PHYSICOCHEMICAL ANALYSIS OF INORGANIC SYSTEMS

# Phase Equilibria, Crystal Structure at 1373 K and Properties of Complex Oxides in the Nd–Co–Fe–O System

T. V. Aksenova\*, Sh. I. Elkalashy, A. S. Urusova, and V. A. Cherepanov

Ural Federal University, Yekaterinburg, 620000 Russia \*e-mail: TV.Aksenova@urfu.ru Received July 21, 2016

Abstract—Phase equilibria in the Nd–Co–Fe–O system were systematically studied at 1373 K in air. The homogeneity range and crystal structure of solid solution NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> ( $0.0 \le x \le 1.0$ ) have been studied by the X-ray powder diffraction method. The structural parameters of complex oxides have been refined by the full-profile Rietveld method. It was shown that all oxides reveal practically stoichiometric oxygen composition within the entire temperature range under investigation. The values of thermal expansion coefficients for the cobaltites NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7) have been calculated within the wide temperature range in air. Chemical stability of NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7) in respect to the solid electrolyte materials (Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2-\delta</sub> and La<sub>0.88</sub>Sr<sub>0.12</sub>Ga<sub>0.82</sub>Mg<sub>0.18</sub>O<sub>3-\delta</sub>) was examined. Electrical conductivity of NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7) was measured as a function of temperature within the range 300–1373 K in air. It was shown that substitution of cobalt for iron leads to the decrease of conductivity. The isothermal-isobaric cross-section of the phase diagram for the Nd–Co–Fe–O system at 1373 K in air has been presented.

DOI: 10.1134/S0036023617080022

Perovskite-related manganites, ferrites and cobaltites of  $LnMO_{3\pm\delta}$  and  $Ln_2MO_{4\pm\delta}$ , compositions, where Ln = La-Y, M = Mn, Fe, Co, find a variety of practical applications as materials for fuel cell electrodes, oxygen membranes, cathodes of CO<sub>2</sub> lasers, catalysts [1–6]. Varying the composition by a partial replacing of components in both sublattices allows the creation of materials with a certain set of properties necessary for practical use. High-temperature chemistry and thermodynamics of neodymium ferrites and neodymium cobaltites is the subject of many publications. The phase equilibria and the crystal structure of oxides formed in the Nd–M–O (M = Fe, Co) and Co–Fe–O quasi-binary systems are the most studied items up to date.

Three ternary oxides: NdCoO<sub>3</sub>, Nd<sub>4</sub>Co<sub>3</sub>O<sub>10</sub> and Nd<sub>2</sub>CoO<sub>4</sub> are known to exist in the Nd–Co–O system [5–17]. Only NdCoO<sub>3</sub> is stable at 1373 K in air; cobaltite Nd<sub>4</sub>Co<sub>3</sub>O<sub>10</sub> had been prepared within the temperature range 1373–1423 K in the atmosphere with lower oxygen pressure  $10^{-2.6}$ – $10^{-4.5}$  atm [14–16], and oxide Nd<sub>2</sub>CoO<sub>4</sub> was synthesized at 1473 K in the atmosphere of purified nitrogen [17].

Neodymium cobaltite NdCoO<sub>3</sub> is crystallized in the cubic cell with the parameter a = 3.76 Å [8, 9] or in the orthorhombic cell with the parameters: a =5.3316 Å, b = 7.5457 Å, c = 5.3434 Å [6], which is in good agreement with the data reported in [7, 10]. NdCoO<sub>3</sub> exhibit semiconducting *p*-type conductivity [8]; the value of total conductivity at room temperature is equal to  $\approx 7 \times 10^{-3}$  S/cm [7].

The only complex oxide NdFeO<sub>3</sub> has formed in the Nd–Fe–O system [18, 19]. Neodymium ferrite NdFeO<sub>3</sub> possesses the orthorhombically distorted perovskite structure with the unit cell parameters: a = 5.576 Å, b = 7.756 Å, c = 5.447 Å (sp. gr. *Pnma*) [20]; it is a semiconductor which exhibit paramagnetic behavior with the Néel temperature  $T_N = 687$  K [20, 21].

CoFe<sub>2</sub>O<sub>4</sub> is known to exist in the Co-Fe-O system [22–29]. Cobalt ferrite  $CoFe_2O_4$  was prepared by the solid state synthesis [22], by using the citrate technique [23], by the thermal decomposition of hydroxides [24] or polymer composites [23], by the co-precipitation method [25] and by the hydrothermal method [26].  $CoFe_2O_4$  possesses the reversed spinel structure [22, 24]. Based on  $CoFe_2O_4$  a series of solid solutions with the general formula  $Co_x Fe_{3-x}O_4$  have been prepared. The homogeneity range of  $Co_x Fe_{3-x}O_4$ at 1373 K in air was reported as  $0.6 \le x \le 1.2$  [28], but according to [27] the composition of the both boundaries are enriched by cobalt  $1.0 \le x \le 1.35$ . The study of phase equilibria at 1373 K in air for the  $CoO-Fe_2O_3$ system [29] has revealed the formation of three types of solid solutions:  $\text{Co}_{1-y}\text{Fe}_y\text{O}$  (0.0  $\leq y \leq$  0.15) with the NaCl-type structure (sp. gr.  $Fm\overline{3}m$ ),  $Fe_{2-u}Co_uO_3$ within the range  $0.0 \le u \le 0.06$  (sp. gr.  $R\overline{3}c$ ) and

 $Fe_{3-z}Co_zO_4 c \ 0.84 \le z \le 1.38$  with the spinel structure (sp. gr. *Fd3m*).

