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Synthesis and Properties of Polycharge Phases in the System La-Li-M-Co-O (M=Ca, Sr, Ba)

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Samples of La$_{1-3x}$Li$_x$M$_{2x}$CoO$_{3-\delta}$ (M = Ca, Sr, Ba; $0 \leq x \leq 0.1$) were synthesized by co-precipitation method. It is shown that the region of their homogeneity lies in the range of substitutions $0 \leq x \leq 0.05$. The volume of the unit cell increases with the size of the alkaline earth metal that replaces lanthanum. Surface morphology of the obtained mixed oxides was studied by SEM. In all samples (except strontium - containing) paramagnetic Co^{2+} ions from the impurity Co$_3$O$_4$, which are in different local environments and have different degrees of exchange interaction with each other, are contained in the form of chain fragments -Co^{2+}-O^{2-}-Co^{2+}-O^{2-}-Co^{2+}-O$^{2—}$ and contain defective centers Co^{2+}, which are formed during the desorption of lattice oxygen from the surface, or in the process of diffusion of oxygen from the volume of material to the surface. In strontium-containing samples La$_{0.85}$Li$_{x0.05}$Sr$_{0.01}$CoO$_{3-\delta}$ there are mainly ferromagnetic clusters Co^{3+}-Co^{4+}.

Keywords: LaCoO$_3$; mixed oxides; lanthanum cobaltates; perovskite-like structure; surface morphology; FMR; diffuse reflection spectra; cluster spin glass.

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Introduction

In multicomponent oxide systems Ln – Co – O, wide fields of homogeneity of unlimited solid solutions are observed, and their ordering takes place with the formation of phases with a perovskite-like structure. During heterovalent cationic substitution, the primary structure remains unchanged, but there is an uncompensated conditional electric charge of the cationic sublattice.

Muhumuza et al. and Ao et al. proved that it is the uncompensated electric charge that causes the unique electrophysical and catalytic properties of these materials [1, 2].

Currently, there is no unambiguous understanding of the mechanisms of uncompensated electric charge in the phases of complex oxides. Among the most probable assumptions are: the occurrence of defects (vacancies) in the anionic oxygen lattice, changes in the apparent degree of oxidation of Co, changes in the coordination of the oxygen environment of cations with changes in the length of the metal-oxygen bond and partial curvature of the primary perovskite-like structure. In our opinion, the latter mechanism is the most correct in terms of structural chemistry and practically combines the two previous ones.

The unique electrophysical properties of cobaltates are conditioned by the competition of low-spin, intermediate spin and high-spin states. Despite the significant amount of work in this direction, the mechanism of spin transitions and the influence of the simultaneous introduction of polyvalent substituents on the properties of the samples, which is of both theoretical and practical interest, has not been clearly established.

Therefore, we can assume that the main purpose of the synthesis of such materials is to create phases with the most uncompensated conditional electric charge.

This can be achieved by heterovalent replacement of the cation with a lower charge in the maximum possible amount, which does not dramatically change the perovskite-like structure and does not shift the phase composition outside the homogeneity region. The maximum possible amount of doped cation is determined by the principle of tolerance and depends on its radius and crystallographic position (coordination) in the structure of perovskite.

The aim of this work was the synthesis of perovskite-like phases and the establishment of the influence of the type and amount of the heterocharging substitution cation on the polycharging of cobalt cations.

Currently, there is a wide range of methods for obtaining complex rare earth cobaltates of different size ranges: from nano- to micro-size. Depending on the requirements for the physicochemical properties of ceramics, it is obtained either by the solid-phase method or by the methods of chemical homogenization from solutions. For example, catalysis requires ceramics with submicron particle size, and this is achieved through the use of methods of chemical homogenization from solutions: co-precipitation method, sol-gel method. Both ceramic method and methods of chemical homogenization from solutions methods are most often used to obtain superconducting compounds, as well as ferrites and complex oxides with dielectric properties.

Synthesis methods that use chemical homogenization have significant advantages over ceramic. Synthesis from solutions in comparison with synthesis from oxides or their solid salts requires much lower annealing temperatures and provides homogenization at the ionic-molecular level, which allows to obtain materials with a high degree of homogeneity. In addition, using chemical methods of homogenization can increase the specific surface area of complex oxides and thus improve their catalytic properties.

However, when using methods of chemical homogenization from solutions we should also take into account some preparative features of the synthesis. In particular, in some cases, co-precipitation causes a problem associated with different rates of deposition of individual components of the solution. Therefore, for the method of co-precipitation of components one of the main criteria is the choice of precipitator and pH of precipitation.

