

In this work, the different aspects of the manganite with colossal magnetoresistance were studied, in an attempt to understand their physics. The physics properties of these systems are principally based on the double exchange interaction (*DE*) between  $\text{Mn}^{3+}$ -O- $\text{Mn}^{4+}$  and the influence of the cation substitutions that alter, for example, the Jahn-Teller distortion. Thus, the magnetic phase diagram is modified if changes are induced on the magnetic sublattice.

A thorough study was carried out to evaluate the changes on the Mn sublattice due to the partial substitution of this cation. This study involves two different systems: La-Sn-Mn-O and La-Cr-Mn-O.

Samples with an initial nominal composition  $\text{La}_{1-x}\text{Sn}_x\text{MnO}_{3+\delta}$  and  $\text{LaMn}_{1-x}\text{Sn}_x\text{O}_{3+\delta}$  were analyzed through the characterization by complementary experimental techniques. The main goals were to establish the structural site that Sn really occupied, its valence and how the magnetic properties were modified by the presence of close shell ion.

In order to evaluate the crystallographic site and the oxidation state of Sn, measurements of X-ray diffraction (XRD), scanning electron microscopy (SEM) with EDS, transmission electron microscopy (TEM) with EDS, Mössbauer spectroscopy (ME) and Redox titration were carried out. The results obtained showed that Sn always substitutes the Mn ion as  $\text{Sn}^{4+}$ . It was determined by these previously mentioned, that the real composition of the analyzed samples were  $\text{La}_{\frac{1-x}{1+x}}\text{Sn}_{\frac{x}{1+x}}\text{Mn}_{\frac{1}{1+x}}\text{O}_{3+\delta}$  and  $\text{LaMn}_{1-x}\text{Sn}_x\text{O}_{3+\delta}$ . Apart from this, it was only possible to obtain single phase materials when the temperature of synthesis was  $T_S \leq 750^\circ\text{C}$ . For higher temperatures of synthesis a multiphase one was obtained and the segregated phases depended on the initial composition of the studied samples.

Magnetic measurements as a function of temperature ( $T$ ) and applied magnetic field ( $H$ ) and electrical resistivity ( $\rho$ ) with and without  $H$  were made in order to understand the variation on the magnetic and electrical transport properties induced by the the substitution of a magnetic ion by a close shell one. It could be established that the observed properties were dependents on the La/(Sn+Mn) relationship. So, when the relationship -La/(Mn+Sn)- was equal to one, the samples showed the presence of superparamagnetic cluster size distribution, whose sizes depended on the Sn concentration.

The formation of these clusters could be due to the interruption of the Mn-O-Mn bonds with  $\text{Sn}^{4+}$  ion, being this the cause of the ferromagnetic region isolation.

As a consequence for all the Sn concentration, the samples were insulating and non-magnetoresistives, showing the impossibility for the electron to hop among Mn rich regions.

When the La/(Sn+Mn) relationship was less than one, the formed clusters could align easily among them when a magnetic field was present, showing a hysteresis loop characteristic of a ferromagnetic material. The electrical resistivity curves showed a strong

dependence on the applied magnetic field, indicating both the growth of ferromagnetic regions and their connection, allowing the hopping of the itinerant electrons, thus showing a magnetoresistance phenomenon. In this way, the cation vacancy effect -not generated by oxygen excess- becomes evident on the magnetic properties of the samples studied in this system.

In the La-Mn-Cr-O system, it was analyzed the influence of an ion with identical electronic structures of  $Mn^{4+}$  to the  $Cr^{3+}$  one. This mentioned ion has a similar ionic radius to the  $Mn^{3+}$ , but it is not a Jahn-Teller one, and the  $e_g$  and  $t_{2g}$  orbitals present a higher separation related to the  $Mn^{3+}$ .

Due to the existing discrepancies in the bibliography, the kind of interaction looked for, was to establish which was the one between the  $Cr^{3+}$  and the  $Mn^{3+}$  ions.

Thermogravimetric studies were made to determine the oxygen non-stoichiometry on the  $LaMn_{1-x}Cr_xO_{3+\delta}$  samples as a function of  $x$ . Due to the important non-stoichiometry shown, the system was divided in two parts in order to diminish the variables involved and to provide an easier interpretation of the results.

Following this idea, on the one hand, stoichiometric samples of  $LaMn_{1-x}Cr_xO_{3,00}$  nominal composition with  $x = 0, 0,05, 0,10, 0,15, 0,25, 0,33,$  and  $0,50$  were prepared to study both, the induced effect on the crystal structure by the decrease of the Jahn-Teller distortion and the differences between cations radii, and the  $Mn^{3+}$ -O- $Cr^{3+}$  interaction without the  $Mn^{4+}$  interference. On the other hand, samples of  $LaMn_{1-x}Cr_xO_{3+\delta}$  compositions with  $x = 0, 0,05, 0,10,$  and  $0,15$  were synthesized by thermal treatments under determined conditions obtained through the thermogravimetric curves. This part of the research was focused on the determination of the  $Mn^{4+}$  influence on the magnetic properties of Cr doped samples, and the structural differences owing to the substitution of two different non Jahn-Teller ions ( $Cr^{3+}$  and  $Mn^{4+}$ ).

Using experimental techniques such as, XRD, SEM with EDS, d.c. magnetization, a.c. susceptibility, neutron diffraction and electrical transport measurements with and without  $H$ , it was possible to determine the established interaction between  $Mn^{3+}$  and  $Cr^{3+}$  ions as a Ferromagnetic one and of the Double Exchange type. Nevertheless, the holes introduced by the presence of  $Cr^{3+}$  are less favourable to the itinerant electron hopping than the  $Mn^{4+}$  generated one. Basing it on all this, it was possible to establish that the  $Mn^{3+}$ -O- $Mn^{4+}$  *DE* interaction could be stronger than the  $Cr^{3+}$ -O- $Mn^{3+}$  one due to the energy difference between  $e_g$  levels. The existence of Magnetoresistance in the stoichiometric samples evidenced that the coupling is a *DE* interaction instead of a superexchange one. Even though, all the samples were strongly insulators.

The experimental results obtained about the kind of interaction were supported by those found by a theoretical model developed by the Solid Theory Group (CAB).

The magnetic behavior shown by these samples made clear the system complexity, due to the different interactions taking part resulting in the magnetic frustration and spin disorder as it can be observed in the development of the studied made.

From the point of view of the Jahn-Teller effect, an interesting result was the dependence on the cationic radius of the  $B$  site of the perovskite structure. The suppression of the cooperative effect appeared at, approximately the same  $\text{Mn}^{4+}$  concentration for all the analyzed samples, independent of the Cr content present in them.