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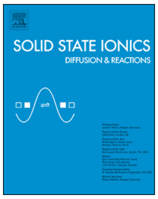

Ruddlesden-Popper phases $Sr_3Ni_{2-x}Al_xO_{7-\delta}$ and some doped derivatives: Synthesis, oxygen nonstoichiometry and electrical properties

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ABSTRACT

The Ruddlesden-Popper phases $Sr_3Ni_{2-x}Al_xO_{7-\delta}$ ($0.5 < x \leq 0.75$) were synthesized in the system Sr–Al–Ni–O for the first time. They show 2*P*/*RS* structure, in which two perovskite layers (*P*) are stacked in between rock-salt layers (*RS*). The composition $Sr_3Ni_{2-x}Al_xO_{7-\delta}$ with $x = 0.5$ was stabilized by partial substitution of Sr^{2+} for Ba^{2+} to give $Sr_{2.8}Ba_{0.2}Ni_{1.5}Al_{0.5}O_{7-\delta}$. This substitution allowed to reduce the synthesis duration and to lower its temperature. The study of specific electrical resistivity of $Sr_3Ni_{2-x}Al_xO_{7-\delta}$ ($0.5 < x \leq 0.75$) and $Sr_{2.8}Ba_{0.2}Ni_{1.5}Al_{0.5}O_{7-\delta}$ ($x = 0.5$) showed that it decreased with decreasing aluminum content. The specific resistivity of yttrium-modified phases $Sr_{2.8-y}Y_yBa_{0.2}Ni_{1.5}Al_{0.5}O_{7-\delta}$ was found to decrease with increasing y and reaches a minimum value for $y = 0.1$. Oxygen nonstoichiometry of limiting representatives in single phase range $0.5 < x \leq 0.75$ was estimated by iodometric titration at 20 °C, which gave the oxygen deficiency δ of 1.02 ($x = 0.75$) and 0.78 ($x = 0.5$), showing the decrease of δ with decreasing aluminum content. The temperature range of semiconductor-to-metal transition (350–450 °C) was determined by thermal analysis and electrical measurements. All synthesized compounds were analyzed by X-ray powder diffraction for identification of crystalline phases.

1. Introduction

A large group of layered complex oxides $Sr_3M_2O_{7-\delta}$ ($\delta \geq 0$), where M is Ti [1], Fe [2], Co [3], Mn [4] and other 3*d*- and 4*d*-elements [5–7], is well-known due to their good transport, electrochemical, magnetic, catalytic properties and *etc*. These oxides belong to the Ruddlesden-Popper phase with *2P/RS* structure, in which two perovskite layers (*P*) are stacked in between rock-salt layers (*RS*). The Ruddlesden-Popper-structured oxides are promising for application in different areas of industry, in particular energy production and information technology. Scientific importance and application fields of new synthesized compounds $Sr_3M_2O_7$ will expand.

In [8] Z. Zhang et al. synthesized $La_3Ni_2O_7$ at high oxygen pressure. M.A. Bobina et al. [9] established low solubility of strontium in this oxide. According to [9–11], $Sr_3Ni_2O_7$ cannot be obtained in Sr–Ni–O system.

Our preliminary investigation showed that introduction of Al^{3+} in nickel sublattice promoted the formation of oxygen deficient 2P/RS phase. Although it is well-known that the single phase $Sr_3Al_2O_7$ does not exist in Sr–Al–O system.

So, the aim of the present work was to synthesize stable solid solutions $Sr_3(Ni, Al)_2O_{7-\delta}$ with 2P/RS structure and to study their oxygen nonstoichiometry and electrical properties. In the course of the investigation, solid solutions $(Sr,Ba)_3(Ni, Al)_2O_{7-\delta}$ and $(Sr,Ba,Y)_3(Ni, Al)_2O_{7-\delta}$ were also synthesized and studied.

2. Experimental

2.1. Synthesis

Syntheses of complex oxides $Sr_3(Ni, Al)_2O_{7-\delta}$, $(Sr,Ba)_3(Ni, Al)_2O_{7-\delta}$, and $(Sr,Ba,Y)_3(Ni, Al)_2O_{7-\delta}$ were carried out by the standard solid state reactions. Reagent grade nitrates $Sr(NO_3)_2$, $Ni(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Ba(NO_3)_2$, and $Y(NO_3)_3{\cdot}6H_2O$ were used as starting materials. Some details of the syntheses are described in Subsection 3.1.