The phase relations in the quasi-ternary Nd–Co– Fe–O system are poorly studied [7, 30]. It was reported that Co-substituted complex oxides NdFe<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> with the orthorhombic structure (sp. gr. *Pbnm*) have formed within the range  $0.0 \le x \le 0.5$  [30]. The solid solutions NdFe<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> with x < 0.3 in air exhibit semiconducting *p*-type conductivity within the temperature range 298–673 K, while the oxides with x > 0.3exhibit *n*-type conductivity [7].

The present work aimed to the study of phase equilibria, crystal structure and physicochemical properties of complex oxides formed in the quasi-ternary Nd–Co–Fe–O system.

### **EXPERIMENTAL**

The samples for investigations were synthesized by the glycerol-nitrate technique. Nd<sub>2</sub>O<sub>3</sub> (NO-L qualification), preliminary calcined for the desorption of the adsorbed water and gases, iron oxalate FeC<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O (pure for analysis grade) and metallic Co were used as starting materials. Metallic Co was prepared by the reducing of cobalt oxide Co<sub>3</sub>O<sub>4</sub> (pure for analysis grade) in the hydrogen flow at 673–873 K. Samarium oxide Sm<sub>2</sub>O<sub>3</sub> (SmO-L qualification), lanthanum oxide (LaO-D qualification), magnesium oxide MgO (pure for analysis grade), cerium nitrate Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O (pure for analysis grade), strontium carbonate SrCO<sub>3</sub> (special purity grade), and metallic gallium were used for the synthesis of Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2 -  $\delta$ </sub> and La<sub>0.88</sub>Sr<sub>0.12</sub>Ga<sub>0.82</sub>Mg<sub>0.18</sub>O<sub>3 -  $\delta$ </sub>.

The weights of the starting components in the required stoichiometric amounts were dissolved in dilute nitric acid HNO<sub>3</sub> (special purity grade) while heating. Then an equimolar amount of glycerol  $C_3H_8O_3$  (pure for analysis grade), required for the complete reduction of nitrate ions, was added. The resulting solution was heated in order to evaporate the solvent. Dry residual was slowly heated within the temperature range 298–1273 K. Final annealing was performed in air during 100–120 h with intermediate grindings in the ethanol media after each 10–12 h. The samples were quenched from 1373 K to room temperature (cooling rate of about ~400–500 K/min).

A chemical indifference test for mixed cobaltite-ferrite of neodymium with respect to solid electrolyte materials was carried out using Sm-stabilized ceria and (Sr, Mg)-doped lanthanum gallate, as the examples. In order to prepare  $Ce_{0.8}Sm_{0.2}O_{2-\delta}$  the final annealing was performed at 1373 K in air during 36 h, while  $La_{0.88}Sr_{0.12}Ga_{0.82}Mg_{0.18}O_{3-\delta}$  was annealed at 1573 K during 12 h.

Phase identification of the studied oxides was performed using diffractometers Inel Equinox 3000 with Fe radiation ( $\lambda = 1.93609$  Å) and Shimadzu XRD 7000 with Cu radiation ( $\lambda = 1.5418$  Å) using a monochromator made from the pyrolytic graphite. XRD measurements were performed within the angle range  $20^{\circ} \le 2\theta \le 90^{\circ}$  with the rate  $0.02^{\circ}-0.05^{\circ}$  per minute with the exposition time from 1 to 10 s.

The unit cell parameters were calculated using the Celref 3 software and refined by the Rietveld analysis using Fullprof 2008 package [31, 32].

The measurements of the relative linear thermal expansion were performed using a dilatometer DIL 402 C (Netzsch GmBH) in air within the temperature range 298-1373 K with the heating and cooling rate of 5 K/min.

The oxygen content in the oxides and its changes with temperature have been determined by the thermogravimetric analysis (STA 409 PC, Netzsch GmBH) followed by the samples reducing in the hydrogen flow at 1373 K inside the TG cell and also by the iodometric titration of the samples slowly cooled from 1373 K to room temperature with the rate 1 K/min, reported elsewhere [33].

Since the studied oxides are considered as potential cathode materials for the solid oxide fuel cells the information about their chemical indifference with respect to electrolyte materials become an issue of vital importance. Chemical stability of substituted cobaltites with respect to electrolyte materials was studied by annealing of powder mixtures of NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7) with the solid electrolytes (Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2- $\delta$ </sub> or La<sub>0.88</sub>Sr<sub>0.12</sub>Ga<sub>0.82</sub>Mg<sub>0.18</sub>O<sub>3- $\delta$ </sub>) taken in mass ratio 1 : 1 at 1573 K in air.

