



# Investigation on the structural and electrical properties of $\text{NdSrNi}_{1-x}\text{Cr}_x\text{O}_{4+\delta}$ ( $0.1 \leq x \leq 0.9$ ) system

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## ABSTRACT

The phases  $\text{NdSrNi}_{1-x}\text{Cr}_x\text{O}_{4+\delta}$  ( $0.1 \leq x \leq 0.9$ ) have been synthesized by modified sol-gel method and subsequent annealing at 1250 °C in 1 atm of flowing argon. X-ray diffraction (XRD) analysis and electrical resistivity have been measured at room temperature. Rietveld refinement shows that all compositions with  $x > 0.1$  were found to crystallize in the tetragonal  $\text{K}_2\text{NiF}_4$  type structure in the space group  $I4/mmm$ , while for  $x = 0.1$ , a mixture of two phases with the tetragonal space group  $I4/mmm$  and the orthorhombic space group  $Fmmm$ . Variations of  $a$  and  $c$  parameters show a complex behavior with increasing chromium content. It was established that compounds with chromium content less than  $x \leq 0.5$  are oxygen-deficient, while for  $x > 0.5$  the sample are oxygen-overstoichiometric. The  $\text{NdSrNi}_{0.5}\text{Cr}_{0.5}\text{O}_{4+\delta}$  compound exhibits semiconductive behavior and the electrical transport mechanism agrees with the non-adiabatic small polaron hopping model in the temperature ranges 298–493, 493–573 and 573–703 K separately.

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## 1. Introduction

The mixed ionic and electronic conducting oxides (MIEC) have attracted interest for use in a wide range of applications such as cathodes for solid oxide fuel cell (SOFC), electrodes for electrically driven ceramic oxygen generators (COG) or dense ceramic membranes for pressure driven oxygen separators [1] such as the mixed-conducting complex oxide  $\text{La}_2\text{NiO}_{4+\delta}$  prepared by complex sol-gel method [2]. The  $\text{Ln}_2\text{NiO}_{4+\delta}$  oxides can be good candidates for these types of applications because of the high level of their electronic and ionic conductivities. They are good electronic conductors due to the mixed ( $\text{Ni}^{+3}/\text{Ni}^{+2}$ ) valence of the nickel cations [1]. Oxygen ionic conduction in  $\text{K}_2\text{NiF}_4$ -type compounds may occur via a vacancy mechanism in the perovskite layers and via diffusion of oxygen interstitials in the rock-salt-type layers [3]. On the other hand, many extensive investigations have been carried out on the structural, electrical and magnetic properties on the Sr-doped rare earth nickelates, in particular, the  $\text{Ni}^{II}/\text{Ni}^{III}$   $\text{Nd}_{2-x}\text{Sr}_x\text{NiO}_4$  [4,5,9,10] and  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  compounds [6–8]. All the iodometric and thermogravimetric analysis results established on these series of compounds illustrated that samples with low strontium contents tend to accommodate excess oxygen, while those with high strontium contents are slightly oxygen deficient. Naturally this is to be expected, as the greater the value

of  $x$ , the greater the proportion of  $\text{Ni}^{II}$  which must be oxidized to  $\text{Ni}^{III}$  in the sample in order to preserve overall charge neutrality if the oxygen stoichiometry is maintained [11].

It has also been reported in previous works that the  $\text{Ln}_2(\text{M,Ni})\text{O}_4$  and  $\text{LnSr}(\text{M,Ni})\text{O}_4$  systems (where  $M = \text{Co, Fe, Cr, Cu}$ ) show complete miscibility both at room and at higher temperature [12–21]. The Goodenough [22] rules predict that if two cation species, B and B', with appropriate electron configurations (for example  $d^3$  and  $d^5$  or  $d^5$  and  $d^8$ ) are present in an insulating oxide, then the superexchange interaction between them can be ferromagnetic, provided that the B–O–B' bond angle is close to 180°. According to the model developed by Tan et al. [23], the degree of localization of the transition-metal  $d$  electrons depends on the overlap integrals with the neighboring transition-metal cation's  $d$  states. Moreover, the simultaneous presence of several transition elements in oxide diluted solid solutions usually results in rich properties, such as electrical and magnetic ones. In the study of  $\text{LaSrNi}_{1-x}\text{Cr}_x\text{O}_{4+\delta}$  [16], synthesized under argon atmosphere, Millburn and Rosseinsky have well described the effect of  $\text{Cr}^{3+}$  substitution on the crystal structure, magnetism and chemical reactivity in  $\text{LaSrNiO}_4$ , as an important member of the  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4 \pm \delta}$  solid solutions [24]. They showed that the samples with high chromium content are overstoichiometric in oxygen and the small amounts of excess oxygen may be attributed to the partial oxidation of  $\text{Cr}^{III}$  to  $\text{Cr}^{IV}$ .