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2.2. Analytical procedures

The samples were investigated using powder X-ray diffraction (XRD) on an Empyrean diffractometer (PANalytical, Netherlands) at room temperature (CuKα radiation, $\lambda = 1.5418$ Å).

The oxygen content of single-phase powders was determined by iodometric titration technique at a temperature of 20 °C. For iodometric titration, 50–80 mg of each sample was dissolved in a solution, containing 10 ml of 1 N potassium iodide and 10 ml of diluted (1:2) hydrochloric acid. The iodine formed was titrated against a standard 0.02 N solution of sodium thiosulfate.

Temperature variation of oxygen index was studied by coulometric titration with a multifunctional solid electrolyte device OXYLYT™ (GmbH SensoTech, Germany) over a temperature cycle 20–900–20 °C. The partial pressure of oxygen in flowing gas (Ar) was arbitrarily fixed at 49 Pa. Air was used as a comparison gas. The considered dependences were titration current (*I*) and oxygen index *vs.* time (*t*) and temperature (*T*). The operation regimes of OXYLYT™ and its construction have been reviewed in [12] in detail. Here, it should be noted that the deviation of titration current (*I*), being take place at any oxygen exchange of sample, from the base current value (I_{base}), being correspond to fixed partial pressure of O_2 in flowing gas Ar, allows to calculate the mass change of oxygen according to Faraday's law:

$$\Delta m_{O_2} = \frac{M_{O_2}}{F \times z} \times \int_{t_1}^{t_2} (I_{base} - I)dt = \frac{32}{96485 \times 4} \times \int_{t_1}^{t_2} (I_{base} - I)dt \qquad (1)$$

Thermal analysis was performed on a Netzsch STA429 thermoanalyzer, in a temperature range of 20–900 °C in nitrogen and air flows, using alumina crucibles. Thermogravimetric (TG) curves were obtained at heating rate 5 °C·min^{-1} and gas flow rate 5 l·h^{-1}.

2.3. Electrical measurements

Samples for electrical conductivity measurements were hydrostatically pressed at 400–600 MPa to form parallelepipeds with dimensions 10 × 4 × 4 mm^3, and sintered at 1250–1300 °C for 20 h in oxygen flow. Specific electrical resistivity (ρ) of samples was measured using a standard DC four-point method using double-sided platinum-rhodium electrodes. The dependence of specific electrical resistivity on temperature [ρ(*T*)] was registered at heating/cooling rate of 2.6°C·min^{-1} in air and in oxygen atmosphere.

To establish the influence of temperature as well as atmosphere conditions on electrical properties of the samples, ln σ(Ohm^{-1}·m^{-1}) *vs.* 1000/T(K) was plotted and the effective activation energy of conduction (*E*a) was estimated according to the Arrhenius Eqs. (2) and (2′):

$$\sigma = \sigma_0 \times \exp\left(-\frac{Ea}{RT}\right) \qquad (2)$$

$$1\text{n}\,\sigma = 1\text{n}\,\sigma_0 - \frac{Ea}{R}\frac{1}{T} \qquad (2')$$

where σ is conductivity, or specific conductance (Ohm^{-1}·m^{-1}), σ_0 – pre-exponential factor (Ohm^{-1}·m^{-1}), R – universal gas constant (8.314 J·mole^{-1}·K^{-1}).

In the present work, we analyzed simplified Arrhenius Eqs. (2) and (2′) without any reference to hopping or semiconductor model of the samples conduction. The coefficient (−*E*a/R) was calculated by regression analysis using *Origin 7.0 SRO* software package (OriginLab. Corporation, Northampton, MA, USA). The final value of *E*a was expressed in electron-volt units.

Coefficient of thermal electromotive force (EMF) or the Seebeck coefficient (α) was determined in air with respect to silver and subsequent conversion to microvolt units (with respect to lead). Temperature gradient between hot and cold ends of each sample was 10–15°C.