Electrical conductivity of ceramic complex oxides sintered in a form of rectangular bars with the sizes  $4 \times 4 \times 25$  mm measured by the 4-probe technique in air as a function of temperature within the range 300– 1373 K.

### **RESULTS AND DISCUSSION**

In order to study the phase equilibria in the Nd– Co–Fe–O system at 1373 K in air 26 samples with various ratios of metallic components were prepared using the glycerol-nitrate technique.

### $NdCo_{1-x}Fe_xO_3$ Solid Solutions

In order to determine the homogeneity range and the crystal structure of solid solutions with the general formula NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> the samples with overall compositions x = 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0 have been prepared. According to the XRD results all samples quenched from 1373 K to room temperature were singe phases. XRD patterns for the cobaltites NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> with  $0.1 \le x \le 1.0$  are shown in Fig. 1. The differences in the mutual solubility of cobaltite and ferrite in Ndand La-containing systems (unlimited solubility in the NdCoO<sub>3</sub>-NdFeO<sub>3</sub> system and limited solubility from the both cobaltite and ferrite sides in the LaCoO<sub>3</sub>-



Fig. 1. The XRD patterns for the single phase  $NdCo_{1-x}Fe_xO_3$  solid solutions  $(0.1 \le x \le 1.0)$ .



**Fig. 2.** The XRD patterns for the NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7), refined by the Rietveld method. Points are experimental results; (1) theoretical profile; (2) peak positions with the allowed Miller indices (*hkl*); (3) the difference between experimental data and theoretical profile.

LaFeO<sub>3</sub> system [29]) are explained by the difference in crystal structure distortions. Lanthanum cobaltite LaCoO<sub>3</sub> is the rhombohedrally distorted perovskite while NdCoO<sub>3</sub>, as well as lanthanum ferrite and neodymium ferrite LnFeO<sub>3</sub> (Ln = La, Nd) possess the orthorhombically distorted unit cell.

The splitting of the diffraction peaks observed at the scattering angles  $31^{\circ}-33^{\circ}$ ,  $39^{\circ}-41^{\circ}$  and  $57^{\circ}-60^{\circ}$  increases with the raise of iron replacing cobalt content in NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub>, which indicates an increase of

the orthorhombic distortions of the perovskite lattice. Similarly to undoped NdMO<sub>3</sub> (M = Fe, Co), the XRD patterns for the NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> complex oxides with  $0.1 \le x \le 0.9$  have been indexed within the orthorhombic cell  $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$  (sp. gr. *Pbnm*), where  $a_p$  – is the unit cell parameter for the cubic perovskite, which is in good agreement with the data reported in [30]. Figure 2 demonstrates XRD patterns, refined by the full-profile Rietveld method for the NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> solid solutions with x = 0.3 and 0.7, as an example. However, the ratio of the unit cell parameters  $a, b, c/\sqrt{2}$ and the values of parameter that characterized the orthorhombic distortions *D* that can be calculated according to the formula:

$$D = \frac{1}{3} \sum_{i=1}^{3} \left| \frac{\alpha_i - \overline{\alpha}}{\overline{\alpha}} \right| \times 100\%, \qquad (1)$$

where  $\alpha_1 = a$ ,  $\alpha_2 = b$ ,  $\alpha_3 = c/\sqrt{2}$  and  $\overline{\alpha} = (a \times b \times a)$  $c/\sqrt{2}$ )<sup>1/3</sup>), indicate the appearance of two types of orthorhombic structure: O-type that characterized by the parameter's ratio  $a \le c/\sqrt{2} \le b$  or  $b \le c/\sqrt{2} \le a$ , and O'-type with the parameter's ratio  $c/\sqrt{2} \le b \le a$ . NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> solid solutions with  $0.0 \leq x < 0.1$  and  $0.1 < x \le 1.0$  possess *O*-type orthorhombic cell, while the oxide with x = 0.1 - O'-type. The values of unit cell parameters, unit cell volume and parameter of orthorhombic distortions for NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> with  $0.0 \le x \le 1.0$ are listed in Table 1. One can see that the value of D parameter is minimal for  $NdCo_{0.9}Fe_{0.1}O_3$  and it is significantly increases with the raise of iron concentration. Thus, while the dopant (Fe) content is increasing, an orthorhombic structure of  $NdCo_{1-x}Fe_xO_3$  at 1373 K in air is undergoes the phase transformation: O-type  $\rightarrow$ O'-type within the range x = 0.0-0.1 and the reverse transformation O'-type  $\rightarrow$  O-type within the range x = 0.1-0.2. Often the structural changes in perovskite-like oxides are associated with a change in the oxygen content (oxygen nonstoichiometry). However, according to the available data for neodymium ferrite and neodymium cobaltite [13, 14, 18, 34] and according to the results of thermogravimetric measurements and iodometric titration for the NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> solid solutions (x = 0.3, 0.7), obtained in the present work, all oxides have stoichiometric oxygen composition and oxygen content remained practically unchanged with the variations of sample composition and temperature. The existence of an O'-type structure at small values of x in  $NdCo_{1-x}Fe_xO_3$  is apparently associated with a fine interaction of isolated iron ions via oxygen bridges with the cobalt ions surrounding them. The increase in the iron content and the greater probability of the iron ions neighborhood eliminate this effect, and the structure again returns to the O-type.