Synthesis of oxides by the method of co-precipitation of components was developed in previous works [3-5].

I. Materials and methods

Synthesis of samples in the system $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; $0 \le x \le 0.1$) was performed in two stages. In the first stage, a precursor was obtained by calcining a co-precipitated mixture of cobalt, lanthanum and alkaly hydroxooxalates at 1023 K for 36 hours.

For this purpose, a mixture of co-precipitated hydroxycarbonates of lanthanum, alkaline earth metals and cobalt was obtained by precipitation from aqueous solutions of nitrates of the corresponding metals mixed in the required proportions 1M Na_2CO_3 („CP”) in the ratio 1:1.75.

Coprecipitation was carried out with vigorous stirring on a magnetic mixer. The mother solutions were tested by the methods of qualitative analysis for the absence of sodium cations (reaction with zinc uranyl acetate) [3]. After ageing, the precipitate was filtered off, washed with a water-alcohol (1:1 by volume) mixture, then with a large amount of distilled water and absolute ethyl alcohol. The color of the obtained co-precipitated hydroxycarbonates of lanthanum, alkaline earth metals and cobalt was mainly pink-violet.

The precipitate products were air-dried, ground in an agate mortar and subjected to heat treatment with intermediate grinding after 12 and 24 hours of heat treatment. In the second stage, the resulting mixture was grated with a stoichiometric amount of lithium carbonate Li_2CO_3 (“CP”) and annealed at 1073 K (36 hours with intermediate grinding after 12 and 24 hours of heat treatment) to form the final product. Next, the resulting mixture was homogenized, compressed into tablets at a pressure of 100 MPa and kept for about 36 hours at 1123 K in air.

The structural features of the synthesized phases were studied by X-ray diffraction on Shimadzu LabX XRD-6000 diffractometers (CuKα - radiation, $\lambda = 0.154056$ nm, range of angles $5 \le 2\theta \le 70°$ samples in the form of powders). Shooting was performed at a speed 1-2 °/min.

Further calculations of the obtained X-ray diffractograms (assignment of diffractograms, calculation and refinement of the crystal lattice parameters) were performed using the Match software [6]. The results of the calculations were compared with the data given in the literature, on the basis of which a conclusion was made about the phase composition and structure of the samples. The database of the International Committee for Powder Diffraction Standards (JCPDS PDF-2) was also used to identify the phases in the studied systems.

The average crystallite size of the substituted cobaltates was calculated by the X-ray line broadening method using the Scherrer formula [7]:

$$D_{012} = \frac{K \cdot \lambda}{\beta_{012} \cdot \cos\theta_{012}} , \qquad (1)$$

where D_{012}(nm) is the average size of crystallites along the direction normal to the diffraction plane (012), K is a constant related to crystallite shape, normally equal to 0.9, λ is the x-ray wavelength 0.15406 (nm) of $Cu_{K\alpha}$ radiation, β_{012} is the integral breadth of the peak related to the diffraction plane (012) and θ_{012} is the Bragg angle in radians for the crystallographic plane (012). Taking into account that the integral width of the peak in the diffractogram is approximated by the pseudo-Voigt function with a large (up to 90% or more) contribution of the Lorentz function, the Lorentzian was used to describe the shape of the diffraction reflection at $2\theta \approx 22.8°$. In order to exclude the instrumental broadening $\beta_{inst.}$, a standard silicon (Si) X-ray powder diffraction data is recorded under the same condition. The integral width of the peak was calculated by the formula [8]:

$$\beta_{012} = \beta_{exp} - \beta_{inst}\,, \qquad (2)$$

where β_{exp} is the experimental width of the sample peak at half the maximum intensity; β_{inst} – instrumental broadening of the diffraction line, which depends on the design features of the diffractometer (in radians).

The process of batch decomposition was monitored by IR spectral method. IR absorption spectra of thermolysis products in the range of 400-4000 cm^{-1} were recorded on a Perkin Elmer Spectrum BXFT-IR Spectrophotometer in a tablet mixture with KBr. The error in measuring the oscillation frequencies was ± 2 cm^{-1}.

The morphological features and particle sizes of solid solutions were determined by scanning electron microscopy (SEM) using a Hitachi S-2400 microscope. Image processing and analysis were performed using the ImageJ program.