In order to get more insight of the structural and electrical properties in this family of compounds, we have synthesized and characterized new solid solutions by substituting both strontium

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and chromium into the parent compound  $\text{Nd}_2\text{NiO}_4$ . We describe below our attempts to synthesize this series of compounds, and the subsequent characterization of our reaction products by resistivity and X-ray diffraction techniques. Our results are compared with those obtained on related papers in the literature [16].

## 2. Material and methods

The solid solutions of the  $\text{NdSrNi}_{1-x}\text{Cr}_x\text{O}_{4+\delta}$  system were prepared for all compositions  $x=0.1; 0.3; 0.5; 0.7$  and  $0.9$  using sol–gel method, stoichiometric quantities of  $\text{Nd}_2\text{O}_3$  (99.99%, Aldrich, calcined in air at  $800^\circ\text{C}$  to remove adsorbed water and carbon dioxide),  $\text{SrCO}_3$  (99.99%, Aldrich),  $\text{NiO}$  (99.99%, Aldrich) and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99.99%, Aldrich), as appropriate, were dissolved in a minimum quantity, typically 150 ml, of a 1:1 solution of analar 6 M nitric acid and distilled water. Then, 5 ml of ethylene glycol (99.99%, Aldrich) and one equivalent of citric acid per mole of  $\text{M}^{3+}$  cation (99.99%, Aldrich) were added and the solution was heated at  $150^\circ\text{C}$  on a hot plate with constant stirring for approximately 3 h. The pale green gel thus formed was decomposed by further heating at  $300^\circ\text{C}$  for approximately 24 h. The resulting fine brown powder was ground, and then returned to the furnace in air at  $800^\circ\text{C}$  for between 24 and 48 h. The obtained powder was pressed into 13 mm diameter at 10 ton. The pellets were annealed in a tube furnace at  $1250^\circ\text{C}$  in 1 atm of flowing argon (dried by bubbling through concentrated sulfuric acid) for 6–8 days with several intermittent grindings. The black polycrystalline solid products were allowed to cool under the argon flow at the rate of the furnace, typically 12 h, before being removed.

The X-ray powder diffraction was carried out using the X'Pert Diffractometer operating with  $\text{Cu } K\alpha_1/K\alpha_2$  radiation. Data were collected at each  $0.0167^\circ$  step width for 30 s over a  $2\theta$  range from  $15^\circ$  to  $119^\circ$ . Rietveld refinements of the crystal structure were performed using the FULLPROF program [25]. The line shape of the diffraction peaks was generated by a pseudo-Voigt function. The background was chosen by interpolation between selected points in regions devoid of Bragg reflections. In the final run the following parameters were refined: zero point, U, V, W, background points, pseudo-Voigt, scale factor, unit cell parameters, positional parameters, isotropic thermal factors and preferred orientation parameters.

The oxygen content of all the compositions system has been determined indirectly at room temperature after calculation of the valence average of the transition metal ions obtained by iodometric titration under flowing nitrogen gas taking into account that  $\text{Ni}^{3+}$  and  $\text{Cr}^{4+}$  can be present in the sample with  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$ . In fact, about 100 mg of sample was dissolved in a solution of 6 M hydrochloric acid in the presence an excess of KI, leading to reduction of tri- and tetra-metal transition ions and formation of iodine that was titrated with  $\text{Na}_2\text{S}_2\text{O}_3$  solution using starch as indicator. Sodium thiosulfate solution was standardized using pure copper wire [26].

