Phase equilibria in the La-Co-Ni-O system were studied at 1100°C in air. It was shown that all binary oxides existed at these conditions: LaCoO$_3$, La$_2$NiO$_4$, La$_3$Ni$_2$O$_7$ and La$_4$Ni$_3$O$_{10}$ in quasibinary systems formed corresponding solid solution: LaCo$_{1-x}$Ni$_x$O$_3$ with $0 < x < 0.6$, La$_2$Ni$_{1-y}$Co$_y$O$_4$ with $y = 0.1$, La$_3$(Ni$_{1.2}$Co$_{0.8}$)$_2$O$_7$ with $y = 0.025$ and La$_4$(Ni$_{1-y}$Co$_y$)$_3$O$_{10}$ with $0 < y < 0.6$. The crystal structure of all single phase samples was refined by Rietveld analysis. The phase equilibria in the examined system illustrated in the form of phase diagram.
EXPERIMENTAL

Lanthanum oxide La$_2$O$_3$ (99.99% purity), nickel oxide NiO of "special purity" grade and cobalt oxide Co$_3$O$_4$ of "pure for analysis" grade were used as starting materials. All were dried in air: La$_2$O$_3$ at 1200°C, Co$_3$O$_4$ and NiO at 700°C during 3 hours.

Different routes were used for the sample preparation. First route was a traditional ceramic technique. Samples were prepared by mixing the reactants in appropriate ratios, ground in an agate mortar, and fired in air at 850°C for 24 hrs, at 950°C for 24 hrs, and finally at 1100°C for 70-360 hrs with intermediate grinding in alcohol every 20 hrs. Another routes involved preparation through precursors. Because Co$_3$O$_4$ slowly dissolve in acid it was preliminary reduced in the flow of H$_2$ to metallic Co. Desired amounts of La$_2$O$_3$, NiO and Co were dissolved in diluted nitric acid, which was taken in small excess in respect to stoichiometry. Next step was performed in two different ways for different samples. (i) In the first way some amount of 5% polyvinyl alcohol solution was added to the nitrate solution; (ii) in the second case small excess of citric acid in respect to stoichiometric amount in order to transform nitrates to citrates was added. Then in both cases solutions were dried in air until they burned. Obtained ashes were placed to the crucible and slowly heated up to 1100°C. Total duration of this anneals was about 70 hrs.

In order to identify the phase compositions, all samples were examined by X-ray diffraction, using a DRON-3 diffractometer with Cu-Kα$_1$ radiation. The crystal structure of some samples was examined by neutron diffraction measurements. Powder neutron profiles were measured using two neutron diffractometers D7a (wavelength 1.5152 Å) and D3 (wavelength 2.425 Å) at the research reactor IVV-2, located near Ekaterinburg, Russia. The equilibrium state was considered to be reached when the phase composition (i.e. X-ray patterns) remained unchanged during last few stages of firing.

RESULTS AND DISCUSSION

LaCo$_{1.3}$Ni$_{0.7}$O$_4$

The samples of the general composition LaCo$_{1.4}$Ni$_{0.6}$O$_3$ (0≤x≤0.6) in step 0.1 and (0.6≤x≤0.7) in step 0.05 were prepared by ceramic technique. According to XRD a single phase with rhombohedrally distorted perovskite structure was found in the range 0≤x≤0.6. All samples with x>0.6 contained La$_4$(Ni$_{1.7}$Co$_{0.3}$)O$_{10}$ and Ni$_{1.8}$Co$_2$O as additional phases. It was shown that rhombohedral distortions of perovskite-type structure increase as the nickel content increases in LaCo$_{1.3}$Ni$_{0.7}$O$_4$. It caused by the tendency of nickel to decrease an average oxidation state of 3d-transition metals in B-site (by means of the oxygen nonstoichiometry increase). An ionic radius of Ni$^{2+}$ ions is larger than ionic radius of Co$^{3+}$. The changes of the unit cell parameters versus composition are shown in Fig.1.