| x   | a, Å     | b, Å     | c, Å     | <i>V</i> , Å <sup>3</sup> | $c/\sqrt{2}$ , Å | Parameters relation        | Type<br>of structure | D, %  |
|-----|----------|----------|----------|---------------------------|------------------|----------------------------|----------------------|-------|
| 0.0 | 5.345(1) | 5.331(1) | 7.549(1) | 215.13(1)                 | 5.33795          | $b \le c / \sqrt{2} < a$   | 0                    | 0.087 |
| 0.1 | 5.354(1) | 5.348(1) | 7.561(2) | 216.51(1)                 | 5.34643          | $c \big/ \sqrt{2} < b < a$ | 0'                   | 0.056 |
| 0.3 | 5.375(1) | 5.394(1) | 7.606(1) | 220.54(1)                 | 5.37825          | $a < c/\sqrt{2} < b$       | 0                    | 0.143 |
| 0.5 | 5.396(1) | 5.444(1) | 7.649(1) | 224.71(3)                 | 5.40866          | $a \le c / \sqrt{2} < b$   | 0                    | 0.341 |
| 0.7 | 5.419(1) | 5.498(1) | 7.695(1) | 229.28(3)                 | 5.44119          | $a < c/\sqrt{2} < b$       | 0                    | 0.552 |
| 0.9 | 5.440(1) | 5.553(1) | 7.738(1) | 233.78(2)                 | 5.47159          | $a \le c / \sqrt{2} < b$   | 0                    | 0.785 |
| 1.0 | 5.453(1) | 5.581(1) | 7.763(2) | 236.27(3)                 | 5.48927          | $a < c / \sqrt{2} < b$     | 0                    | 0.885 |

**Table 1.** The unit cell parameters, type of the orthorhombic structure, and orthorhombic distortion parameter for the NdCo<sub>1</sub>  $_{x}$ Fe<sub>x</sub>O<sub>3</sub> solid solutions ( $0.0 \le x \le 1.0$ ), quenched from 1373 K in air

**Table 2.** Atomic coordinates in the unit cells of  $NdCo_{1-x}Fe_xO_3$  solid solutions ( $0.0 \le x \le 1.0$ ), quenched from 1373 K in air

| Sp. gr. <i>Pbnm</i> : Co/Fe (0.5, 0, 0); Nd ( <i>x</i> , <i>y</i> , 0.25); O1 ( <i>x</i> , <i>y</i> , 0.25); O2 ( <i>x</i> , <i>y</i> , <i>z</i> ) |            |           |            |           |           |            |            |
|--|------------|-----------|------------|-----------|-----------|------------|------------|
| x  | 0.0        | 0.1       | 0.3        | 0.5       | 0.7       | 0.9        | 1.0        |
| x(Nd)  | -0.0094(9) | -0.007(1) | -0.0082(1) | -0.007(1) | -0.008(1) | -0.0089(9) | -0.0079(7) |
| <i>y</i> (Nd)  | 0.0334(5)  | 0.0347(6) | 0.0372(1)  | 0.0408(6) | 0.0435(6) | 0.0473(6)  | 0.0480(4)  |
| <i>x</i> (O1)  | 0.095(6)   | 0.073(8)  | 0.070(2)   | 0.066(4)  | 0.088(9)  | 0.099(8)   | 0.092(6)   |
| <i>y</i> (O1)  | 0.493(4)   | 0.495(6)  | 0.486(1)   | 0.481(6)  | 0.485(6)  | 0.465(6)   | 0.477(4)   |
| <i>x</i> (O2)  | -0.241(6)  | -0.282(1) | -0.285(2)  | 0.292(7)  | 0.288(6)  | 0.285(6)   | 0.290(4)   |
| <i>y</i> (O2)  | 0.180(3)   | 0.286(1)  | 0.289(2)   | 0.260(8)  | 0.278(6)  | 0.284(5)   | 0.276(4)   |
| <i>z</i> (O2)  | -0.015(4)  | 0.029(9)  | 0.034(1)   | 0.048(5)  | 0.043(4)  | 0.045(4)   | 0.051(3)   |
| <i>R</i> <sub>Br</sub> , %   | 4.50       | 2.80      | 2.08       | 5.80      | 4.61      | 6.49       | 5.67       |
| $R_{\rm f},\%$   | 6.47       | 3.23      | 2.97       | 7.05      | 7.25      | 8.14       | 7.90       |
| $R_{\rm p}, \%$  | 4.77       | 8.80      | 5.71       | 11.02     | 11.10     | 12.4       | 11.01      |

The atomic coordinates for the unit cells of  $NdCo_{1-x}Fe_xO_3$  solid solutions  $(0.0 \le x \le 1.0)$  refined by the full-profile Rietveld method are listed in Table 2.