Diffuse reflectance spectra in the 400–800 nm range were recorded on a UV/VIS Varian Cary 5000 spectrophotometer; magnesium oxide was used as the reflectance standard.

Electron paramagnetic resonance spectra of polycrystalline samples were recorded at room temperature on a Bruker Elexsys E580 spectrometer. Experiment parameters: microwave power 2 mW, radiation frequency ~ 9.9 GHz, modulation intensity 2 Gs, modulation frequency 100 kHz, sweep time 300 s, 1024 point sampling 1024 points. The spectra were processed using the WINEPR Bruker program. The concentration of paramagnetic centers was estimated by comparing the integral intensities of the spectra of the studied and reference ($CuSO_4*5H_2O$) samples.

The oxygen index in cobaltates was determined by iodometric titration. A sample of $La_{1-3x}Li_xM_{2x}CoO_{3\pm\delta}$ (M = Ca, Sr, Ba; $0 \leq x \leq 0.1$) m = 0.05 mg was placed in a flask, then were added 10 mL of HCl solution (C_N = 0.7 mol/L) and 10 mL KI solution (C_N = 1 mol/L). The process of sample dissolution lasted on average from 10 to 30 min. The iodine formed after the dissolution of the substituted cobaltate powder was titrated with a $Na_2S_2O_3$ solution (C_N = 0.1 mol/L) using a freshly prepared starch solution as an indicator. The error in determining the oxygen content during iodometric titration is ±0.02.

It is known that KI can be oxidized in the presence of light in the presence of atmospheric oxygen according to the scheme:

$$4KI + O_2 + 2H_2O \rightarrow 2I_2 + 4KOH$$

To minimize the loss of iodine, a so-called "control experiment" (without a sample) was carried out.

The oxygen index, as well as the average oxidation state of the transition metal (in this case, cobalt), were determined in air at room temperature. For complex oxides with a perovskite structure (ABO_3 type), partial substitution in the A and/or B positions can lead to a change in the cobalt oxidation state and/or the formation of oxygen vacancies.

The value of the oxygen index (3-δ) was calculated by the formula:

$$3-\delta = 2.5 - 2\cdot x + \frac{0.001\cdot N\cdot(V_S - V_0)\cdot M_r}{2\cdot m - 0.016\cdot N\cdot(V_S - V_0)}\,, \qquad (3)$$

where N, V_s and V_0 are the concentration (mol/L) and volume (mL) of the $Na_2S_2O_3$ solution used for titration of sample and in "control experiment", respectively; M_r is the molecular weight of the reduced form of the substance $La^{3+}_{1-3x}Li^{+1}_{x}M^{+2}_{2x}Co^{+2}O_{3-\delta}$ (g/mol).

II. Results and discussion

For solid solutions in the system $La_{1-x}Me_xCoO_3$ (Me=Ca, Sr, Ba) it is known that they exist in the whole range of substitutions. The magnitude of the rhombohedral distortion decreases with increasing alkaline earth metal content and at x = 0.5 the compositions take a cubic structure [9-12].

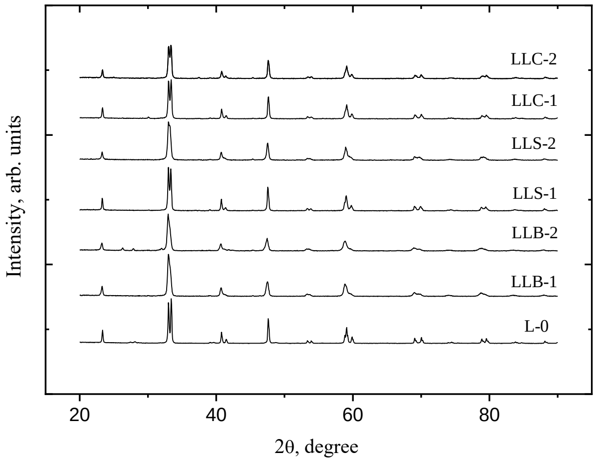


Fig. 1. The X-ray powder diffraction patterns of $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$: L-0 ($x$ = 0),
LLB-1 (M = Ba; x = 0.05), LLB-2 (M = Ba; x = 0.1), LLS-1 (M = Sr; x = 0.05), LLS-2 (M = Sr; x = 0.1), LLC-1 (M = Ca; x = 0.05) and LLC-2 (M = Ca; x = 0.1).