The Electrical direct current resistivity measurements were carried out on sintered pellets using a Lucas Labs 302 four point probe with a Keithley 2400 digital. Source Meter (Keithley Instruments, Inc., Cleveland, Ohio). Measurements were performed at room temperature for all compositions. Impedance spectroscopy measurements of the sample with  $x=0.5$  only, using a sintered polycrystalline disk form, have been carried out in the temperature range 298–682 K. Electrical contacts are made by silver paste. The spectroscopy analyser used is a HP analyser for solid state. The frequency range is from 100 Hz to 10 MHz. Impedance diagrams were analyzed and fitted using the Z view

software [27]. The resistance  $R$  was derived from the low-frequency intersection of a semicircle fit on the complex impedance plane with the real complex axis. The conductivity was calculated using the following relation:

$$\sigma = d/RS[\Omega^{-1} \cdot \text{m}^{-1}]$$

## 3. Results and discussion

### 3.1. Structural study and oxygen stoichiometry analysis

The purity of the samples synthesized  $\text{NdSrNi}_{1-x}\text{Cr}_x\text{O}_{4+\delta}$  ( $0.1 \leq x \leq 0.9$ ) was confirmed by X-ray powder diffraction measurements, which revealed no product impurities or starting materials.

In order to study the variation in the oxygen stoichiometry as function of chromium content we have carried out iodometric titration using  $\text{Na}_2\text{S}_2\text{O}_3$  standard solution. The oxygen nonstoichiometry ( $\delta$ ) is directly correlated to the  $\text{Ni}^{3+}$  and  $\text{Cr}^{4+}$  content according to the formulation  $\text{NdSr}(\text{Ni}_{1-\tau}^{3+} \text{Ni}_\tau^{2+})_{1-x}(\text{Cr}_{1-\tau}^{4+} \text{Cr}_\tau^{3+})_x\text{O}_{4+\delta}$ , with  $\delta=(x-\tau)/2$ . The content  $(1-\tau)$  of the average of cations transition metals  $\text{Ni}^{3+}$  and  $\text{Cr}^{4+}$  was then determined by iodometric titration.  $\text{I}^-$  anions reduce  $\text{Ni}^{3+}$  cations into  $\text{Ni}^{2+}$  and  $\text{Cr}^{4+}$  cations into  $\text{Cr}^{3+}$ . The titration of the resulting  $\text{I}_2$  by a solution of  $\text{Na}_2\text{S}_2\text{O}_3$  sodium thiosulfate leads to determine ( $\tau$ ) and therefore ( $\delta$ ) whose values are reported in Table 1. The obtained results indicate that compounds with chromium content less than ( $x \leq 0.5$ ) are oxygen-deficient, while for  $x > 0.5$  the sample are oxygen-overstoichiometric.

The crystal structures of samples with  $x > 0.1$  were refined, from powder X-ray data, in the  $I4/mmm$  tetragonal space group; this is the same space group adopted by the parent compounds  $\text{NdSrNiO}_4$  and  $\text{NdSrCrO}_4$  [28,29]. The isotropic temperature factors for the oxygen sites could not be refined and so the values were fixed, at  $0.02 \text{ \AA}^2$ , in the final refinements. The positional and thermal parameters obtained are shown in Table 2. We have chosen the X-ray diffraction profiles of the composition  $\text{NdSrNi}_{0.5}\text{Cr}_{0.5}\text{O}_{4+\delta}$  to be displayed in Fig. 1. The X-ray pattern of the  $x=0.1$  sample showed a shift of some Bragg reflections that was indicative of a unit cell of lower symmetry. Two distortions of the  $I4/mmm$   $\text{K}_2\text{NiF}_4$  aristotype cell to orthorhombic symmetry are known,  $Fmmm$  and  $I mmm$ , depending on which of the  $\langle 100 \rangle$  and  $\langle 110 \rangle$  sets of mirror planes and twofold axes are lost together with the fourfold axis when the symmetry is lowered. Inspection of the X-ray pattern indicates that the  $h0l$  reflections remain unsplit. Such an observation suggested refinement of the data in the  $Fmmm$  space group with unit cell related to the tetragonal structure ( $I4/mmm$ ) by  $a_o \approx b_o \approx \sqrt{2}a_t$  and  $c_o \approx c_t$ . However, Rietveld refinement of the powder X-ray data for the  $x=0.1$  sample in  $Fmmm$  produced an unsatisfactory fit. Refinement was then attempted with a two-phase model, in which an undistorted  $I4/mmm$  structure is introduced as a second phase. Such an attempt has been encountered in the study of

**Table 1**

Oxygen content and average transition metal oxidation state valence for all compositions.

Chromium content ( $x$ )	Oxygen content	Average transition metal oxidation state
0.1	3.85	2.70
0.3	3.95	2.90
0.5	3.98	2.96
0.7	4.02	3.04
0.9	4.03	3.06

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