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STRUCTURAL AND ELECTRONIC PROPERTIES OF $La_{2-x}Sr_xNiO_{4-\delta}$

G.Tavizón, E. Orgaz* and R. Escudero*

Facultad de Estudios Superiores Cuautitlán
*Instituto de Investigaciones en Materiales.
Universidad Nacional Autónoma de México. AP 70-360, CP 04510, México, D.F. México.

$La_{2-x}Sr_xNiO_{4-\delta}$ solid solution is isostructural to the superconducting family $La_{2-x}Sr_xCuO_{4-\delta}$. In this work we present recent structural and electronic studies for the $La_{2-x}Sr_xNiO_{4-\delta}$, $(0 \leq X \leq 1.2)$ series. Our results show that the electrical resistivity varies with the Sr content, exhibiting a maximum at $x = 0.30$, which is on the boundary of the maximum value of the extreme elongation of the c lattice parameter $(x = 0.45)$. We correlated this variation of the c parameter with the change of the electrical properties in terms of a Jahn-Teller distortion.

1 Introduction

The K_2NiF_4 structures La-Ni-O and La-Cu-O are systems with stoichiometry sensitive properties. Recently, with the discovery of the superconducting cuprates, their properties have been studied and compared. It is worth mentioning that the existing similarities between both compounds, induce to investigate if the superconducting behavior can also be found or not in these nickel compounds. $La_{2-x}Sr_xNiO_{4-\delta}$ solid solution gives us the excellent opportunity to investigate and compare much of the physical properties that occur between this compound and the same family of the corresponding cuprates. The compound La_2NiO_4, is formed by intergrowth of rock salt $La-O$ structure and the cubic perovskite unit $LaNiO_3$. This compound has been under investigation for the last 20 years[1]. The electronic and magnetic properties are strongly influenced by the two-dimensional arrangement of $Ni-O_2$ planes, as occur in all the members of the K_2NiF_4 family. One of the central problems of this nickel based compound seems to be directed to explain the complex mechanism involved in the metal - semiconductor transition, which may be associated to a Jahn-Teller distortion.

2 Experimental

The $La_{2-x}Sr_xNiO_{4-\delta}$ solid solution was prepared by pyrolisis of the coprecipitated metallic oxalates. La_2O_3, NiO and $SrCO_3$ were used to prepare the corresponding nitrates. The oxalates were obtained from a stoichiometric mixture of titrated metallic nitrates.

This mixture was fired in air at 900 ^0C for about 12 h. In the final step, pellets were formed and fired at 1350 ^0C for a period of 18 h. and then quenched to room temperature. The samples showed coloration ranking from black to black-redish, depending on the Sr content. Two sets of samples were prepared, one annealed in air, and the other one in oxygen atmosphere, both for about 15 h. at 800 ^0C. X-ray diffractograms showed pure phases. It is important to note that our samples show long term stability. After one month, these samples show reproducible electric and structural properties. $Ni(III)$ and the oxygen content were determined by iodometric titration. In all the samples discussed here the oxygen non-stoichiometry δ is close to zero. Electrical resistivity measurements were made using the standard four point technique.

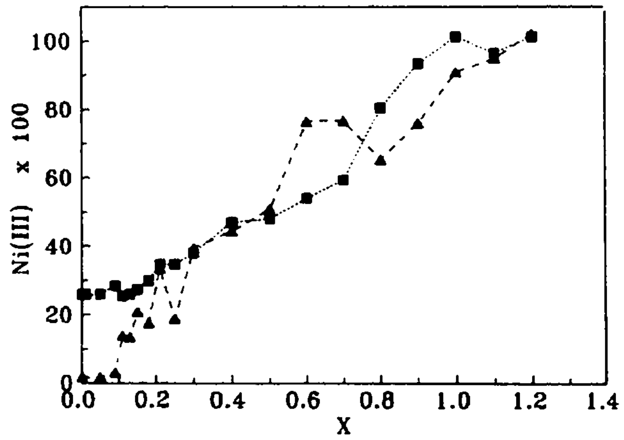

Figure 1: Ni(III) fraction of the total nickel as a function of Sr content. Squares (triangles) represent oxygen (air) annealed samples.

3 Results and Discussion

The samples showed tetragonal symmetry for the entire range of Sr content. No evidence of 5a x 5a tetragonal supercell reflections were observed[2]. The behavior of a and c parameters is in agreement with earlier studies[3,4]. It is worth note that this behavior is not monotonic in x and is in opposition to the Vegard's rule. Similar observations were found for the oxygen and air annealed samples. Figure 1 shows the fraction of the nickel in the 3^+ state with respect to the total nickel in $La_{2-x}Sr_xNiO_{4-\delta}$, as a function of Sr content. It seems that the formal 3^+ charge state of Ni is stabilized. In figure 2 we show the values of the resistance at 200 K (normalized to the value at 250 K) as a function of the Sr content. It is clear that a maximum is present at $x \approx 0.30$. This property shows the same trend as the c/a tetragonal ratio.

Recent Mössbauer spectroscopy results[5], in addition to our observations, point to a cooperative Jahn-Teller tetragonal distortion mechanism present in the $x \leq 0.5$ range. A clear transition from the low $(t_{2g})^6(d_{z^2})^1$ ($x \leq 0.5$) to the high $(t_{2g})^5(e_g)^2$ ($x > 0.5$) spin state of Ni^{3+} supports this assertion. The electron in the d_{z^2} orbital (Ni^{3+}) is localized, while in the high spin configuration one electron is in d_{z^2} and the other is now in $d_{x^2-y^2}$ which is itinerant. This new electron configuration is responsible of the change in the transport properties as we showed in figure 2. We conclude that the main electronic and structural properties of these materials are dominated by the presence of $Ni(III)$.

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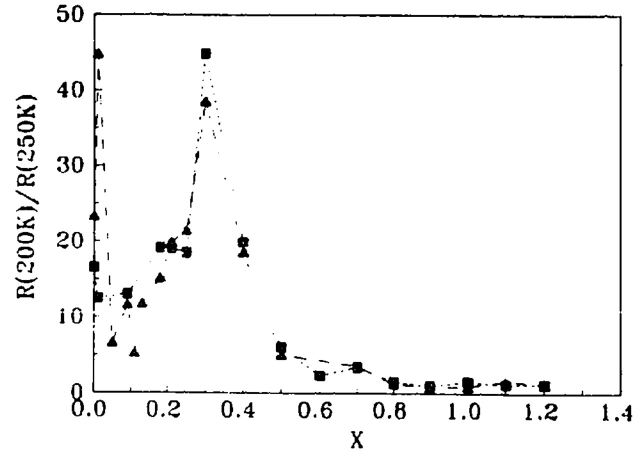

Figure 2: Resistance at 200 K normalized at 250 K as a function of the Sr content. Squares (triangles) represent oxygen (air) annealed samples. Note the maximum value of resistance at $x \approx 0.3$ and the monotonic decrease as the Sr content increases.