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The crystal structure and homogeneity range of the solid solutions in La–Sr–Co–Ni–O system

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Abstract

Two types of samples of general composition: $La_{1-x}Sr_xCo_{1-y}Ni_yO_{3-\delta}$ and $(La_{1-x}Sr_x)_2Co_{1-y}Ni_yO_4$ with various values of x and y were prepared by standard ceramic technique. Final annealing was performed at 1100 °C in air. Total duration of these anneals was 240–360 h. Identification of phase composition was made by powder XRD method. Crystal structure refinement was performed using Rietveld analysis. The homogeneity ranges of solid solutions were determined and presented in the composition fields.

Keywords: Electrode materials; Gas–solid reactions; X-ray diffraction; Thermal analysis

1. Introduction

Complex oxides with the general formula ABO_3 and A_2BO_4 with rare earth elements on the A sites and 3d-transition metals on the B sites, are well known for their catalytic activities, wide range of magnetic and electrical properties. A unique set of these properties makes them useful as electrode materials in the different electrochemical devices. Further investigations on these oxides have been carried out in order to find appropriate compositions with the best set of necessary properties. The traditional way of modifying the properties of materials is by partial substitution in different sublattices. In the present work the homogeneity ranges and crystal structure of solid solutions $La_{1-x}Sr_xCo_{1-y}Ni_yO_{3-\delta}$ and $(La_{1-x}Sr_x)_2Co_{1-y}Ni_yO_{4\pm\delta}$ were studied at 1100 °C in air.

The homogeneity range for $La_{1-x}Sr_xCoO_{3-\delta}$ at 1100 °C in air was found within $0 \leq x \leq 0.8$ [1] and for $LaCo_{1-y}Ni_yO_{3-\delta}$ within $0 \leq y \leq 0.6$ at the same conditions [2]. The rhombohedral distortions of perovskite-type structure decrease while the Sr-content increase in $La_{1-x}Sr_xCoO_{3-\delta}$ [1,3] (solid solutions with $x \geq 0.5$ possess ideal cubic structure) and increase as the nickel content increases in $LaCo_{1-x}Ni_xO_{3-\delta}$ [2]. $LaNiO_{3-\delta}$ can be obtained either at 1100 °C in an environment with higher oxygen pressure than in air or in air but at lower temperature ($T < 900$ °C).

The homogeneity range for $(La_{1-x}Sr_x)_2CoO_{4\pm\delta}$ was found at $0.3 \leq x \leq 0.55$ [1]. Solid solutions of $(La_{1-x}Sr_x)_2NiO_{4\pm\delta}$ general composition were synthesized by different authors [4–8] in different conditions. However, there is no information concerning the homogeneity range of this solid solution in air at 1100 °C. La_2CoO_4 can be synthesized at 1100 °C only at an oxygen partial pressure of $PO_2 < 10^{-4}$ atm. The limit of partial substitution of Ni by Co in $La_2Co_yNi_{1-y}O_{4\pm\delta}$ lies within $y = 0.1$–0.15 [2]. All single phases obtained in air possess tetragonal K_2NiF_4 type structure.

2. Experimental

Lanthanum oxide La_2O_3 (99.99% purity), nickel oxide NiO of 'special purity' grade, cobalt oxide Co_3O_4 of 'pure for analysis' grade and strontium carbonate $SrCO_3$ of 'special purity' grade were used as starting materials. The initial materials were dried in air: La_2O_3 at 1200 °C, Co_3O_4 and NiO at 700 °C and $SrCO_3$ at 600 °C during 3 h.

Samples were prepared by mixing the reactants in appropriate ratios, ground in an agate mortar, and fired in air at 850 °C for 24 h, at 950 °C for 24 h, and finally at 1100 °C for 240–360 h with intermediate grinding in alcohol every 20 h. All samples were quenched after firing.

In order to identify the phase compositions and to define

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the unit cell parameters, all samples were examined by X-ray diffraction, using DRF-4.0 and DRON-UM1 diffractometers with Cu Kα radiation. The equilibrium state was considered to be reached when the phase composition (i.e. X-ray patterns) remained unchanged during the last few stages of firing. The full profile Rietveld analysis using FULLPROF program [9] was used for the crystal structure refinement.

3. Results and discussion

3.1. $La_{1-x}Sr_xCo_{1-y}Ni_yO_{3-\delta}$

Thirty samples of different composition within the general formula $La_{1-x}Sr_xCo_{1-y}Ni_yO_{3-\delta}$ were prepared and analyzed. The homogeneity range of solid solution changes in such a way that while the nickel content increases the limiting strontium content decreases. This is in good agreement with the fact that strontium substitution in general increases the average oxidation state of 3d-transition metal, while nickel substitution leads to decrease it. The field of phase stability is shown in Fig. 1.

