PRODUCTION SYSTEM AND STRUCTURAL CHARACTERIZATION $CAMN_{1-x}TI_xO_3$ (WITH X = 0.0, 0.25, 0.5, 0.75 AND 1.0)

PRODUCCIÓN Y CARACTERIZACIÓN ESTRUCTURAL DEL SISTEMA $CAMN_{1-x}TI_xO_3$ (CON X=0.0, 0.25, 0.5, 0.75 Y 1.0)

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ABSTRACT

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In this work, we report the production of new composite perovskite manganite system $CaMn_{1-x}Ti_xO_3$ with doping x = 0.25, 0.5 and 0.75, reaction sintering method solid state. Structural characterization was performed using the technique of X-ray Diffraction (XRD) and the Rietveld method, obtaining a tetragonal structure, with Pnma spatial group (# 62) (a=5.3586Å y a=5.2997Å; b=7.5041Å y b=7.5526Å; c=5.3182Å y c=5.3278Å). In this paper takes the discussion on possible structural changes with changes in the system titanium $CaMn_{1-x}Ti_xO_3$.

Key words: Manganites, perovskite, structural analysis.

RESUMEN

En éste trabajo se reporta la producción del nuevo sistema tipo perovskita compuesta manganita $CaMn_{1-x}Ti_xO_3$ con dopajes x= 0.25, 0.5 y 0.75, sinterizado por el método estándar de reacción de estado sólido. La caracterización estructural se realizó a través de la técnica de Difracción de Rayos X (DRX) y el método de Refinamiento Rietveld, obteniendo una estructura tetragonal, con grupo espacial Pnma (#62) (a=5.3586Å y a=5.2997Å; b=7.5041Å y b=7.5526Å; c=5.3182Å y c=5.3278Å). En este paper se realiza la discusión sobre los posibles cambios estructurales con la variación del titanio en el sistema $CaMn_{1-x}Ti_xO_3$.

Palabras clave: Manganitas, perovskita, análisis estructural.

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I. Introduction

The manganites have been studied extensively in recent years, mainly due to the discovery advance property of colossal magneto resistance (CMR) and the discovery of high temperature superconductors (**Raveau *et al.*,** 1998; **Raveau *et al.*,** 2000). These also show extraordinary and varied transport properties (**Helmolt Von *et al.*,** 1993; **Kuwahara H. *et al.*,** 1998). Two types of behavior can be set to the manganites doped with holes, have CMR and electron-doped manganites showing CMR properties in a narrow range of composition and only for small cations, in this way substitution in Mn sites of these compounds doped generate great potential for inducing properties of the films **(Nagaev E. L. 2001).** As the metal insulator transition and CMR effects.

Recent studies (**Nagaev E. L.** 2001; **Raveau B *et al.*,** 2000). Show that partial substitution of pentavalent or hexavalent elements by Mn (IV) presenting induce electron doped double exchange phenomenon Mn^{3+} - O - Mn^{4+} (**Gil de Muro Izaskun *et al.*,** 2005) as it was shown for the system $CaMn_{1-x}Ln_xO_3$, besides that the manganite doped with electrons in the system $CaMn_{1-x}M_xO_{3-\delta}$ with M = Nb, Ta, W, Mo [2,8], almost semimetallic exhibit behavior over a wide range of composition below 30K and significant ferromagnetic interaction also demonstrated the existence of CMR at low temperatures in the range of 4-50K (**Ochoa Burgos R. *et al.*,** 2012; **Roa-Rojas *et al.*,** 2008). Thus, in the continuing search for understanding the inherent properties multiferroicidad and the discovery and production of new materials that exhibit this effect, generated the idea of producing the $CaMn_{1-x}Ti_xO_3$ new system, which has a complex perovskite structure $CaMn_{1-x}Ti_xO_3$. Initially system meets some of the requirements of the materials being multiferroics combining two simple perovskite dielectric $CaTiO_3$ magnetic $CaMnO_3$. This paper focuses primarily on the production and structural characterization $CaMn_{1-x}Ti_xO_3$ system by the Rietveld refinement technique (**Yung R. A.** 1993). In order to establish the structural characteristics of that system.

