A STUDY OF NONSTOICHIOMETRIC OXIDES IN THE Ln-Ni-O (Ln=La, Pr, Nd) SYSTEM

Sergiy Nedilko[a], Olexander Dziazko[a], Vadym Kulichenko[b], Victoria Chornovol[b]

[a] *Department of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska Street, 64/13, Kyiv 01601, Ukraine}*

[b] *Department of Chemistry, Kyiv National University of Building and Architecture, Povitroflotsky pr., 31, Kyiv 03680, Ukraine*

contacting e-mail dziazko@mail.univ.kiev.ua

Keywords: *coprecipitation method, non-stoichiometric compositions, nickelates, rare earth oxides, K_2NiF_4.*

The non-stoichiometric compositions $Ln_{2-x}NiO_{4-3x/2+\delta}$ (Ln=La, Pr, Nd, $0 \le x \le 0,4$) were obtained using coprecipitation method from nitrates solutions by K_2CO_3 followed by calcination of the obtained blend at 950°C. According to X-ray phase analysis compositions in the range $La_2NiO_{4.17}$ – $La_{1.6}NiO_{3.63}$ are monophase and crystallize in tetragonal symmetry K_2NiF_4, space group I4/mmm. $Nd_{2-x}NiO_{4-y}$ and $Pr_{2-x}NiO_{4-y}$ in the range $0 \le x \le 0,2$ are monophase and have orthorombic and monoclinic(correspodingly) distorted K_2NiF_4 structure. Samples with $0,2 < x \le 0,4$ are polyphase and contain Ln_2NiO_4 (Ln=Pr, Nd), NiO and rare earth oxides. Electrical conductivity of obtained samples has semiconducting behavior and it is strongly depended to nonstoichiometric oxygen content.

Introduction

Search for new oxide compounds based on nickelates of rare-earth elements with important physico-chemical properties for the modern science and technology is a topical issue today. The mentioned above oxide compositions have potential to be used in microelectronics, catalysis and sensor technology [1-4]. Most of the rare-earth elements form only $RNiO_3$ compositions. Lanthanum, Praseodymium and Neodymium form Ruddlesden-Popper phases $Ln_{n+1}Ni_nO_{3n+1}$. It has been reported that using sol-gel method of synthesis gives an opportunity to obtain phases with Lanthanum deficiency $La_{1.9}NiO_4$ [5]. The goal of the research was synthesis of nonstoichiometric phases $Ln_{2-x}NiO_{4-y}$ and studying their characteristics.

Results and discussion

The combined thermogravimetric and IR-spectroscopic studies showed that the

decomposition of the blend proceeds in the following three stages:

1 – decomposition of the hydrooxocarbonate groups, accompanied by a loss of water and CO_2, at 150–160 °C;

2 – decomposition of the carbonate groups, accompanied by a loss of CO_2, at 450–460 °C;

3 – crystallization in the 880–900 °C temperature range.

Taking into account the results of these studies, we have chosen a calcination temperature of 950°C for the sample synthesis. The blend was calcined during 10 h in alundum crucibles. The pellets were calcined during 8 h. All the synthesized samples were black powders that could easily be dissolved in mineral acids.

According to X-ray phase analysis compositions in the range $La_2NiO_{4.17}$ – $La_{1.6}NiO_{3.63}$ are monophase and crystallize in tetragonal symmetry K_2NiF_4, space group I4/mmm. Crystal lattice parameters of $La_2NiO_{4.17}$ – a= 0,384(3)nm and c=1,26(3)nm.

Samples $Nd_{2-x}NiO_{4-y}$ with $0 \le x \le 0,2$ are monophase and have orthorombic distorted K_2NiF_4 structure. Samples with $0,2 < x \le 0,4$ are polyphase and contain Nd_2NiO_4 phase, NiO and Nd_2O_3. Crystal lattice parameters of $Nd_2NiO_{4,20}$ are a=0,545(0)nm, b=0,536(8) nm, c=0,123(3) nm.

Compositions $Pr_{2-x}NiO_{4-y}$ with $0 \le x \le 0,2$ are monophase and have monoclinic distorted K_2NiF_4 structure. Crystal lattice parameters of $Pr_2NiO_{4.20}$ are a=0.383(1) nm, b=0.384(1) nm and c=1.243(2) nm, γ=90.4(1)°. Similar to neodymium system samples with $0,2 < x \le 0,4$ are polyphase and contain Pr_2NiO_4, rare earth and nickel oxides.

The stabilization of non-stoichiometric nickelate phases most likely is due to ion vacancies formation. In other words we can consider formation of those phases as isomorphous substitution of rare earth ions to vacancies - $Ln_{2-x}\square_xNiO_{4-y}$.

Electrical conductivity of obtained samples have semiconducting behavior and it is strong depended to nonstoichiometric oxygen content (Fig.1).

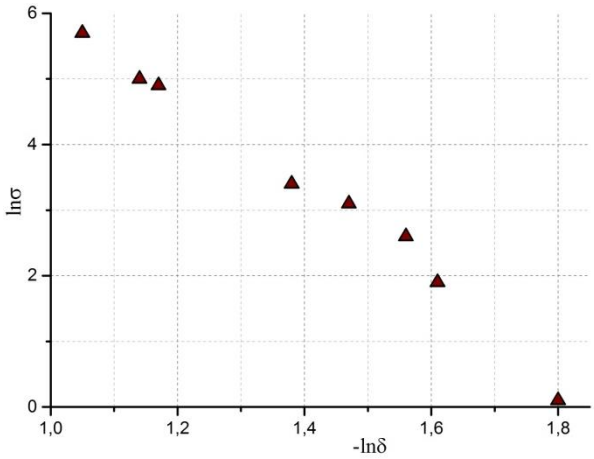

Figure 1. The dependence of conductivity on nonstoichiometric oxygen content δ in samples $La_xNiO_{1,5x+1+\delta}$ at T=293.