Similar to the lanthanum strontium cobaltates the rhombohedral distortions of $La_{1-x}Sr_xCo_{1-y}Ni_yO_{3-\delta}$ decrease while the Sr content increases, but with a lower rate. Thus, the composition $La_{0.5}Sr_{0.5}Co_{0.9}Ni_{0.1}O_{3-\delta}$ still has some small rhombohedral distortions, whereas 'pure' cobaltate is already cubic at Sr content $x=0.5$ (Fig. 2).

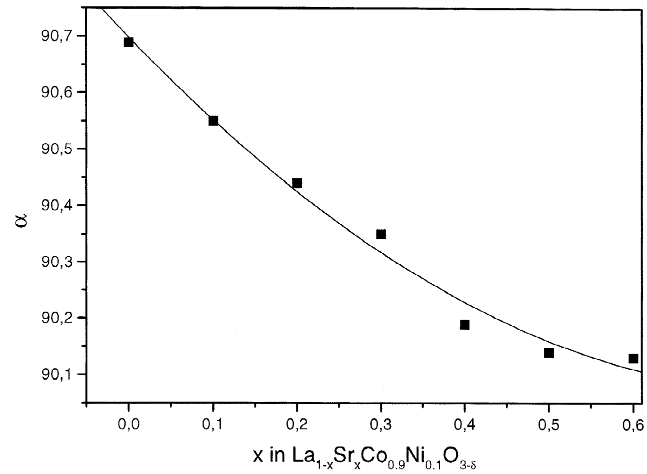

Fig. 2. The angle of pseudo-cubic cell of $La_{1-x}Sr_xCo_{0.9}Ni_{0.1}O_{3-\delta}$ with the perovskite-type structure.

3.2. $(La_{1-x}Sr_x)_2Co_{1-y}Ni_yO_{4\pm\delta}$

Forty-four samples of different composition with the general formula $(La_{1-x}Sr_x)_2Co_{1-y}Ni_yO_{4\pm\delta}$ were prepared and analyzed. The phase composition of all samples confirmed practically linear boundaries of the homogeneity ranges of $(La_{1-x}Sr_x)_2Co_{1-y}Ni_yO_{4\pm\delta}$ (Fig. 3). Obtained results correspond well to the homogeneity ranges of $(La_{1-x}Sr_x)_2CoO_{4\pm\delta}$ and $La_2Co_{1-y}Ni_yO_{4\pm\delta}$ found earlier [1,2]. The value of limiting composition of $(La_{1-x}Sr_x)_2NiO_{4\pm\delta}$ in air at 1100 °C was estimated within the range $0.4<x<0.45$.

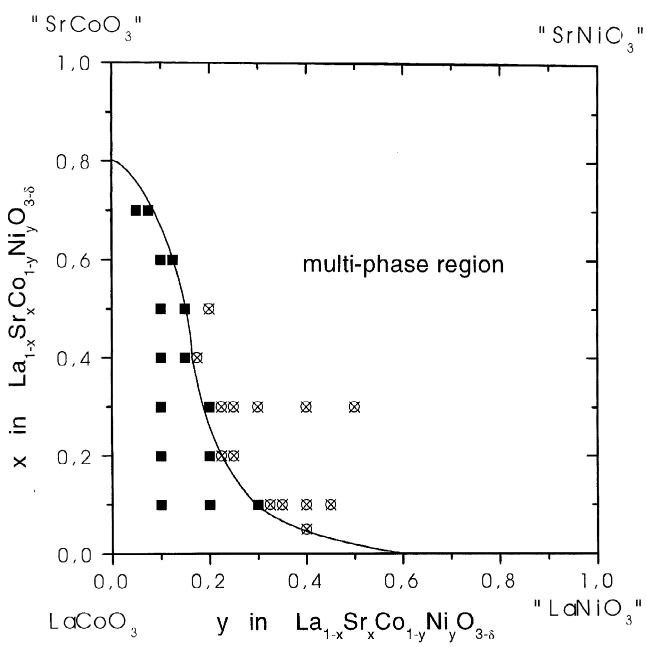

Fig. 1. The region of single phase stability of $La_{1-x}Sr_xCo_{1-y}Ni_yO_{3-\delta}$ at 1100 °C in air.