La$_2$Ni$_{1.4}$Co$_{0.4}$

The samples of the general composition La$_2$Ni$_{1.5}$Co$_9$O$_4$ with y=0.1, 0.15, 0.2, 0.3 and 0.4 were prepared by ceramic technique described above. Total annealing time at the last stage was about 250 hrs. A single phase samples of La$_2$Ni$_{1.5}$Co$_9$O$_4$ composition were
obtained only for y=0.1. It has tetragonal K₂NiF₄-type structure. Structural parameters refined by Rietveld method are listed in Table 1.

![Graph showing the unit cell parameters versus composition of LaCo₁₋ₓNiₓO₃₋₀.]

**Fig. 1.** The unit cell parameters versus composition of LaCo₁₋ₓNiₓO₃₋₀.

**TABLE 1**

| Structural parameters for La₂(Ni₁₋ₓCoₓ)O₄, sp.gr. I₄/mmm: |
|-------------------------------------------------------------|
| La – (0,0,z); Ni(Co) – (0,0,0); O₁ – (0,0.5, 0); O₂ – (0,0,z) |
| La₂NiO₄ | La₂Ni₀.₉Co₀.₁O₄ |
| z, La | 0.3603(3) | 0.3607(2) |
| z, O₂ | 0.1770(3) | 0.1763(2) |
| L(Ni-O₁), Å | 1.9303(2) | 1.9327(1) |
| L(Ni-O₂), Å | 2.2427 | 2.2277 |
| L(La-O₁), Å | 2.6190 | 2.6140 |
| L(La-O₂), Å | 2.3225 | 2.3300 |
| a, Å | 3.8606(2) | 3.8653(1) |
| c, Å | 12.6707(8) | 12.6358(5) |
| R_{Br} | 5.19 | 4.08 |
| R_{f} | 4.74 | 2.87 |

**TABLE 2**

| The unit cell parameters for La₃(Ni₁₋ₓCoₓ)₂O₇ (sp.gr. Cmcm) obtained from XRD |
|--------------------------------------------------------------------------------|
| a, Å | b, Å | c, Å | V, Å³ | R_{f} | R_{Br} |
| La₃Ni₂O₇ | 5.4491(2) | 5.3995(9) | 20.4971(1) | 603.072(1) | 7.21 | 10.2 |
| La₃Ni₁.₉Co₀.₀₅O₇ | 5.4466(3) | 5.3966(4) | 20.5020(7) | 602.616(4) | 2.32 | 1.64 |

**La₃(Ni₁₋ₓCoₓ)₂O₇**

Neither La₃Ni₂O₇ nor La₃(Ni₁₋ₓCoₓ)₂O₇ solid solutions were obtained as a single phases by ceramic technique. Only wet methods using nitrates with polyvinil alcohol solutions or citrates as precursors allowed to prepare single phase samples for y=0, 0.025 after 75-170 hrs firing at 1100°C. Both samples possess orthorhombic (Cmcm space...
group) structure which is in good agreement with results obtained in (11). The unit cell parameters refined by Rietveld method are listed in Table 2.

Using the results of neutron diffraction measurements it was shown that the lowering of symmetry from tetragonal in ideal $A_3B_2O_7$ to orthorhombic in obtained oxides caused by significant distortion of the oxygen octahedrons in $La_3(Ni_{1-x}Co_y)O_7$. There are four different Ni-O interatomic distances in NiO$_6$ octahedron (Table 3).

**TABLE 3**
Crystal structure data for $La_3Ni_2O_7$ (*Cmcm*) from d7a neutron powder data at 300 K and interatomic distances

| x    | y    | z    | B$_i$ Å$^2$ | n  |
|------|------|------|-------------|----|
| 0    | 0.268(2) | 0.25 | 0.25(9)    | 1  |
| 0.3170(3) | 0.269(2) | 0.25 | 0.25(9)    | 2  |
| 0.0964(3) | 0.259(2) | 0.25 | 0.99(9)    | 2  |
| 0.297(3) | 0.257(9) | 0.25 | 0.84(3)    | 2  |
| 0.2030(6) | 0.2141(2) | 0.25 | 1.41(22)   | 2  |
| 0.1044(6) | 0.5    | 0    | 0.42(11)   | 2  |
| 0.0899(6) | 0.297(3) | 0.5  | 0.42(11)   | 2  |

| Bond type | Bond length | Bond type | Bond length |
|-----------|-------------|-----------|-------------|
| La1-O1    | 2.543(9)    | La2-O3    | 2.557(9)    |
| x1        | 2.907(8)    | x2        | 2.679(7)    |
| x2        | 2.722(2)    | Ni-O1     | 1.988(7)    |
| x4        | 2.911(7)    | Ni-O2     | 2.188(8)    |
| x4        | 2.596(7)    | Ni-O3     | 1.891(7)    |
| x1        | 2.366(9)    | Ni-O4     | 1.958(7)    |
| x1        | 3.023(8)    | x2        | 2.730(2)    |
| x1        | 2.486(8)    |           |             |