II. Experimental

The preparation process $CaMn_{1-x}Ti_xO_3$ samples (with x = 0.25, 0.5 and 0.75.) Was made by the standard method of solid state reaction (**Gil de Muro Izaskun *et al.*,** 2005) from the mixture of the precursor oxides of high purity titanium oxide TiO_2 (99.999%), manganese oxide MnO_2 (99.99%), calcium carbonate CaCO3 (**Raveau B. *et al.*,** 1998) (97.00%). These oxides were weighed in amounts calculated stoichometry, dried at a temperature of 120 ° C for 12 hours and macerated manually mixed in an agate mortar to obtain fine particles and to ensure a homogeneous mixture. These samples thus prepared were divided into two series preparing tablets with a diameter of 0.8cm and a thickness of 0.5 cm in a hydraulic press with pressure of 5 ton/cm^2 approximate which were subjected to two heat treatments calcined at a temperature of 900 °C for 36 hours and sintering at 1360 °C for 84 hours. Structural analysis was done by XRD technique using XPERT-PRO diffractometer PANalytical with λ = 1.54064 Å copper Kα line, step 2Theta: 0.001 Position with a Start position [° 2Th.] 20.0100 and End Position [° 2Th.] 79.9900. At diffractograms were asked to Rietveld software GSAS input crystallographic data were taken from references reported and these were adjusted PCW23 program, necessary for the software GSAS refinement. The experimental results presented correspond to the three values of doping respectively.

The figure 1. Displays the x-ray diffractogram theorists. Calculated at Spuds program and plotted on PCW theoretical modeled $CaMn_{1-x}Ti_xO_3$ system.

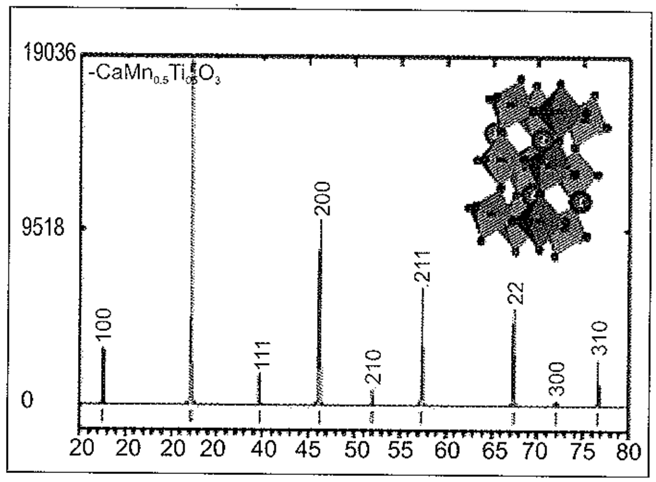

Figure 1. Theoretical Difragtograma of $Mn_{0.25}Ti_{0.75}O_3$.

III. Results and discussion

Figure 2 shows the experimental x-rays for the threedoped $CaMn_{1-x}Ti_xO_3$ system, clearly shows that the three belong to the same structural phase. Structural analysis of the samples was done using the Rietveld refinement technique (**Yung R. A.** 1993) through the GSAS program.

Comparing the diffraction patterns being theoretical and experimental adjustment necessary data manually until the best correlation between these using the PCW program, critical for the initiation process of refinement by Rietveld method. In Figure 3 are shown the data obtained by Rietveld refinement $CaMn_{1-x}Ti_xO_3$ system (with x = 0.75). The data marked with crosses represent the experimental result in continuous

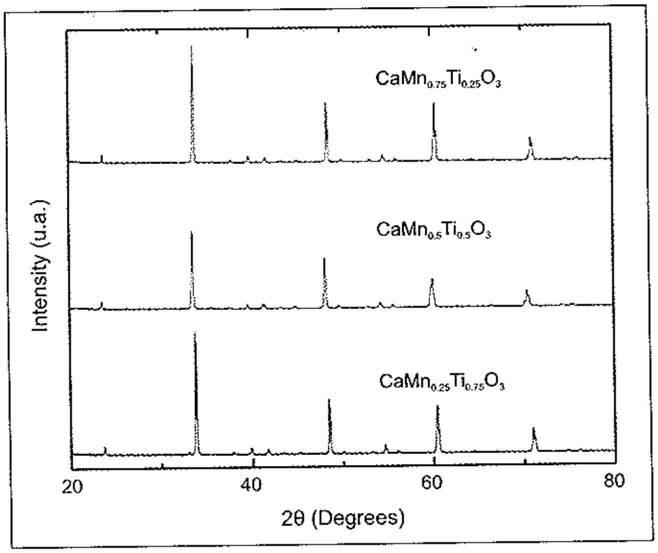

Figure 2. XRD diffractograms. Theoretical $CaMn_{1-x}Ti_xO_3$ system. For the three doped.

red line represents the theoretical diffractogram, green line and blue Background the difference between theoretical and experimental diffractograms. Also shown in Figure 4. Appropriate system-$CaMn_{1-x}Ti_xO_3$ (with x = 0.5) and Figures 5. $CaMn_{1-x}Ti_xO_3$ system (with x = 0.25.)