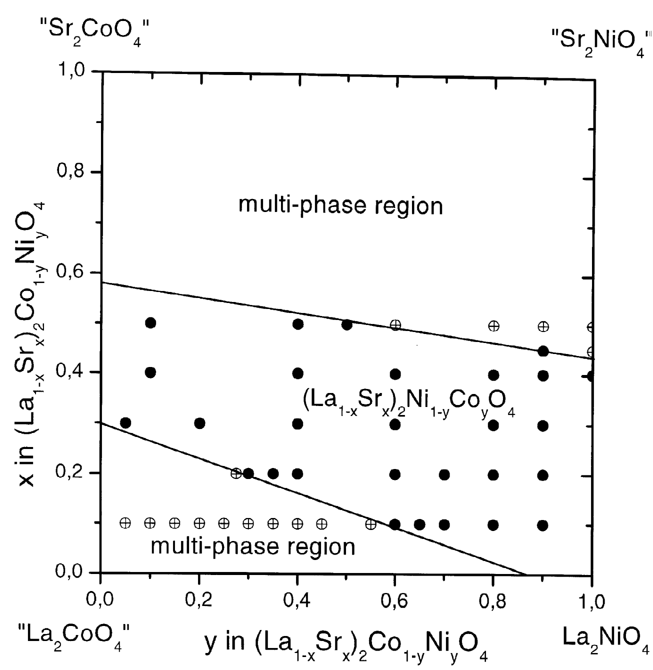

Fig. 3. The region of single phase stability of $(La_{1-x}Sr_x)_2Co_{1-y}Ni_yO_{4\pm\delta}$ at 1100 °C in air.

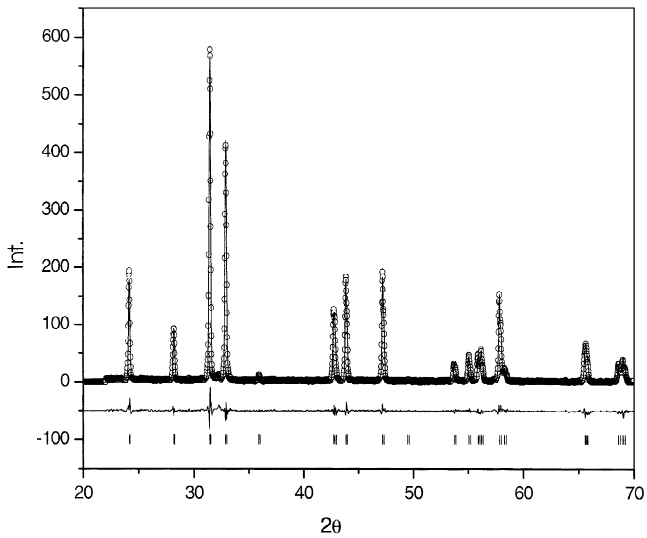

Fig. 4. X-ray diffraction powder pattern for $(La_{0.9}Sr_{0.1})_2Co_{0.1}Ni_{0.9}O_4$ refined by Rietveld analysis.

All solid solutions $(La_{1-x}Sr_x)_2Co_{1-y}Ni_yO_{4\pm\delta}$ within the homogeneity range have tetragonal K_2NiF_4 type structure (space group *I4/mmm*). The results of Rietveld structure refinement for $(La_{0.9}Sr_{0.1})_2Co_{0.1}Ni_{0.9}O_4$ is shown in Fig. 4 as an example.

Fig. 5 illustrates that partial substitution of Ni ions by Co at a constant La/Sr ratio leads to the decrease of the volume of the unit cell of $(La_{1-x}Sr_x)_2Co_{1-y}Ni_yO_{4\pm\delta}$ and parameter c, while parameter a slightly increased. This can be explained by the dimension factor. The ionic radius of cobalt ion is smaller than that of nickel ion (r^{2+}_{Co}=0.65 Å; r^{2+}_{Ni}=0.70 Å, c.n.=6) [10]. Structural parameters for the $(La_{0,9}Sr_{0,1})_2Co_xNi_{1-x}O_4$ are listed in Table 1 as an example.

Substitution of lanthanum for strontium leads to the increase of limiting cobalt content in $(La_{1-x}Sr_x)_2Co_{1-y}Ni_yO_{4\pm\delta}$ (Fig. 3). Introduction of Sr decrease the average oxidation state of cations in A-position, while cobalt reveals susceptibility to have higher oxidation state then +2 in conditions under investigation.

The complex changes of the unit cell parameters with the Sr content at constant Co/Ni ratio (Fig. 6) are caused