3. Results and discussion

3.1. Synthesis and XRD study

According to [9–11], the oxide with the exact composition $Sr_3Ni_2O_7$ cannot be obtained due to the fact that the oxidation state +4 is not typical of nickel ions. Some Ruddlesden-Popper phases show exact composition $Sr_3M_2O_7$, as in the case of $Sr_3Ti_2O_7$ [13, 14], which became a traditional example of Ruddlesden-Popper compounds $Sr_3M_2O_7$ (titanium ion is in oxidation state +4). Other Ruddlesden-Popper phases, such as $Sr_3Fe_2O_{7-\delta}$ and $Sr_3Co_2O_{7-\delta}$, revealed large oxygen deficiency, because cobalt and iron ions do not attain oxidation state +4. For example, in $Sr_3Co_2O_{7-\delta}$ [3], the oxygen deficiency δ was found to be close to 1.

It was found in the course of the present investigations, that the introduction of Al^{3+} in Sr–Ni–O system is the factor, stabilizing oxygen deficient 2*P*/*RS*-structure. The investigation showed that single phase oxides $Sr_3Ni_{2-x}Al_xO_{7-\delta}$ could be synthesized by partial substitution of Ni-sites by Al^{3+} only in the range $0.5 < x \leq 0.75$. Synthesis of such phases were prepared with a step $\Delta x = 0.05$ by the following way. An aqueous solution of starting nitrates, taken in corresponding ratio, was evaporated by slow heating from 20°C to 350°C. The obtained mixture of solid products was grinded and sintered at 750°C for 5 h to complete decomposition of nitrates. As a result, fine powder oxide was formed. Subsequent sintering of the powder at 1100–1150°C in oxygen-rich atmosphere enhanced the reaction between oxides to form precursors. The precursors were grinded and sintered at 1300–1320°C for 30 h in oxygen flow to give the resulting sample. As showed XRD powder patterns of the obtained samples with $0.5 < x \leq 0.75$, all they are single phases $Sr_3Ni_{2-x}Al_xO_{7-\delta}$ with Ruddlesden-Popper 2*P*/*RS*-structure, crystallizing in the tetragonal space group *I*4/*mmm*. Fig. 1a shows XRD powder pattern of $Sr_3Ni_{1.25}Al_{0.75}O_{7-\delta}$, being the representative with the highest aluminum content. Its unit cell dimensions was found to be $a = 3.8198(2)$ Å and $c = 20.325(2)$ Å.

The samples, synthesized for $x > 0.75$ and $x \leq 0.5$, were found to be multiphase. So, according to XRD powder data, the sample with $x = 0.8$ contained a small amount of $Sr_3Al_2O_6$. Oxides NiO and SrO were observed in the sample obtained for $x < 0.5$, and very small amount of these oxides was found in the sample with $x = 0.5$. To facilitate single phase synthesis for $x = 0.5$, partial substitution of Sr-sites by Ba^{2+} was performed. Final stage of the sample synthesis (*i.e.* formation of 2*P*/*RS*-structure) could be performed by sintering the sample at 1270–1280°C for 18–20 h. As a result, single phase

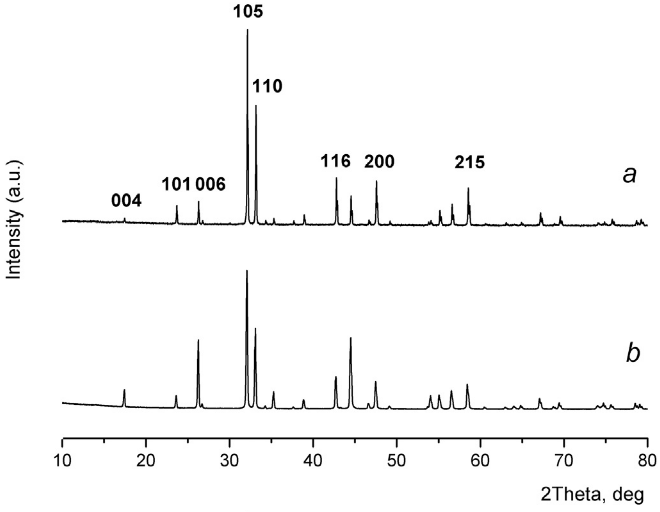

Fig. 1. XRD powder patterns of the samples with nominal compositions $Sr_3Ni_{1.25}Al_{0.75}O_{7-\delta}$ (a) and $Sr_{2.8}Ba_{0.2}Ni_{1.5}Al_{0.5}O_{7-\delta}$ (b).