb_x\, Ca_{1-x}MnO_{3(s)} + (4+x)NO_{2(g)} + \left(\frac{1}{2} + \frac{1}{2}x\right) O_{2(g)} \quad (1)$$

The stoichiometric amounts of the salts precursors were individually dissolved as required in a predetermined amount of ethanol. Subsequently, all precursors were mixed to form a single solution, kept stirred during a period of time at 60° C until their complete dissolution. Afterwards, sodium hydroxide (NaOH, 99%, Aldrich) drops were added until pH (9 or 10). Good dispersion was achieved by doing an ultrasonic bath. Then, the compounds were dried at 100 ° C for 2 hours and then heat treatments were applied.

X-ray powder diffraction was performed by employing CuKa radiation (λ = 1.54 Å), with an Inel diffractometer with 2θ in a range of 20 to 80 ° C. Electron paramagnetic resonance (RPE), using the RE3X JES ESR spectrometer was employed to characterize the electronic magnetic properties of the samples. Thermogravitric analysis using the TGA/SDTA 851e Mettler Toled was used to corroborate the heat treatment temperature.

Results and discussion

The samples were characterized for their single-phase by X-ray diffraction. The samples did not show single-phase nature by varying the temperature of the heat treatment (800, 900, 1200° C) as shown in Fig. 1. But the diffraction patterns showed that the ideal temperature to work must be equal to or greater than 1000° C, where is easy to observe that after 1000° C the predominant formation of the distorted orthorhombic structure of the solid phase begins as confirmed by thermogravimetric characterization technique (which results are not shown in this paper).

Then, the pH variation of the nitrate solution was performed to find the suitable pH for obtaining the solid phase purity. The pH 9 was used with different concentrations (x=0.35, 0.66) and the results are shown in Fig. 2., indicates that at those concentrations and at that pH the single-phase nature and the distorted orthorhombic structure could not be reached alone without the presence of secondary phases.

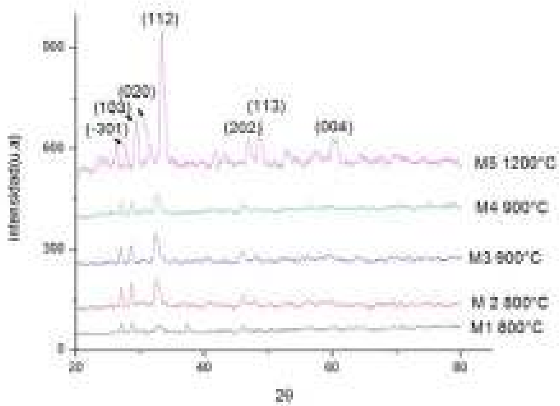

Fig. 1. XRD patterns of calcium and terbium manganite obtained by chemical coprecipitation method to different heat treatment temperatures (800, 900 and 1200 ° C).

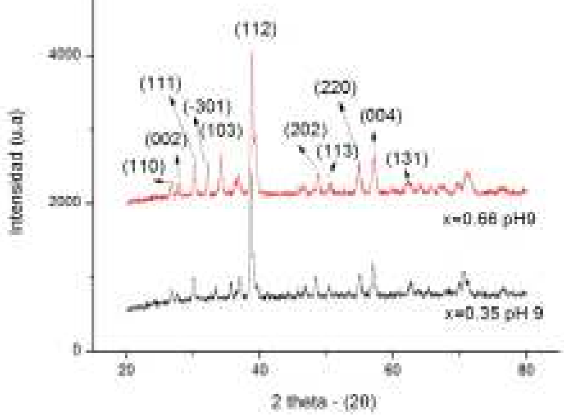

Fig. 2. XRD patterns of calcium and terbium manganite obtained by chemical coprecipitation method at pH = 9.

Once the suitable temperature was known, the pH 10 was chosen, with the variation of x aiming to find the ideal concentration in order to obtain the single-phase purity without the presence of secondary phase. Fig.3 shows the XRD of $Tb_xCa_{1-x}MnO_3$ samples. It revealed, for the first time, that it has a single perovskite-type phase with the distorted orthorhombic structure with space group pbnm with PDF file number (01-087-1092) under the following condition: terbium concentration should be in the range of (x = 0.35, 0.40, 0.45). As can be seen that the diffraction patterns peaks slightly change position to the left due to the modification of the crystal lattice because of the increasing Tb concentration. However, in Fig. 4 as can be seen that at a higher concentration of terbium (x = 0.65 and 0.65), it is more difficult to obtain the single-phase purity, PDF number (00-041-0313).