Within the homogeneity range, an increase of the concentration of iron replacing cobalt in NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> leads to a gradual raise of the unit cell parameters and unit cell volume, which is related to the size effect: the radius of cobalt ions ( $r_{Co}^{3+} = 0.75$  Å, CN = 6) is less than the radius of iron ions ( $r_{Fe}^{3+} = 0.785$  Å, CN = 6) [35] (Fig. 3).

### Thermal Properties of the $NdCo_{1-x}Fe_xO_3$ Oxides

In order to determine the linear thermal expansion coefficients (LTEC) by means of high-temperature dilatometry the powder samples of  $NdCo_{1-x}Fe_xO_3$  oxides (x = 0.3, 0.7) were pressed into bars with the sizes  $4 \times 4 \times 25$  mm and sintered at 1632 K in air during 24 h, followed by slow cooling to room temperature with the rate of 1 K/min. Same ceramic bars

were used for the conductivity measurements. The relative density of cobaltites NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> was ranged as 90–93% from theoretical value. Temperature dependences of the relative linear expansion of NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7) within the range 298– 1373 K in air, obtained in the heating and cooling modes, completely coincide and are shown in Fig. 4. Isobaric dependencies  $\Delta L/L_0 = f(T)$  are non-linear. In order to describe the obtained  $\Delta L/L_0 = f(T)$  curves the equation of third-degree polynomial was used:

$$\frac{\Delta L}{L_0} = a + b_1 T + b_2 T^2 + b_3 T^3, \qquad (2)$$

where T is absolute temperature (K);  $a, b_1, b_2$  and  $b_3$  are constants.

Isobaric linear thermal expansion coefficients ( $\alpha_p$ ) were calculated using following equation:

$$\alpha_{\rm P} = \frac{1}{L_0} \left( \frac{d\Delta L}{dT} \right) = b_1 + 2b_2T + 3b_3T^2.$$
(3)

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY Vol. 62 No. 8 2017

The coefficients in the equation (2) and the values of LTEC within the temperature range 298–1373 K in air, calculated by means of equation (3) are listed in Table 3. The value of LTEC noticeably decreases with the raise of content of iron substituting cobalt in the neodymium cobaltite NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> from 21.8 × 10<sup>-6</sup> down to  $16.1 \times 10^{-6}$  K<sup>-1</sup>.

Significant increase of the slope for the linear thermal expansion dependencies with temperature that observed for the related cobaltites-ferrites of rare earth elements and barium LnBaCo<sub>2-x</sub>Fe<sub>x</sub>O<sub>5+ $\delta$ </sub> (Ln = Nd-Y) caused by the high temperature oxygen release from the crystal lattice and, as a consequence, by the decrease of average oxidation state of 3d metal in oxide [36, 37]. This contribution to the relative expansion of oxides is called as "chemical expansion" [38-40]. The temperature dependencies of thermal expansion for  $NdCo_{1-x}Fe_xO_3$  (x = 0.3, 0.7) also exhibit noticeable increase of slope at temperature higher than 600 K. However, as it was mentioned above, it was found that the oxygen content in NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7) has not changed within the temperature range 298-1373 K in air according to the results of high temperature thermogravimetry. In this case the non-linear shape of  $\Delta L/L_0 = f(T)$  plot can be explained by the transition of  $\mathrm{Co}^{3+}$  from the low spin (LS) to the high spin (HS) state ( $r_{Co}^{3+}(LS) = 0.685 \text{ Å}, r_{Co}^{3+}(HS) = 0.75 \text{ Å}$ [35]); its possibility for the  $Co^{3+}$  ions was reported in  $NdCoO_3$  [41] and also in the other related complex oxides [42].

In order to study the chemical stability of the cobaltites NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7) in the contact with the electrolyte material the mixtures of NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> with Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2- $\delta$ </sub> or La<sub>0.88</sub>Sr<sub>0.12</sub>Ga<sub>0.82</sub>Mg<sub>0.18</sub>O<sub>3- $\delta$ </sub> in the 1 : 1 mass ratio were annealed during 1 h at 1573 K in air. It was found that NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7) has not react with Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2- $\delta$ </sub> (Fig. 5a).

Chemical reaction occurs when  $NdCo_{1-x}Fe_xO_3$  (x = 0.3, 0.7) is contacted with  $La_{0.88}Sr_{0.12}Ga_{0.82}Mg_{0.18}O_{3-\delta}$ ; the solid solution based on neodymium gallate  $NdGaO_3$  has been detected as the main product of this interaction (Fig. 5b).



Fig. 3. The unit cell parameters and the unit cell volumes versus iron content for the NdCo<sub>1 – x</sub>Fe<sub>x</sub>O<sub>3</sub> solid solutions  $(0.0 \le x \le 1.0)$ .