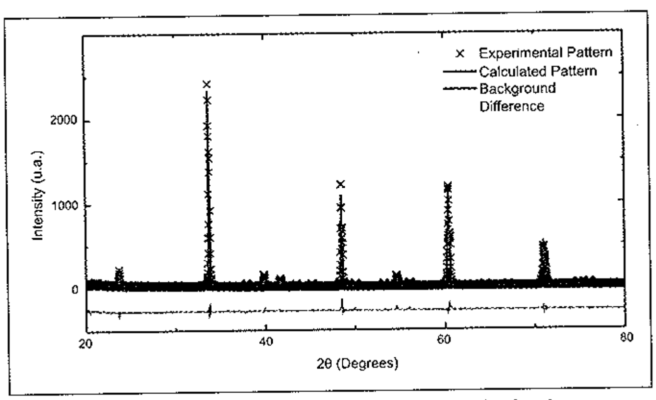

Figure 3. Rietveld refinement results obtained for the sample $CaMn_{0.25}Ti_{0.75}O_3$.

The refining process identified corresponding to a single phase$CaMn_{1-x}Ti_xO_3$ compound. Perovskite-type compound which crystallizes with orthorhombic structure with Pnma space group number 62.

In the Table 1, we identify the lattice parameters a, b, c structural angles α, β, γ; χ^2 R_{Bragg}, Rf^2, f.o factor and spatial positions x, y, z obtained by Rietveld refinement for the sample $CaMn_{0.25}Ti_{0.75}O_3$. In Figure 3, there is obtained quality refinement so that the calculated curve of peak intensities is set

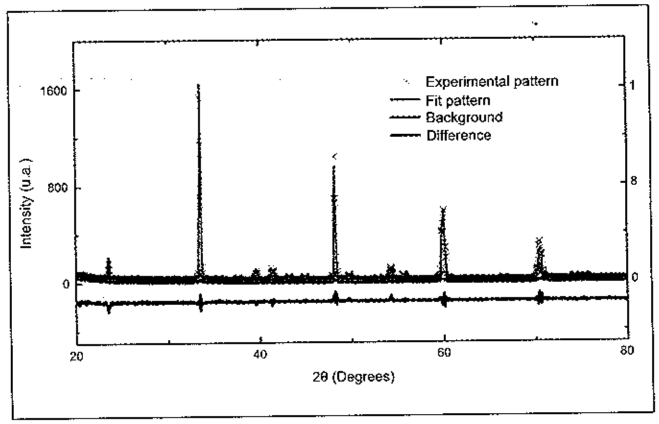

Figure 4. Rietveld refinement results obtained for the sample CaMn0.5Ti0.5O3.

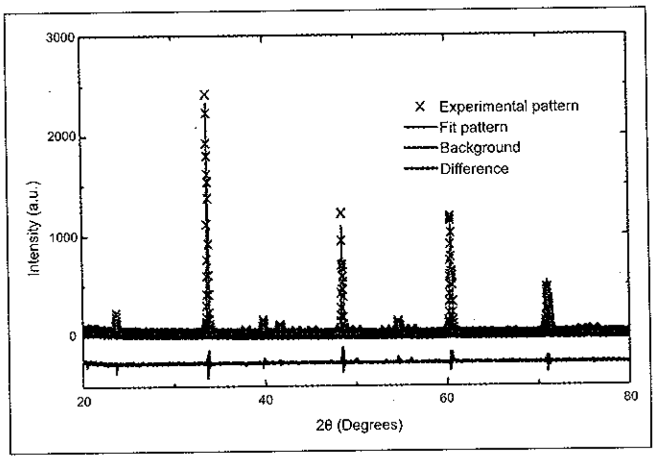

Figure 5. Rietveld refinement results obtained for the sample CaMn0.75Ti0.25O3

with good approximation to the observed intensities curve, obtained as a result of variance values: Rf^2= 12.72% and χ^2= 1.974 showing the reliability of the process, and it is observed that all the diffraction peaks correspond to a single phase of the compound and do not manifest secondary phases of impurities.