$La_4(Ni_{1-x}Co_y)O_{10}$

Single phase solid solutions were obtained in the range $0 \leq y \leq 0.6$. It should be noted that Co-rich samples (within the composition range $0.25 \leq y \leq 0.6$) prepared more easily even by ceramic route. Meanwhile the samples within the composition range $0 \leq y \leq 0.2$ need either incredibly long annealing time or usage of precursors. All single phase samples were described in *Cmca* space group. The unit cell parameters are listed in Table 4.

Two different type of oxygen octahedrons were found in $La_4Ni_3O_{10}$ according to the neutron diffraction measurements – practically ideal octahedron, centered by Ni1, surrounded by distorted octahedrons, centered by Ni2 ions. There are two approaches for estimation of the ion oxidation state in the oxides based on the crystallographic data. First take into account average cation-anion distance (14); second, so-called bond
valence approach, treated each bond as an individual and hence irregularities or distortions in coordination environments can be taken into account (15).

### TABLE 4
The unit cell parameters for La₄(Ni₁₋ₓCoy)₃O₁₀ (sp.gr. Cmca) obtained from XRD

| y  | a, Å   | b, Å   | c, Å   | V, Å³  | R_Br  | R_f  |
|----|--------|--------|--------|--------|-------|------|
| 0  | 5.408(1)| 5.465(1)| 28.037(2)| 828.7(1)| 2.51  | 1.98 |
| 0,1| 5.412(1)| 5.465(1)| 27.961(2)| 827.0(1)| 3.11  | 2.19 |
| 0,2| 5.414(1)| 5.466(1)| 27.948(2)| 827.0(1)| 4.01  | 3.14 |
| 0,3| 5.414(1)| 5.464(1)| 28.086(4)| 830.7(2)| 4.84  | 2.76 |
| 0,4| 5.416(1)| 5.468(1)| 28.033(4)| 830.3(2)| 5.58  | 2.88 |
| 0,5| 5.413(1)| 5.465(1)| 27.817(2)| 822.8(1)| 3.02  | 2.02 |
| 0,6| 5.412(1)| 5.463(1)| 27.766(2)| 821.1(1)| 3.48  | 2.25 |

### TABLE 5
Crystal structure data for La₄Ni₃O₁₀ (Cmca) from d3 neutron powder data at 300 K

| x  | y  | z   | B, Å⁻² | n  |
|----|----|-----|--------|----|
| Ni1| 0  | 0   | 0.41(6)| 1  |
| Ni2| 0  | 0.1382(4)| -0.0035(9)| 0.41(6)| 2  |
| La1| 0  | 0.4347(4)| -0.0066(9)| 0.41(6)| 2  |
| La2| 0  | 0.2997(4)| -0.0096(9)| 0.41(6)| 2  |
| O1 | 0.25| 0.0061(7)| 0.25| 0.41(6)| 2  |
| O2 | 0  | 0.0682(6)| 0.9554(9)| 0.41(6)| 2  |
| O3 | 0.25| 0.1353(7)| 0.25| 0.41(6)| 2  |
| O4 | 0  | 0.2188(8)| 0.0273(9)| 0.41(6)| 2  |
| O5 | 0.25| 0.1436(9)| 0.25| 0.41(6)| 2  |