Fig. 4. The relative linear thermal expansion versus temperature for NdCo<sub>1 - x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7) in air.

## Electrical Conductivity of $NdCo_{1-x}Fe_xO_3$

Isobaric dependencies of electrical conductivity for  $NdCo_{1-x}Fe_xO_3$  (x = 0.3, 0.7) versus temperature are presented in Fig. 6. One can observe the raise of conductivity with increasing temperature for the studied oxides that indicates a semiconducting nature of con-

**Table 3.** The coefficients in the equations corresponding to the isobaric  $\Delta L/L_0 = f(T)$  dependencies and the average values of LTEC for NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7) in air

| x   |                          | $\frac{\Delta L}{L_0} = a + b_1$ | $\alpha_{\rm p} \times 10^6,  {\rm K}^{-1},$ | <i>R</i> ^2                |          |         |
|-----|--------------------------|----------------------------------|--|----------------------------|----------|---------|
|     | а                        | $b_1$                            | <i>b</i> <sub>2</sub>                        | <i>b</i> <sub>3</sub>      | 298-1373 |         |
| 0.3 | $6.74934 \times 10^{-4}$ | $-1.54932 \times 10^{-5}$        | $4.84008 \times 10^{-8}$                     | $-1.82986 \times 10^{-11}$ | 21.8     | 0.99984 |
| 0.7 | $3.53385 \times 10^{-4}$ | $-8.49185 \times 10^{-6}$        | $2.7599 \times 10^{-8}$                      | $-9.05099 \times 10^{-12}$ | 16.1     | 0.99992 |



**Fig. 5.** The XRD patterns for the mixtures:  $NdCo_{0.3}Fe_{0.7}O_3 + Ce_{0.8}Sm_{0.2}O_{2-\delta}$  (a) and  $NdCo_{0.7}Fe_{0.3}O_3 + La_{0.88}Sr_{0.12}Ga_{0.82}Mg_{0.18}O_{3-\delta}$  (b), after high temperature treatment at 1573 K in air refined by the Rietveld method.

ductivity in the doped neodymium cobaltites. Introduction of iron into the cobalt sites leads to a significant decrease of electrical conductivity of the parent NdCoO<sub>3</sub> at temperature higher than 600 K, which is in good agreement with the data reported in [7]. The values of the conductivity activation energies, listed in Table 4, were calculated from the tangent of the  $log(\sigma T) = f(1/T)$  dependences' slope (see the inset in Fig. 6). The activation energies of conductivity for the undoped neodymium cobaltite and neodymium ferrite [43, 44] are presented in the same table for comparison. The values of conductivity activation energy for all oxides are typical for the hopping polaron mechanism of charge transfer. Since the stoichiomet-

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY Vol. 62 No. 8 2017



**Fig. 6.** The isobaric dependencies of electrical conductivity versus temperature for NdCoO<sub>3</sub> according to data from [43], NdFeO<sub>3</sub> according to data from [44] and NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7)—present work. The insert illustrates log( $\sigma T$ ) =  $f(10^3/T)$  dependencies for NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub>.

ric oxygen composition remains unchanged for all oxides the appearance of charge carriers can be associated with the disproportionation process, which is characteristic for this type of oxides:

$$2M^{3+} = M^{4+} + M^{2+}.$$
 (4)

Significant raise of conductivity at temperature higher 600 K for NdCoO<sub>3</sub> and NdCo<sub>0.7</sub>Fe<sub>0.3</sub>O<sub>3</sub> and slight increase of conductivity for NdCo<sub>0.3</sub>Fe<sub>0.7</sub>O<sub>3</sub> allow assuming that mainly cobalt ions are disproportionate predominantly while iron ions involved in this process to much lesser extent.

### Phase Diagram for the Nd-Co-Fe-O System at 1373 K

The phase diagram of the four-component system in isobaric-isothermal conditions should be represented as a three-dimensional tetrahedron. However, the presentation of such systems on the plane in the form of a triangle, where the sample composition are expressed in terms of the molar fraction of metal components, and the vertices of the triangle correspond to the simple oxides  $1/2Nd_2O_3$ , CoO and  $1/2Fe_2O_3$  that exist under these conditions, is more convenient for practical use. The oxygen content in the condensed phases cannot be determined from the diagram. The resulting image is a projection of the isobaric-isothermal phase diagram of the Nd-Co-Fe-O system having a tetrahedron shape on the Nd-Co-Fe face. The information for the phase equilibria on the  $CoO-1/2Fe_2O_3$  side at 1373 K in air has been taken from [29]. Based on the XRD results for 26 samples quenched to the room temperature, the phase diagram for the Nd-Co-Fe-O system at 1373 K in air has been divided into six phase fields (Fig. 7).