The X-ray powder diffraction patterns of $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; $0 \leq x \leq 0.1$) samples are shown in Figure 1. It can be seen that the cobaltates of lanthanum, modified by alkali earth metals and lithium, have at room temperature rhombohedrally distorted perovskite cell (SG *R-3c*) with the parameters shown in Table 1. When lithium and alkali earth metal ions are introduced into the structure of the initial $LaCoO_{3-\delta}$, there is a slight increase in the parameters of the unit cell associated with the change in the ionic radius of the substituent. It should be noted that due to the slight difference in the ionic radii of the La^{3+} and Ca^{2+} cations, the lattice parameters do not really change during the transition from the initial matrix to Ca-containing cobaltates.

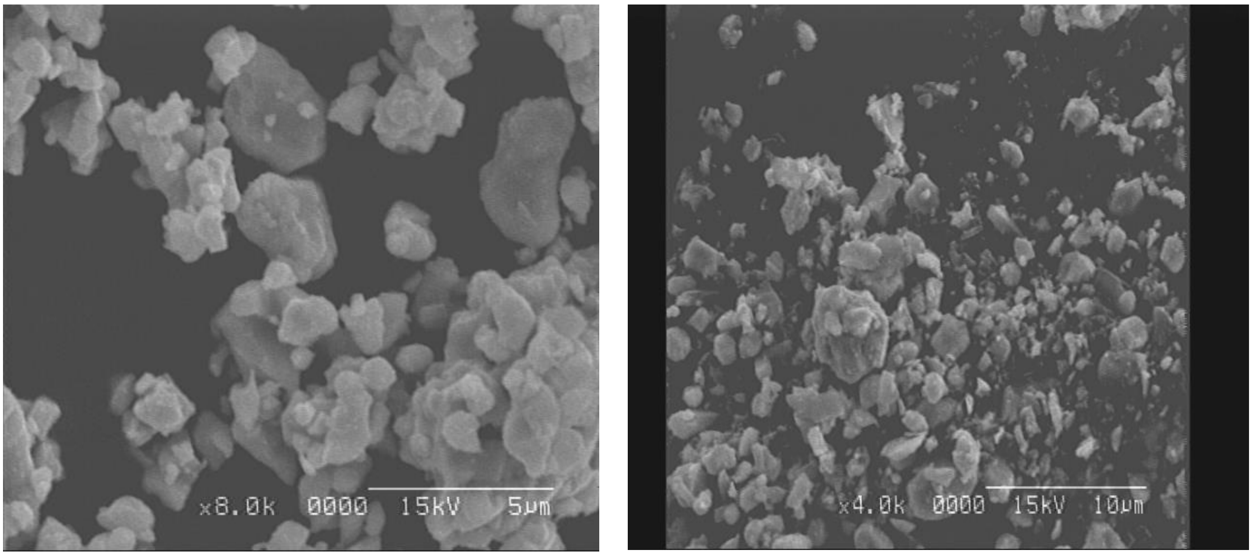
The crystallites size D of (102) planes of complex oxides were calculated from X-ray diffraction data on the expansion of the diffraction maximum with an angle of $2\theta \approx 23.3$. As can be seen from Table 1, the average value of D_{102} varied from 32 nm to 73 nm depending on the steric factor of the modifying additives. Thus, the obtained data confirm the fact of formation of nanoparticles of substituted cobaltates of lanthanum.

Figure 2 shows SEM images of the surface of nanocrystalline solid solutions $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; $0 \leq x \leq 0.05$). Based on these data, it can be validated that the grains of substituted cobaltates are

Table 1

Unit cell parameters and grain sizes of oxides with perovskite structure $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; $0 \le x \le 0.1$).

Sample	Unit cell parameters			D_{102}, nm	D_{SEM}, nm
	a, nm	*c*, nm	*V*, nm^3		
$LaCoO_{3-\delta}$	0.5438(7)	1.3085(9)	0.3351(1)	73	910
$La_{0.85}Li_{0.05}Ca_{0.1}CoO_{3-\delta}$	0.5438(2)	1.3084(7)	0.3351(3)	56	810
$La_{0.7}Li_{0.1}Ca_{0.2}CoO_{3-\delta}$	0.5436(1)	1.3083(4)	0.3353(6)	52	750
$La_{0.85}Li_{0.05}Sr_{0.1}CoO_{3-\delta}$	0.5441(3)	1.3100(3)	0.3358(2)	48	570
$La_{0.7}Li_{0.1}Sr_{0.2}CoO_{3-\delta}$	0.5434(2)	1.3162(6)	0.3366(3)	36	430
$La_{0.85}Li_{0.05}Ba_{0.1}CoO_{3-\delta}$	0.5437(4)	1.3130(4)	0.3362(5)	37	440
$La_{0.7}Li_{0.1}Ba_{0.2}CoO_{3-\delta}$	0.5443(1)	1.3136(4)	0.3370(6)	32	380



a) b)