| Bond type | multiple | Bond length | Bond type | multiple | Bond length |
|-----------|----------|-------------|-----------|----------|-------------|
| La1-O1    | x2       | 2.791(9) Ni1-O1 | x4       | 1.926(2) |
|           | x2       | 2.519(8)       |           | 1.928(9) |
| La1-O2    | x1       | 2.928(9) Ni1-O2 | x2       | 1.970(8) |
|           | x1       | 2.515(4)       |           | 1.934(2) |
| La1-O3    | x2       | 2.725(9) Ni2-O2 | x1       | 2.270(7) |
| La1-O5    | x2       | 2.898(9) Ni2-O3 | x2       | 2.193(9) |
| La2-O3    | x1       | 2.620(9) Ni2-O4 | x1       | 2.193(9) |
| La2-O4    | x1       | 2.377(9) Ni2-O5 | x2       | 2.72   |
|           | x1       | 2.573(8)       |           | 2.72   |
|           | x1       | 2.966(9) Val(Ni2) | x2       | 2.72   |
|           | x2       | 2.756(5)       |           | 2.72   |
|           | x2       | 2.483(7)       |           | 2.72   |
Nickel ions in all complex oxides under investigation have coordination number 6. Therefore average bond length for Ni positions can characterized their oxidation states. Estimation of the oxidation state of Ni ions was made assuming linear change of bond length with oxidation state based on two points for L(Ni-O): 2.088 Å for Ni^{2+} and 1.962 Å for Ni^{3+}. Oxidation state of nickel ions obtained from the values of bond length increase from La$_2$NiO$_4$ to La$_4$Ni$_3$O$_{10}$ in a same way as it follows from calculations based on chemical formulas. However Ni ions in nonequivalent sites in La$_4$Ni$_3$O$_{10}$ have different oxidation states (Table 5). Thus it is possible to claim that Ni$^{3+}$ preferably occupied NiI sites, i.e. it is possible to assume some charge ordering inside lattice.

Both samples of the nominal composition La$_4$(Ni$_{1-y}$Co$_y$)$_3$O$_{10}$ with $y$=0.65 and 0.7 consisted of La$_4$(Ni$_{0.4}$Co$_{0.6}$)$_3$O$_{10}$, LaCo$_{1-x}$Ni$_x$O$_{3.8}$ with fixed x and La$_2$O$_3$.

The phase diagram

The results of XRD patterns of more than 70 samples of different composition allowed us to divide the phase triangle as shown in Fig.2. Fixed composition of perovskite phase coexisted in the samples within field II, which is determine the phase boundary between fields I – II and II – IX was estimated as $x$=0.12 and found based on the concentration dependence of unit cell parameters of LaCo$_{1-x}$Ni$_x$O$_{3.8}$.

CONCLUSION

It was shown that each binary oxide existed in the La-Co-O and La-Ni-O systems at 1100°C in air formed correspondent solid solution: LaCo$_{1-x}$Ni$_x$O$_{3.8}$ ($0 \leq x \leq 0.6$), La$_2$Ni$_{1-y}$Co$_y$O$_4$ with $y$=0.1, La$_3$(Ni$_{1-y}$Co$_y$)$_2$O$_7$ with $y$=0.025 and La$_4$(Ni$_{1-y}$Co$_y$)$_3$O$_{10}$ with $0 \leq y \leq 0.6$. The phase equilibria in the system represented in the form of phase diagram (Gibbs triangle).