In the Table 2, we identify the lattice parameters a, b, c, structural angles α, β, γ; χ^2, R_{Bragg}, Rf^2, f.o factor and spatial positions x, y, z, obtained by Rietveld refinement for the sample $CaMn_{0.5}Ti_{0.5}O_3$. In Figure 4, like in figure 3 show the results of Rietveld refinement of variance values: Rf^2 = 14.79% and χ^2 = 1.435.

In the Table 3, we identify the network parameters a, b, c structural angles α, β, γ; χ^2, R_{Bragg}, Rf^2, f.o factor and spatial positions x, y, z, Rietveld structural refinement obtained for the sample $CaMn_{0.75}Ti_{0.25}O_3$. In Figure 5 in the same way as in Figures 3 and 4 shows the results of the Rietveld refine-

Table 1. Spatial positions and structural parameters obtained through the Rietveld refinement technique for the system $CaMn_{0.25}Ti_{0.75}O_3$

$CaMn_{0.25}Ti_{0.75}O_3$ Sample

	a = 5.3013 Å α = 90.00 χ^2= 1.974	b =7.5053 Å β = 90.00 R_{Bragg}=0 .1978	c = 5.3181 Å γ = 90.00 R_f^2= 0.1272	
	X	Y	Z	F.O.
Ca	0.0155	0.2500	1.0010	1.000
Mn	0.0000	0.0000	0.5000	0.250
Ti	0.0000	0.0000	0.5000	0.750
O	0.4778	0.2500	0.0282	1.000
O	0.2998	0.6273	0.7096	1.000

Table 2. Spatial positions and structural parameters obtained through the Rietveld refinement technique for $CaMn_{0.5}Ti_{0.5}O_3$ system.

$CaMn_{0.5}Ti_{0.5}O_3$ Sample

	a = 5.3586 Å α = 90.00 χ^2 = 1.435	b = 7.5526 Å β =90.00 R_{Bragg}=0.1978	c=5.3278 Å γ =90.00 R_f^2=0.1479	
	X	Y	Z	F. O.
Ca	0.0269	0.2500	0.9886	1.006
Mn	0.0000	0.0000	0.5000	0.497
Ti	0.0000	0.0000	0.5000	0.497
O	0.4831	0.2500	0.0451	0.959
O	0.2895	0.0475	0.7081	1.029

Table 3. Spatial positions and structural parameters obtained through the Rietveld refinement technique for the system $CaMn_{0.75}Ti_{0.25}O_3$

$CaMn_{0.75}Ti_{0.25}O_3$ Sample

	a = 5.2997 Å α = 90.00 χ^2 = 1.622	b = 7.5041 Å β = 90.00 R_{Bragg} = 0.1978	c = 5.3167 Å γ = 90.00 R_f^2=0.1080	
	X	Y	Z	F.O.
Ca	0.0139	0.2500	1.0038	1.028
Mn	0.0000	0.0000	0.5000	0.726
Ti	0.0000	0.0000	0.5000	0.250
O	0.4767	0.2500	0.0215	0.971
O	0.3004	0.0635	0.7034	0.993

ment with values results in disagreement: Rf^2 = 10.94% and χ^2 = 1.620 again showing the reliability of the process.

IV. Conclusions

We produced the Compound the $CaMn1_{-x}Ti_xO_3$ (with x = 0.25, 0.5 and 0.75) system. Through the technique of solid state reaction. This material has a double perovskite structure which corresponds to the number 62 group Pnma.

Rietveld refinement analysis established that $CaMn_{1-x}Ti_xO_3$ system presents a single phase orthorhombic structure with lattice parameters between a = 5.3586Å and a = 5.2997Å, b = 7.5041Å and b = 7.5526Å and c = 5.3278Å and c = 5.3182Å for stoichiometries (with x = 0.25, 0.5 and 0.75) respectively.

In the graphs shows refinement quality obtained so that the curves calculated from the peak intensities adjusted with good approximation to the observed intensities curve, showing that the reliability of the process and the presence of a single phase of the compound and confirming the absence of secondary phase impurities.

V. References

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