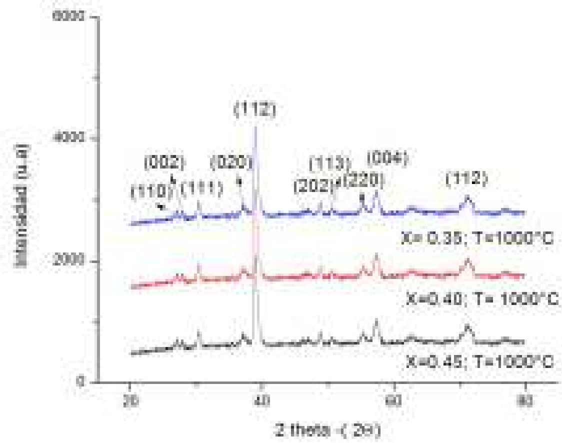

Fig. 3. XRD patterns of calcium and terbium manganite obtained by chemical coprecipitation method at different concentrations (0.35, 0.40 and 0.45).

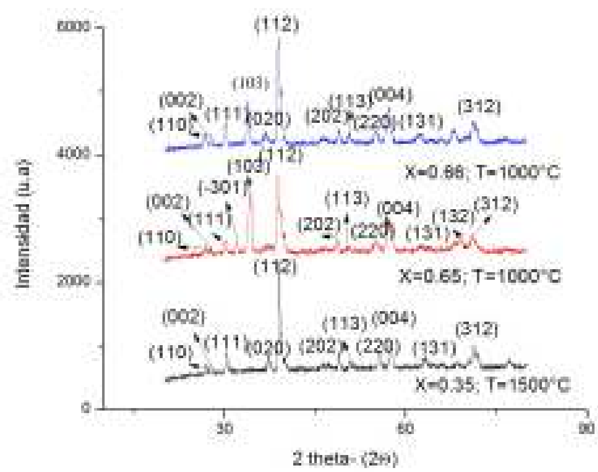

Fig. 4. XRD patterns of calcium and terbium manganite obtained by chemical coprecipitation method at different concentrations (x=0.65, 0.66) compared to the concentration of x = 0.35.

In order to confirm the validity of the pure single phase of the compounds, EPR were performed. Fig.5 and 6 show the Electron paramagnetic resonance patterns which determined the paramagnetic behavior due to the typical Mn^{2+} manganite calcium with X = 0.35 and x= 0.40 obtained at pH 10, where were revealed the resonance field of 3400 (fig.5) and 3200 Gauss (fig.6) associated to Mn^{2+}, the line width changes suggesting a change in magnetic interaction due to increment of dipole moments caused by the presence of the electronic environment of Tb. Where Tb induces an structural distortion as consequence one originates exchange interaction. In both spectra only one absorption due to the pure single phase of manganite is observed.

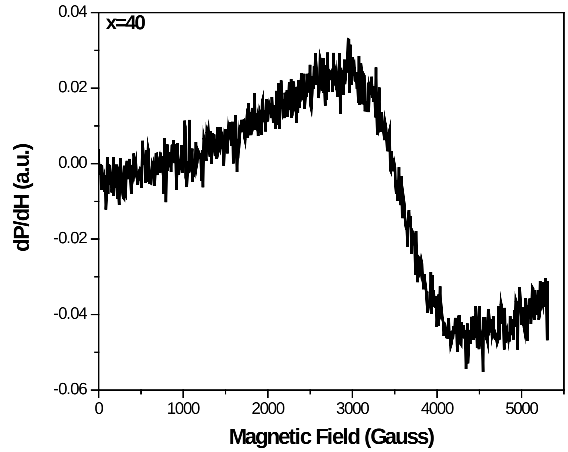

Fig. 6. EPR of calcium and terbium manganite obtained at pH = 10 for x = 0.40.

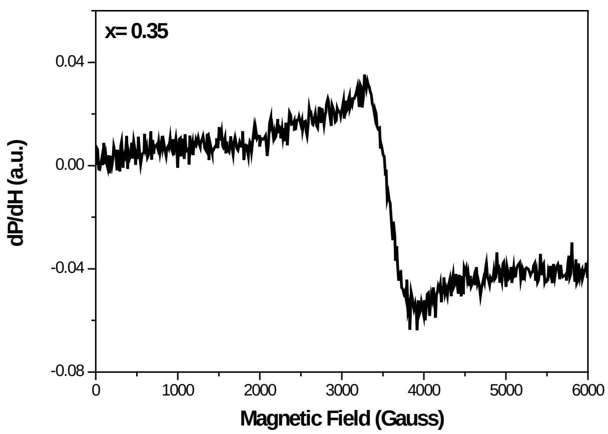

Fig. 5. EPR of calcium and terbium manganite at pH 10 for x=0.3

Summary

This paper presented a detailed study of different parameters for the calcium and terbium manganite. Polycrystalline samples of calcium and terbium manganites with a variation of different pH values (pH 9 and 10), different heat treatment temperature (800, 900, 1200 °C) and different values of x (x=0.35,0.40,0.45,0.65,0.66) were prepared by the chemical coprecipitation method, aiming to find the right parameters in order to obtain for the first time, the single phase purity of the samples. XRD studies indicated that the samples with a low concentration of Tb when x (x=0.35, 0.40 and 0.45) at pH 10 and sintered at 1000°C showed the orthorhombic symmetry expected as a structural perovkiste patterns. EPR confirmed the validity of the pure single phase by revealing the change in the manganese electronic environment due to the presence of terbium for x=0.35 and 0.40 at pH 10.