Fig. 2. Surface morphology of a) ($LaCoO_{2.91}$) and modified b) ($La_{0.85}Li_{0.05}Ca_{0.1}CoO_{2.93}$) lanthanum cobaltates.

plates with the morphology of a hexagonal prism. The average size of individual particles is of the order of hundreds of nanometers and decreases with heterovalent substitution. Comparison of the results of SEM studies and data on grain sizes obtained from the diffraction experiment (D_{102}) (Table 1) shows that most particles are in an aggregated state.

The IR spectrum of lanthanum cobalt $LaCoO_{3-\delta}$ (Fig. 3) consists of two bands of valence vibrations (ν_1 = 605 cm^{-1}, ν_2 = 565 cm^{-1}) and one band of deformation vibrations (ν_b = 430 cm^{-1}).

According to research [13], in the rhombohedrally distorted structure of $LaCoO_3$ perovskite, two types of Co^{3+} (Co_I, Co_{II}) are distinguished in oxygen octahedra, and the distance Co_I – O is shorter than the distance Co_{II} – O, i.e. the Co_I – O bond is stronger than the Co_{II} – O bond. Therefore, the higher frequency of valence oscillations ν_1 refers to the oscillations of the Co_I – O bond; the lower frequency ν_2 is determined by the oscillations of the less strong Co_{II} – O. The band with a frequency of 430 cm^{-1} can be attributed to La-O bond oscillations dodecahedral coordination [14].

With an increase in the content of cobaltates and lithium in the base matrix in the IR spectra there is a noticeable shift of the frequencies ν_1 and ν_2 in opposite directions, and then their fusion ($\nu_s \approx$ 600 cm^{-1}) in the spectra of solid solutions $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; $0 \le x \le 0.05$). In addition, in the spectra of substituted cobalts of lanthanum revealed a narrow arm of about 670 cm^{-1}, the appearance of which in accordance with [15] is associated with the formation of Co^{4+} ion. The shift of this band to the high-frequency region is caused by an increase in the force constant of the Co-O bond due to an increase in the electric charge of the cobalt ion.

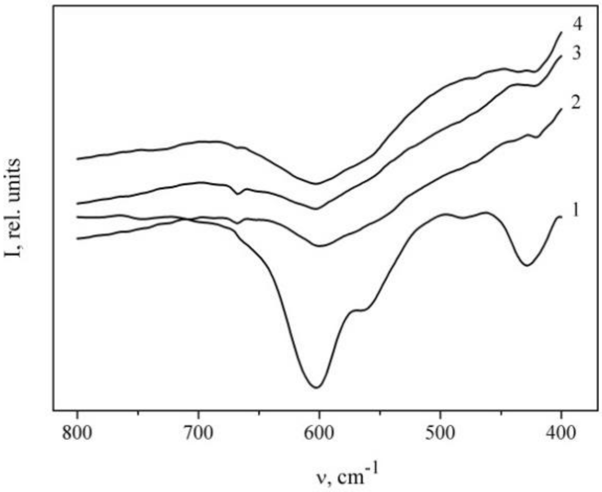


Fig. 3. IR spectra of solid solutions of the system $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$:1 – $LaCoO_{3-\delta}$; 2 – $La_{0,85}Li_{0,05}Ba_{0,1}CoO_{3-\delta}$; 3 – $La_{0,85}Li_{0,05}Sr_{0,1}CoO_{3-\delta}$; 4 – $La_{0,85}Li_{0,05}Ca_{0,1}CoO_{3-\delta}$.

Since, as is known from the literature, nonstoichiometry by oxygen has a significant effect on the electrophysical properties of complex cobalt oxides, we determined the value of nonstoichiometry by oxygen for samples of the studied system. The results of the analysis given in Table 2, show that the existence of Co^{4+} ions in the compounds was confirmed by chemical analysis, which correlates well with the data of IR spectroscopy. With increasing x, δ oxygen decreases by approximately 0.09 for all compositions.

Table 2

Oxygen nonstoichiometry and valence state of cobalt in system samples
$La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; $0 \le x \le 0.1$).