Conclusions

Samples of the $Ln_{2-x}NiO_{4-y}$ (Ln=La, Pr, Nd) systems were obtained using coprecipitation from aqueous solutions of rare-earth metal and nickel nitrates with K_2CO_3

solution, followed by calcination of the blends obtained this way.

It is shown that in compositions $Ln_{2-x}NiO_{4-y}$ in the ranges $0 \le x \le 0.4$ (Ln=La) and $0 \le x \le 0.2$ (Ln=Pr and Nd) nonstoichiometric compounds are obtained.

Electrical conductivity of obtained samples have semiconducting behavior and it is strong depended to nonstoichiometric oxygen content. It is can be explained by dominating role of –Ni-O- layers in the electron transport processes.

Experimental part

To prepare solutions, we used La, Ni and Ca nitrates ("pure for analysis") as starting substances. A trilonometric analysis of the metal content in the solutions was performed according to the techniques described in [6-8]. A 0.25 M solution of K_2CO_3 ("chemically pure") was used for the precipitation.

We studied the coprecipitation processes using a model mixture of $La(NO_3)_3$ and $Ni(NO_3)_2$ solutions. The ratio between the La^{3+} and Ni^{2+} concentrations was $La^{3+}:Ni^{2+} = 3:2$, for the total concentration $[La^{3+}] + [Ni^{2+}] = 0.10$ M. It was shown that a complete precipitation of metal ions with K_2CO_3 solution is achieved at a molar fraction of the sum of precipitated ions with respect to the precipitator $n = 1.75$ in the range pH = 10–10.2.

To prepare the blend, the metal solutions were mixed (at the required ratios) in a beaker using a magnetic mixer. The required amount of the precipitator was quickly added to the well-stirred solution. Then the whole mixture was agitated during 1–2 h. The coprecipitated hydrooxocarbonates were held for 3 days to age the precipitate. After this, the degree of metal ion precipitation was analyzed. Then the precipitates were filtered off, washed in distilled water, a 1:1 water-acetone mixture, pure acetone and dried in air. The dried blend was exposed to thermal treatment at 900 °C for 10 h. After this it was ground, pressed into pellets and calcined in air at 1000 °C for 8 h. Then the blend was cooled down to room temperature in the oven.

The IR spectra taken from the pressed into pellets mixed with KBr ("special purity, class 3–4") in the 400–4000 cm^{-1} frequency range using a UR-10 instrument. Thermogravimetric studies of the coprecipitated blend were performed with a derivatograph Q-1500 produced by MOM (Hungary). We studied blend pieces of about 0.2–0.4 g. The sample heating rate was 10°C/min. X-ray powder diffraction (XRD) studies of the samples were performed using a DRON-3 instrument ($Cu_{K\alpha}$-radiation, Ni filter).

The excess oxygen content was determined by iodometric titration techniques [9-10]. The conductivity of the samples (12×2 mm pellets with deposited In–Ga contacts) was measured in the 300–78 K temperature range using the four-probe technique with a ASTS-R

(Automated System for Superconductors Testing – R) plant.

References

[1] M. Hrovat, N. Katsarakis, K. Reichmann et all. *Solid State Ionics.* **1996**, Vol. 83. № 1-2. P. 99-105.

[2] H. Zhao, Q. Li, L.P. Sun, Science China Chemistry, **2011**, Volume 54, Issue 6, pp 898-910

[3] M. L. Faro, D. L. Rosa, I. Nicotera, V. Antonucci, A. S. Aricò, Applied Catalysis B: Environmental, **2009**,Volume 89, Issues 1–2, 3 P. 49-57

[4] M.C. Álvarez-Galván, V.A. de la Peña O'Shea, G. Arzamendi, B. Pawelec, L.M. Gandía, J.L.G. Fierro, Applied Catalysis B: Environmental, **2009**, Volume 92, Issues 3–4, P. 445-453

[5] E.Boehm, J.M. Bassat, P.Dordor et al. Solid State Ionics, **2005**, v.176, 2717-2725.

[6] G. Schwarzenbach, H. Flaschka, *Die komplexometrische Titration*, Ferdinand Enke Verlag, Stuttgart (1965) (in German).

[7] F. Umland, A. Janssen, D. Thierig, G. Wünsch, *Theorie und praktische Anwendung von Komplexbildern*, Akademische Verlagsgesellschaft, Frankfurt am Main (1971) (in German).

[8] R. Přibil, *Komplexony v chemické analyse*, Nakladatelství Československé Akademie Věd, Prague (1953) (in Czech).

[9] G. Charlot, *Les méthodes de la chimie analytique, analyse quantitative minérale*, Masson et Co. (1961) (in French).

[10] V.A. Kulichenko, S.A. Nedilko, A.G. Dziazko, *Visn. Kievs. Univ. Khim*. **33** (1996) 130 (in Ukrainian).