ACKNOWLEDGMENTS

The research described in this publication was made possible in part by award No REC 005 of the US civilian Research & Development Foundation for the Independent States of Former Soviet Union (CRDF), by grant No 00-03-32070 of the Russian Basic Science Foundation and by grants from the Russian State Scientific and Technical Program division “Neutron Investigations of Condensed Matter” (project N°4), “Physics of quantum and wave processes” division “Statistical Physics” (project N VIII-6).
Fig. 2. The phase diagram of La-Co-Ni-O system at 1100°C in air. The phase composition in the fields are: I - La$_2$O$_3$ + La$_{1,2}$Ni$_{0,9}$O$_{3,5}$ (0≤x≤0.12); II - La$_2$O$_3$ + La$_{0,88}$Ni$_{0,12}$O$_{3,5}$ + La$_4$(Ni$_{0,4}$Co$_{0,6}$)$_3$O$_{10}$; III - La$_2$O$_3$ + La$_4$(Ni$_{0,7}$Co$_{0,3}$)$_3$O$_{10}$ (0.43≤y≤0.6); IV - La$_2$O$_3$ + La$_4$(Ni$_{0,57}$Co$_{0,43}$)$_3$O$_{10}$ + La$_2$Ni$_{0,88}$Co$_{0,12}$O$_4$; V - La$_2$O$_3$ + La$_2$Ni$_{1,0}$Co$_{0,4}$O$_4$ (0≤y≤0.12); VI - La$_2$Ni$_{0,88}$Co$_{0,12}$O$_4$ + La$_4$(Ni$_{0,57}$Co$_{0,43}$)$_3$O$_{10}$ + La$_2$(Ni$_{0,975}$Co$_{0,025}$)$_2$O$_7$; VII - La$_2$Ni$_{1,0}$Co$_{0,4}$O$_4$ (0≤y≤0.12) + La$_3$(Ni$_{1,3}$Co$_{0,7}$)$_2$O$_7$ (0≤y≤0.025); VIII - La$_4$(Ni$_{1,3}$Co$_{0,7}$)$_3$O$_{10}$ (0≤y≤0.025) + La$_4$(Ni$_{1,3}$Co$_{0,7}$)$_3$O$_{10}$ (0≤y≤0.43); IX - La$_2$(Ni$_{1,3}$Co$_{0,7}$)$_3$O$_{10}$ (0.3y≤0.6) + La$_4$(Ni$_{1,3}$Co$_{0,7}$)$_3$O$_{10}$ (0.12≤x≤0.6); X - La$_4$(Ni$_{1,3}$Co$_{0,7}$)$_3$O$_{10}$ + La$_4$(Ni$_{1,3}$Co$_{0,7}$)$_3$O$_{10}$ + Co$_{0,02}$Ni$_{0,98}$O; XI - La$_4$(Ni$_{1,3}$Co$_{0,7}$)$_3$O$_{10}$ (0≤y≤0.3) + Co$_{1,2}$Ni$_2$O (0.98≤z≤1); XII - La$_{1,3}$Ni$_{0,9}$Co$_{0,1}$O$_{3,5}$ (0≤x≤0.6) + Co$_{1,2}$Ni$_2$O (0≤z≤0.98).

REFERENCES:

1. J. J. Janecek, G. P. Wirthz, *J. Amer. Chem. Soc.*, 61, 242 (1978).
2. M. Seppanen, M. Kyto, P. Taskinen, *Scand. J. Met.*, 8, 199 (1979).
3. A. N. Petrov, V. A. Cherepanov, E. M. Novitsky, V. M. Zhukovsky, *Russian J. Phys. Chem.*, 58, 2662 (1984).
4. A. N. Petrov, V. A. Cherepanov, A. Yu. Zuev, V. M. Zhukovsky, *J.Solid State Chem.*, 75, 1 (1988).
5. A. Rabenau, F. Eckerlin, *Acta Crystallogr.*, 11, 304 (1958).
6. M. Seppanen, *Scand. J. Met.*, 8, 191 (1979).
7. J. Drennan, C. P. Tavares, B. C. H. Steele, *Mat.Res.Bull.*, 17, 621 (1982).

464 Electrochemical Society Proceedings Volume 2001-16
(8) Z. Zhang, M. Greenblatt, J. B. Goodenough, *J. Solid State Chem.*, 108, 402, (1994).
(9) Z. Zhang, M. Greenblatt, *J. Solid State Chem.*, 117, 236, (1995).
(10) M. D. Carvalho, F. M. A. Costa, I. S. Pereira, A. Wattiaux, J. M. Bassat, J. C. Grenier, M. Pouchard, *J. Mater Chem.*, 7, 2107 (1997).
(11) C. D. Ling, D. N. Argyriou, G. Wu, J. J. Neumeier, *J. Solid State Chem.*, 152, 517 (1999).

(12) J. Gopalakrishnan, G. Colsmann, B. Reuter, *Z. Anorg. Allg. Chem.*, 424, 155 (1976).

(13) S. Aasland, H. Fjellvag, B. C. Hauback, *J. Solid State Chem.*, 135, 103 (1998).

(14) P. Poix in *Seminaires de Chimie de l'Etat Solide: Relationship between anion-cation distance and unit cell parameters*, J.P. Suchet Editor, p.49, translated from French, Metallurgy, Moscow, (1972).

(15) Brown I.D. and Aldermatt D., *Acta Crystallogr.*, B41, 244 (1985).