According to the XRD data, the samples from the phase fields 3 and 5 were three-phase. In accordance with the Gibbs rule, coexistence of three phases in the quasi-ternary system under consideration at a fixed

**Table 4.** The values of activation energy of conductivity for the  $NdCo_{1-x}Fe_xO_3$  complex oxides

| Composition  | Temperature<br>range, K        | $E_{\rm a}$ , eV        | Reference    |  |
|--|--------------------------------|-------------------------|--------------|--|
| NdCoO <sub>3</sub>                                   | 473–523<br>523–673<br>673–1073 | 0.32<br>0.69<br>0.22    | [43]         |  |
| NdCo <sub>0.7</sub> Fe <sub>0.3</sub> O <sub>3</sub> | 367–417<br>417–916<br>916–1369 | 0.51<br>0.72<br>0.32    | Present work |  |
| NdCo <sub>0.3</sub> Fe <sub>0.7</sub> O <sub>3</sub> | 417—916<br>916—1369            | 0.63<br>0.83            |              |  |
| NdFeO <sub>3</sub>                                   | 323–398<br>398–690<br>690–1073 | 0.461<br>0.276<br>0.242 | [44]         |  |



**Fig. 7.** The isobaric-isothermal cross-section of the phase diagram for the Nd–Co–Fe–O system at 1373 K in air. The phase composition inside the fields are: (1) Nd<sub>2</sub>O<sub>3</sub>, NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (0.0 ≤ x ≤ 1.0); (2) NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (0.0 ≤ x ≤ 0.9), Co<sub>1-y</sub>Fe<sub>y</sub>O (0.0 ≤ y ≤ 0.15); (3) Co<sub>0.85</sub>Fe<sub>0.15</sub>O, Co<sub>1.38</sub>Fe<sub>1.62</sub>O<sub>4</sub>, NdCo<sub>0.1</sub>Fe<sub>0.9</sub>O<sub>3</sub>; (4) Co<sub>2</sub>Fe<sub>3-z</sub>O<sub>4</sub> (0.84 ≤ z ≤ 1.38), NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (0.9 ≤ x ≤ 1.0); (5) NdFeO<sub>3</sub>, Co<sub>0.84</sub>Fe<sub>2.16</sub>O<sub>4</sub>, Fe<sub>1.94</sub>Co<sub>0.06</sub>O<sub>3</sub>; (6) NdFeO<sub>3</sub>, Fe<sub>2-u</sub>Co<sub>u</sub>O<sub>3</sub> (0.0 ≤ u ≤ 0.06).

temperature and oxygen pressure means that it is nonvariant, and therefore the compositions of all the coexisting phases within a given phase field are fixed. The composition of the solid solution  $NdCo_{0.1}Fe_{0.9}O_3$ coexisting with  $Co_{0.85}Fe_{0.15}O$  and  $Co_{1.38}Fe_{1.62}O_4$  in the field 3 of the isobaric-isothermal section of the phase diagram was determined as follows: the refined by the Rietveld method unit cell parameters of the orthorhombic perovskite solid solution coexisting with other phases in the samples from field 3 were compared with the concentration dependence of the unit cell parameters that have been obtained in the study of the  $NdCo_{1-x}Fe_xO_3$  cross-section ( $0.0 \le x \le 1.0$ ). In a similar way, it was shown that the perovskite phase coexisting with  $Co_{0.84}Fe_{2.16}O_4$  and  $Fe_{1.94}Co_{0.06}O_3$  in the field 5 is the practically unsubstituted neodymium ferrite NdFeO<sub>3</sub>.

### CONCLUSION

It is shown that a continuous series of solid solutions of NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> ( $0.0 \le x \le 1.0$ ) is formed in the Nd-Co-Fe-O system, orthorhombic distortions increase with increasing of iron content. Structural transitions of the  $O \rightarrow O' \rightarrow O$  type within the orthorhombic syngony framework occur within the compo-

sition range x = 0.0-0.1 and x = 0.1-0.2, respectively. All oxides are stoichiometric in oxygen content within the temperature range 298–1373 K in air. The average values of thermal expansion coefficients for NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> (x = 0.3, 0.7) are calculated. It was found that NdCo<sub>1-x</sub>Fe<sub>x</sub>O<sub>3</sub> solid solutions are semiconductors, and the substitution of cobalt for iron leads to a significant decrease of electrical conductivity. The calculated values of activation energies indicate the small polaron conductivity mechanism. An isobaric–isothermal section of the phase diagram of the quasi-ternary Nd–Co–Fe–O system at 1373 K in air has been constructed.

### ACKNOWLEDGMENTS

The work has been done within the framework of the project part of the State task of the Ministry of Education and Science of the Russian Federation and with partial financial support by Act 211 Government of the Russian Federation, (agreement no. 02.A03.21.0006).

#### REFERENCES

- 1. M. Dokiya, Solid State Ionics 152–153, 383 (2002).
- 2. H. J. M. Bouwmeester, Catal. Today 82, 141 (2003).