Sample	3-δ	Co^{n+}
$LaCoO_{3-\delta}$	2.91	2.82
$La_{0.85}Li_{0.05}Ca_{0.1}CoO_{3-\delta}$	2.93	3.06
$La_{0.7}Li_{0.1}Ca_{0.2}CoO_{3-\delta}$	2.79	2.97
$La_{0.85}Li_{0.05}Sr_{0.1}CoO_{3-\delta}$	2.96	3.13
$La_{0.7}Li_{0.1}Sr_{0.2}CoO_{3-\delta}$	2.82	3.04
$La_{0.85}Li_{0.05}Ba_{0.1}CoO_{3-\delta}$	2.97	3.13
$La_{0.7}Li_{0.1}Ba_{0.2}CoO_{3-\delta}$	3.01	3.42

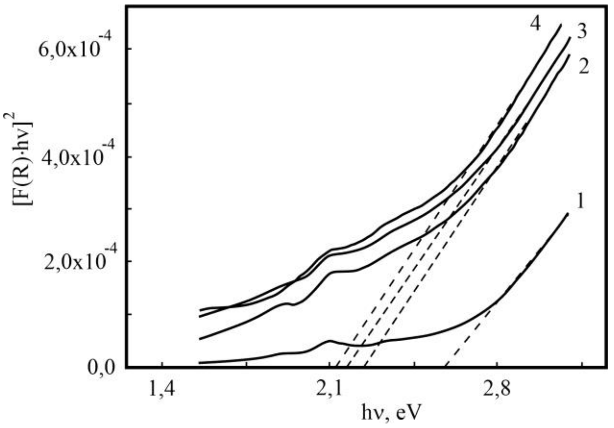


Fig. 4. Diffuse reflection spectra for solid solutions $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$: 1 – $LaCoO_{2.91}$;
2 – $La_{0.85}Li_{0.05}Ca_{0.1}CoO_{2.93}$; 3 – $La_{0.85}Li_{0.05}Sr_{0.1}CoO_{2.96}$;
4 – $La_{0.85}Li_{0.05}Ba_{0.1}CoO_{2.97}$.

Diffuse reflection spectroscopy (DRS) allow us to identify information about the local environment. The valence state of cobalt ions, as well as to assess the relationship between the nature of the alkaline earth ion and the optical properties of solid solutions $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; $0 \le x \le 0.05$). Diffuse reflection data (Fig. 4) in the visible part of the optical spectrum are presented in the coordinates of the Kubelka – Munk F(R) function [16]:

$$F(R) = \frac{(1-R)^2}{2R} = \frac{\alpha}{S}, \tag{4}$$

where R – diffuse reflection of the layer of the test sample relative to the layer of powder of standard non-absorbent material (MgO «CP»); the value of α and S are the absorption and scattering coefficients of the sample. The optical band gap (E_g) of the studied complex oxides was determined from the ratio:

$$\alpha E = K\left(E - E_g\right)^{\eta}, \tag{5}$$

where E – photon energy ($h\nu$); K – constant; degree η (in the case of a direct allowed optical transition takes the value of ½S) [16].

According to this equation, the width of the optical slit can be found by extrapolating the linear section of the dependence $F(R)E = f(E)$ to the intersection with the abscissa axis (Fig. 4).

The obtained values of the optical slits of the band gap for the samples $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; x=0.05) and pure $LaCoO_{3-\delta}$ are 2.14; 2.07; 2.01 and 2.43 eV, respectively. As the ionic radius of the substituent increases, the width of the optical gap of the band gap narrows. It is known that the introduction of $LaCoO_3$ alkali earth metals and lithium leads to an increase in oxygen vacancies. As a result, there is an increase in the concentration of carriers, and, accordingly, the approach of the Fermi level to the conduction band of the semiconductor with the subsequent expansion of the band gap. The band on the spectra with $E = 2.07 eV$ corresponds to the d-d-transition of the Co^{2+} ion in the tetrahedral oxygen environment characteristic of spinel Co_3O_4 [17]. Low E_g values indicate the possibility of using lanthanum cobaltates as potential photocatalysts along with classical TiO_2 (E_g = 3.2 eV) [18-19].

Investigation of magnetic properties of complex cobalt oxides $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; $0 \le x \le 0.1$) was performed in a wide temperature range (20-300 K) by ferromagnetic resonance [20] (Fig. 5).