References

Arnache, O., Hoffmann, A. & Giratá, D. (2008). Síntesis y Caracterización Estructural y Magnética de Manganitas La2/3Ca1/3MnO3 dopadas con Fe. Revista Colombiana de Física, 40,34.

Bolarín, A. M., Sánchez F., Palomares, S., J. A. Aguilar, G., & Torres-Villaseñor. (2007). Synthesis of calcium doped lanthanum manganite by mechanosynthesis. Journals of Alloys and

Compounds, 43, 335-340.

Coey, J.M.D., Viret, M., and von Molna, S. (1999). Mixed valence manganites. Advances Physics, 48(2), 167.

Chezhina, N. V. & Fedorova, A. V. (2007). Estado de los átomos y las interacciones interatómicas en la perovskita a partir de óxidos: XXII.2 efecto de la relación de intercambio de radio del Ca-Sr en Manganitas lantano dopado con calcio y el estroncio, 807-811.

Chezhina, N. V. and Fedorova, A. V .(2006). Estados de los átomos y las interacciones interatómicas en Perovskita a partir de óxidos:XXI.1 Efecto de la naturaleza dopantes en las propiedades magnéticas de Manganitas de lantano, 860-863.

Cerón, M. L. E. (2011). Síntesis y caracterización de la manganita tipo $La_{1-X}Ca_XMnO_3$ efecto de la urea y el ácido cítrico como combustibles, Tesis-Universidad Autónoma de Hidalgo, 74,78-80.

Gutiérrez, M.P. (2005). Influencia del método de síntesis en la respuesta de resonancia paramagnética electrónica en manganitas, sociedad mexicana de ciencias y tecnología de superficies y materiales, superficies y vacío, 18,6-10.

Ivanov, E., and Surynarayana, C.(2000). Materials and process design through mechanochemical routes. Journal of Materials, Synthesis and Processing, 8(3-4), 235-244.

Komarneni, S. (2003). Nanophase materials by hydrothermal, microwavehydrothermal and microwave-solvothermal methods. Current Science, 85, 1730-1734.

Krivoroutchko, K. A., Kulik., Fadeeva, V.I. and Portnoy, V.K. (2002) Journal of Alloys and Compounds: 333, 225.

Moritomo, Y., Asamitsu, A., Kasai, M., Kumai, R., Kuwahara,H., & Tokura, Y., .(1996). Giant magnetoresistance of manganese oxides with a layered perovskite structure. Nature Publishing Group, 6570(380), 141-144.

Malavasi, L., Mozzati, M.C., Polizzi S., Azzoni, C.B., & Flor, G.(1999). Nanosized sodium-doped lanthanum manganites: Role of the synthetic route on their physical properties, 1-2.

Paucar, C., Gaviria, J. (1998). Preparación de manganitas con propiedades de magnetorresistencia, Congreso Nacional de Química UIS, Bucaramanga, Universidad Nacional de Colombia Sede Medellín. Facultad de Ciencias. Departamento de Química, 2-3.

Richerson W. D. (1992). Modern Ceramic Engineering.

Suryanarayana, C., Ivanov, E., & Boldyrev, V.V. (2001). The science and technology of mechanical alloying. Materials science and engeering.A. 304,151-158.

Tahmineh Sodaee, Ali Ghasemi & al. (2013). The role of terbium cation substitution on the magnetic properties of cobalt ferrite nanoparticles. Journal of magnetism and magnetic Materials, 330, 169-173.

Tokura, Y., & Tomioka, Y. (1999). Colossal magnetoresistive manganite. Journal of Magnetism and Magnetic Materials, 200(1-3)1-23.

Tokura, Y., Tomioka, Y.,. Kuwahara, H., A. Asamitsu, A. Moritomo, Y., & Kasai, M. (1996). Origins of Colossal magnetoresistance in perovskite-type manganese oxides. Journal of Applied Physics, 79(8),5288-5291.

Tomioka Y., Asamitsu, A., Moritomo., Kuwahara H., & Tokura, Y. (1995). Collapse of a charge – ordered state under a magnetic field in $Pr_{1/2}Sr_{1/2}MnO_3$. Physical Review Letter, 74, 5108.

Tokunaga, M., Miura, N., Tomioka, Y., & Tokura, Y. (1998). High-magnetic-field study of the phase transitions $R_{1-x}Ca_xMnO_3$(R=Pr, Nd). Physical Review B, 57(2), 5259.

Varshney, D., & Kaurav, N. (2004). Analysis of low temperature specific heat in the ferromagnetic state of the Ca-doped manganites. The European. Physical Journal., 37(3), 301-309.

Wang, S., Zhai Y., X. Li, Li Yan, & Wang. K. (2006). Coprecipitation Synthesis of MgO-Doped ZrO2 Nano Powder. Journals American Ceramics, 89, 3577-81.