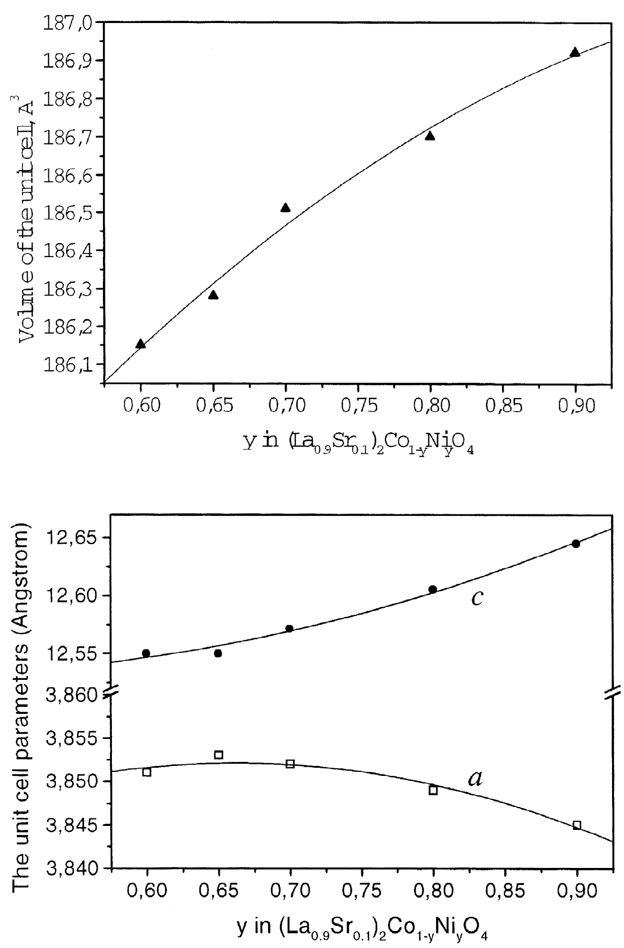

Fig. 5. The volume and unit cell parameters of $(La_{0.9}Sr_{0.1})_2Co_{1-y}Ni_yO_{4\pm\delta}$.

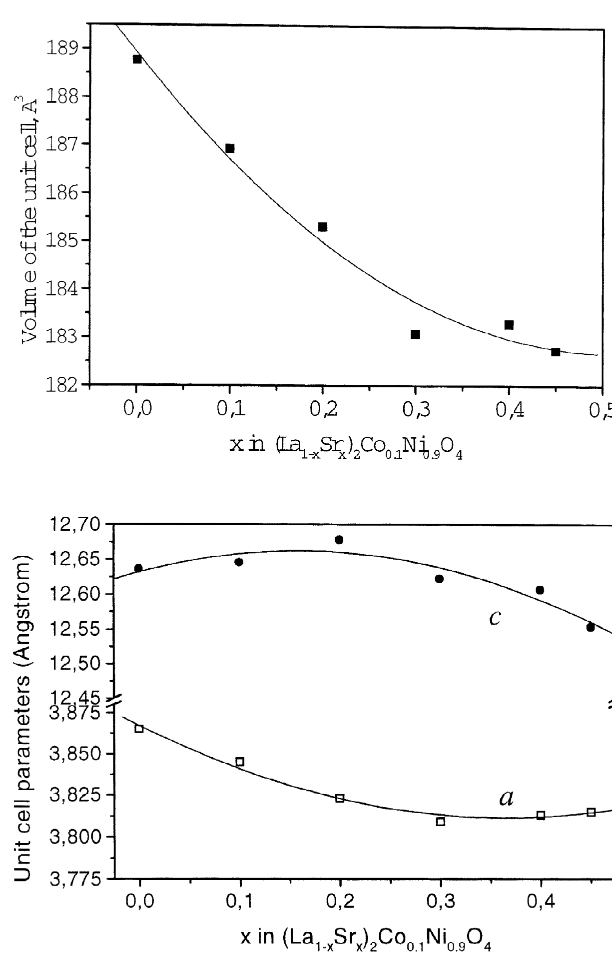

Fig. 6. The volume and unit cell parameters of $(La_{1-x}Sr_x)_2Co_{0.1}Ni_{0.9}O_{4\pm\delta}$.

Table 1
Structural parameters of $(La_{0.9}Sr_{0.1})_2Co_xNi_{1-x}O_4$, quenched from 1100 °C in air, space group *I4/mmm*: La(Sr), (0,0,*z*); Co(Ni), (0,0,0); O1, (0,0.5,0); O2, (0,0,*z*)

	Ni content (*x*)				
	0.1	0.2	0.3	0.35	0.4
Z, La(Sr)	0.362(0)	0.362(0)	0.362(0)	0.362(0)	0.362(1)
Z, O2	0.172(1)	0.172(1)	0.173(1)	0.175(2)	0.171(2)
L (Co–O1) (Å)	1.922(0)	1.924(0)	1.926(0)	1.926(1)	1.926(1)
L (Co–O2) (Å)	2.170(1)	2.164(1)	2.176(1)	2.193(0)	2.146(0)
L (La–O1) (Å)	2.594(1)	2.595(1)	2.591(1)	2.588(1)	2.591(1)
L (La–O2) (Å)	2.411(1)	2.397(1)	2.377(1)	2.353(0)	2.396(1)
R_{Br}	2.91	3.33	3.46	4.77	6.97
R_f	2.11	2.06	2.08	4.32	5.43

by two opposite tendencies. From the one hand the radii of strontium ions are larger than radii of lanthanum ion, however the increase of Sr content leads to the increase of average oxidation state of 3d-transition metals on B-sites with smaller ionic radii.

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