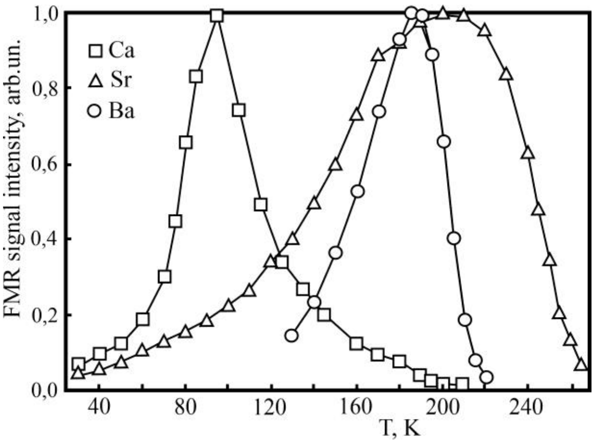


Fig. 5. Temperature dependence of the integral intensity of the FMR signal for samples $La_{0.7}Li_{0.1}M_{0.2}CoO_{3-\delta}$, where M = Ca, Sr, Ba.

It is shown that the dependences of the integral intensity of the FMR signal, which is proportional to the magnetic susceptibility of the samples, have the form of a curve with a maximum, the position of which is significantly influenced by the nature of the alkaline earth metal. This behavior can be explained by the formation of a state of the type "cluster spin glass".

The values of the double integrals of FMR signals, normalized to the mass of the samples, indicate the antiferromagnetic nature of the exchange interaction between cobalt ions.

The parameters of the signals on the electron paramagnetic resonance spectra and the characteristics of the signals for samples $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ are shown in Table 3.

The line in the electron paramagnetic resonance

Table 3

Parameters of signals on the electron paramagnetic resonance spectra for samples $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; $0 \le x \le 0.1$) [23].

Signal	*g*-factor	ΔH, G	Signal characteristics
1	5.00	680	isolated Co^{2+} ions in an octahedral oxygen environment – structural defect centers
2	2.80	1250	ferromagnetic clusters Co^{3+}-Co^{4+}
3	2.25	1500	paramagnetic Co^{2+} ions from the impurity Co_3O_4 that are in different local environments and have different degrees of exchange interaction with each other; contained in the form of chain fragments $-Co^{2+}-O^{2-}-Co^{2+}-O^{2-}-Co^{2+}-O^{2-}-$
4	2.14	40	surface complexes of adsorbed anion radical $O_2^{\bullet -}$ (α-oxygen) with ions Co^{3+} – $[Co^{3+}\cdots O_2^-]^\bullet$
5	2.02	1650	defective centers of Co^{2+}, which are formed during the desorption of lattice oxygen (β-oxygen) from the surface $Co^{3+}_{(surf)}O_2^-Co^{3+}_{(surf)} \longrightarrow Co^{2+}_{(surf)}V_OCo^{2+}_{(surf)} + \frac{1}{2}O_2\,(g)$ or in the process of oxygen diffusion from the volume of material to the surface $Co^{3+}_{(bulk)}O_2^-Co^{3+}_{(bulk)} + Co^{2+}_{(surf)}V_OCo^{2+}_{(surf)} \longrightarrow Co^{2+}_{(bulk)}V_OCo^{2+}_{(bulk)} + Co^{3+}_{(surf)}O_2^-Co^{3+}_{(surf)}$

spectra with $g_{ef.} = 2.02$ i $\Delta H \approx 1600 - 1700$ *G* is determined by defective centers Co^{2+}, which are formed, according to the authors' assumptions [21-22] based on the data of thermoprogrammed desorption of lattice oxygen (Table 4):

$$Co^{3+}_{(surf)}O_2^-Co^{3+}_{(surf)} \longrightarrow Co^{2+}_{(surf)}V_OCo^{2+}_{(surf)} + \frac{1}{2}O_2\,(g)$$

or in the process of diffusion of oxygen ions from the volume of the material to the surface of the oxide matrix (volume defect):

$$\begin{aligned} &Co^{3+}_{(bulk)}O_2^-Co^{3+}_{(bulk)} + Co^{2+}_{(surf)}V_OCo^{2+}_{(surf)} \longrightarrow \\ &\longrightarrow Co^{2+}_{(bulk)}V_OCo^{2+}_{(bulk)} + Co^{3+}_{(surf)}O_2^-Co^{3+}_{(surf)} \end{aligned}.$$

Table 4.

Narrow line parameters for solid solutions $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$.