- H. M. Zhang, Y. Shimizu, Y. Teraoka, et al., J. Catal. 121, 432 (1990).
- D. N. Zybin, N. I. Lipatov, P. P. Pashinin, et al., Pis'ma Zh. Tekh. Fiz. 12, 622 (1986).
- C. Tealdi, M. S. Islam, C. A. J. Fisher, et al., Prog. Solid State Chem. 35, 491 (2007).
- L. Malavasi, C. Tealdi, G. Flor, et al., Sens. Actuat. 105, 407 (2005).
- 7. Zhang Ru, Hu Jifan, Han Zhouxiang, et al., J. Rare Earths 28, 591 (2010).
- H. Hashimoto, T. Kusunose, and T. Sekino, J. Alloys Compd. 484, 246 (2009).
- Z. Ali, I. Ahmad, B. Amin, et al., Physica A 406, 3800 (2011).
- 10. W. Chen, F. Li, and J. Yu, Mater. Lett. 61, 397 (2006).
- A. N. Petrov, A. Yu. Kropanev, V. M. Zhukovskii, et al., Zh. Neorg. Khim. 26, 3190 (1981).
- 12. J.-P. Coutures, J. M. Badie, R. Berjoan, et al., High Temp. Sci. 13, 331 (1980).
- 13. K. Kitayama, J. Solid State Chem. 76, 241 (1988).
- 14. K. Kitayama, J. Solid State Chem. 137, 255 (1998).
- 15. A. Olafsen, H. Fjellvåg, and B. C. Hauback, J. Solid State Chem. **151**, 46 (2000).
- A. N. Petrov, V. A. Cherepanov, A. Yu. Zuyev, et al., J. Solid State Chem. 77, 1 (1988).
- M. V. Kniga, I. I. Vygovskii, and E. E. Klementovich, Zh. Neorg. Khim. 24, 1171 (1979).
- T. Katsura, T. Sekine, K. Kitayama, et al., J. Solid State Chem. 23, 43 (1978).
- O. Opuchovic, G. Kreiza, J. Senvaitiene, et al., Dyes Pigm. **118**, 176 (2015).
- S. Chanda, S. Saha, A. Dutta, et al., Mater. Res. Bull. 48, 1688 (2013).
- 21. W. Slawiński, R. Przenioslo, I. Sosnowska, et al., Nucl. Instrum. Methods Phys. Res. B **254**, 149 (2007).
- 22. M. I. Godinko, M. A. Catarino, M. I. S. Pereira, et al., Electrochem. Acta **47**, 4307 (2002).
- 23. Y. Xu, J. Wei, J. Yao, et al., Mater. Lett. **62**, 1403 (2008).
- 24. J. Gwak, A. Ayral, V. Rouessac, et al., Micropor. Mesopor. Mater. **63**, 177 (2003).

- I. Sharifi, H. Shokrollahi, M. M. Doroodmand, et al., J. Magn. Magn. Mater. **324**, 1854 (2012).
- J. Mao, X. Hou, X. Wang, et al., Mater. Lett. 161, 652 (2015).
- B. D. Roiter and A. E. Paladino, J. Am. Ceram. Soc. 45, 128 (1962).
- 28. Dong Hoon Lee, Hong Seok Kim, Jeong Yong Lee, et al., Solid State Commun. **96**, 445 (1995).
- N. V. Proskurnina, V. A. Cherepanov, O. S. Golynets, et al., Inorg. Mater. 40, 955 (2004).
- F. Bartolomé and J. Bartolomé, Solid State Sci. 7, 700 (2005).
- V. K. Pecharsky and P. Y. Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Materials (Springer, 2009).
- 32. R. E. Dinnebier and S. J. L. Billinge, RSC Publ., 571 (2008).
- A. S. Urusova, V. A. Cherepanov, T. V. Aksenova, et al., J. Solid State Chem. 202, 207 (2013).
- 34. A. N. Petrov, V. A. Cherepanov, and A. Yu. Zuev, Zh. Fiz. Khim. 61, 630 (1987).
- 35. R. D. Shannon, Acta Crystallogr. Sect. A 32, 751 (1976).
- T. V. Aksenova, L. Ya. Gavrilova, D. S. Tsvetkov, et al., Russ. J. Phys. Chem. A 85, 427 (2011).
- 37. V. A. Cherepanov, L. Yu. Gavrilova, T. V. Aksenova, et al., Solid State Ionics **188**, 53 (2011).
- A. Yu. Zuev, V. V. Sereda, and D. S. Tsvetkov, J. Electrochem. Soc. 159, F594 (2012).
- S. R. Bishop, D. Marrocchelli, N. Perry, et al., ECS Trans. 57 (1), 643 (2013).
- 40. S. B. Adler, J. Am. Ceram. Soc. 84, 2117 (2001).
- 41. X. Liu and C. T. Prewitt, J. Phys. Chem. Solids **52**, 441 (1991).
- 42. S. Shafeie, J. Grins, S. Ya. Istomin, et al., J. Mater. Chem. 22, 16269 (2012).
- 43. K. T. Lee and A. Manthiram, J. Electrochem. Soc. **152**, A197 (2005).
- 44. N. Dasgupta, R. Krishnamoorthy, and J. K. Thomas, Solid State Ionics **149**, 227 (2002).