Sample	g-factor, ±0.0002	Intensity / Mass	ΔH, G
$LaCoO_3$	2.1430	71.9	39.6
$La_{0.85}Li_{0.05}Ca_{0.1}CoO_{3\pm\delta}$	2.1446	40.1	37
$La_{0.7}Li_{0.1}Ca_{0.2}CoO_{3\pm\delta}$	2.1439	410.4	39.1
$La_{0.85}Li_{0.05}Sr_{0.1}CoO_{3\pm\delta}$	2.1436	45.4	36.3
$La_{0.7}Li_{0.1}Sr_{0.2}CoO_{3\pm\delta}$	2.1446	387	39.15
$La_{0.85}Li_{0.05}Ba_{0.1}CoO_{3\pm\delta}$	2.1439	401	37.5
$La_{0.7}Li_{0.1}Ba_{0.2}CoO_{3\pm\delta}$	2.1439	558	41.8

Thus, analyzing the obtained data, we can identify certain correlations, namely to establish the relationship between the average ionic radius of the metal, the average degree of oxidation of cobalt n and the parameters of the jumping conductivity with a variable jump length.

As the radius of the alkaline earth metal and the value of *x* increases, the chemical pressure in the system decreases. This prolongs the Co – O bond and reduces the p-d hybridization of the oxygen and cobalt electron clouds. The effect of the crystal field created by the oxygen environment on cobalt ions weakens, and the energy gap between the t_{2g}- and e_g-levels narrows.

Conclusions

For the first time, solid solutions of $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; $0 \le x \le 0.1$) were synthesized and investigated. It is shown that the region of their homogeneity lies in the range of substitutions $0 \le x \le 0.05$. The volume of the unit cell increases symbate with the size of the alkaline earth metal that replaces lanthanum. A comparison of the results of SEM-studies and data on grain sizes obtained from the diffraction experiment shows that most particles are in the aggregate states. The values of the optical gaps of the band gap were found for samples $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; $x = 0.05$) i and pure $LaCoO_{3-\delta}$ which are 2.14, 2.07, 2.01 and 2.43 eV, respectively. It was found that in all samples (except strontium - containing) paramagnetic Co^{2+} ions from the impurity Co_3O_4, which are in different local environments and have different degrees of exchange interaction with each other, are contained in the form of chain fragments

$-Co^{2+}-O^{2-}-Co^{2+}-O^{2-}-Co^{2+}-O^{2-}$

and contain defective centers Co^{2+}, which are formed during the desorption of lattice oxygen from the surface, or in the process of diffusion of oxygen from the volume of material to the surface. In strontium-containing samples $La_{0.85}Li_{0.05}Sr_{0.01}CoO_{3-\delta}$ there are mainly ferromagnetic clusters Co^{3+}-Co^{4+}.

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Синтез і властивості полізарядних фаз в системі La-Li-M-Co-O (M=Ca, Sr, Ba)

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Методом сумісного осадження компонентів синтезовано зразки $La_{1-3x}Li_xM_{2x}CoO_{3-\delta}$ (M = Ca, Sr, Ba; $0 \leq x \leq 0{,}1$) (M = Ca, Sr, Ba; $0 \leq x \leq 0{,}1$). Показано, що область їх гомогенності лежить в діапазоні $0 \leq x \leq 0{,}05$. Об'єм елементарної комірки збільшується з розміром лужноземельного металу, який заміщує лантан. Морфологію поверхні отриманих змішаних оксидів досліджували методом SEM. У всіх зразках (крім стронцій-вмісних) парамагнітні іони Co^{2+} від домішки Co_3O_4, які знаходяться в різному локальному оточенні мають різний ступінь обмінної взаємодії між собою; містяться у вигляді ланцюгових фрагментів-Co^{2+}-O^{2-}-Co^{2+}-O^{2-}-Co^{2+}-O^{2-} і містять дефектні центри Co^{2+}, які утворюються при десорбції решіткового кисню з поверхні, або в процесі дифузії кисню з об'єму матеріалу на поверхню. В стронцій вмісних зразках $La_{0,85}Li_{0,05}Sr_{0,01}CoO_{3-\delta}$ існують переважно феромагнітні кластери Co^{3+}-Co^{4+}.

Ключові слова: $LaCoO_3$; змішані оксиди; кобальтати лантану; перовскітоподібна структура; морфологія поверхні; FMR; спектри дифузного відбиття; кластер спінового скла.