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Thermal Stability and Features of the Synthesis of Mixed Ceramic Oxides $La_{2-x}Sr_xCoO_4$

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Abstract—Thermal behavior of the mixed oxides $La_{2-x}Sr_xCoO_4$ ($0.1 < x < 1.5$) in the temperature range 1200–1700 K was studied. The use of the ceramic synthesis method makes it possible to obtain homogeneous samples at the calcination temperature of 1673 K. It was found by the high-temperature mass-spectrometry method that a charge can be depleted of cobalt oxide during the high-temperature synthesis.

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Perovskite-like mixed oxides $La_{2-x}A_xCoO_4$ (A are alkaline-earth elements) are of special interest for researches in the chemistry of solids and inorganic chemistry [1–3]. The possibility of lanthanum replacement by elements with oxidation state +2 allows changing an electronic state of cobalt atoms in single crystals and obtaining new data on the features of interactions between these atoms. The tolerance of perovskite-like structures to variations in chemical compositions with homogeneity retention is known for a long time, and this property is widely used for creating materials for electronics on their basis. The use of $La_{2-x}Sr_xCoO_4$ for this purpose is caused, in particular, by a ferromagnetic-antiferromagnetic phase transition. Mixed oxides $La_{2-x}Sr_xCoO_4$ formed become ferromagnetic when strontium is substituted for lanthanum in the lanthanum cobaltate La_2CoO_4, and the fraction of the ferromagnetic contribution is defined by strontium content. It is supposed [2, 4] that as x increases, fields of the uncompensated magnetic order related to the presence of spin correlations are gradually formed, or the temperature of transition into the antiferromagnetic state fast decreases, and it is sharply converted to the ferromagnetic state. It is no wonder that the opinions are different, as it was found for oxides of 3*d*-elements in mixed oxidation states that there are complicated alternations of electron correlation in the form of phases with spin or charge ordering, to which various magnetic phases correspond.

Final conditions of the synthesis of cobaltates are still not determined, as there are rather conflicting data on the conditions of homogeneous samples preparation. Despite differences in methods and conditions of the synthesis, the main resulting phase is $La_{2-x}Sr_xCoO_4$ with a perovskite-like tetragonal structure analogous to that of K_2NiF_4 with a small amount (no more than 3–5%) of an impurity phase [5, 6]. Chemical composition of the admixture can be different. It is supposed that it can be $LaSrCoO_3$ or $La_{0.9}Sr_{0.1}CoO_3$ perovskites or $Sr_6Co_5O_{15}$ or $Sr_3Co_2O_7$ oxides. As a rule authors do not give a detailed analysis of the admixture composition and assign all characteristics obtained to the main phase.

According to our earlier data [5], the calcination of a charge at 1200–1330 K results in a change in the ratio of lanthanum, strontium, and cobalt mole fractions in $La_{2-x}Sr_xCoO_4$, therefore this temperature range cannot be considered as sufficient for the completion of the solid-state reaction. According to the X-ray data, the increase in the temperature of the synthesis up to 1673 K results in the homogenization of oxides and in the formation of the required perovskite-like structure analogous to that of K_2NiF_4. The average composition of samples corresponded to the chemical formula $La_{2-x}Sr_xCoO_4$, which points to their homogeneity on a macro level. However, the analysis of a microscopic structure has shown that on a micro level there are structural submicroinhomogeneities. It is proved by the fact that the ratio of La and Sr mole fractions in different points of a sample is either 2:1 or 1:1. Such ratios correspond, respectively, to perovskite-like tetragonal $La_{2-x}Sr_xCoO_4$ and perovskite $LaSrO_x$ structures.

Furthermore, points corresponding to individual lanthanum oxide La_2O_3 are recorded.

The change in the microscopic structure of samples can be caused by partial losses of initial components during the synthesis at the high-temperature calcination. To check this assumption, we have carried out a mass-spectrometry study of vaporization of both the initial charge with components taken in the stoichiometric ratio for obtaining $La_{1.3}Sr_{0.7}CoO_4$ and the sample synthesized by the ceramic procedure.

To simplify the comparison of the charge and the sample synthesized by the ceramic procedure, we loaded equal masses of the charge and the mixed oxide $La_{1.3}Sr_{0.7}CoO_4$ in effusion cells. Partial pressures of the molecular vapor forms were determined by the method of comparing ionic currents according to Eq. (1).

$$p_1 = \frac{p_2 I_1 T_1 \sigma_2 \gamma_2}{I_2 T_2 \sigma_1 \gamma_1}. \tag{1}$$

Here p is partial pressure; I is ionic current intensity, relative units; T is temperature, K; σ is ionization cross section of a molecule; a is a mass spectrum coefficient. The factor γ represents an effective coefficient of conversion on the first electrode of the secondary-electron multiplier for specified ions, it was accepted to be $1/\sqrt{M}$ in the calculations (M is a molecular weight of an ion). Indexes 1 and 2 refer to a sample and a standard, respectively. The instrumentation was preliminary calibrated by standard pressures of Au [7] and CaF_2 [8].

Preliminary experiments have shown that at a fast increase in the temperature of the cell with samples a strong gas evolution occurs, which is caused by the intensive removal of adsorbed gases and water from a charge surface, and also by the removal of carbon dioxide from strontium carbonate. As in the course of the synthesis temperature of samples increases within 2–3 h from the room temperature up to the temperature of the synthesis beginning, further the chamber with a charge and a sample loaded in it was maintained in isothermal conditions at ~1400 K within 2 h.

Starting from the temperature ~1550 K peaks of Co^+ ions only were detected in the mass spectrum of vapor above both the charge and the sample. The measured appearance energy of the Co^+ ion has shown that this ion is formed as a result of the direct ionization of atomic cobalt present in the vapor, as the measured appearance energy has coincided within the measurement accuracy with the ionization energy of atomic cobalt [9]. As cobalt oxide dissociates by Eq. (2) on heating [10], molecular oxygen was also present in the vapor in addition to atomic cobalt. We did not measure its pressure, as oxygen does not condense on cold parts of the mass spectrometer and can cross the ionization field repeatedly, which considerably deforms the observed data. The oxygen partial pressure can be calculated by Eq. (3), where M is a molar weight.

$$CoO(cr) = Co(gas) + 0.5\ O_2(gas), \tag{2}$$

$$p(O_2) = 0.5p(Co)\sqrt{M(O_2)/M(Co)}. \tag{3}$$

At the isothermal maintaining of the sample at ~1600–1625 K partial pressure of atomic cobalt remained constant within the measurement accuracy, however the partial pressure of cobalt vapor above preliminary calcined charge was slightly higher than that above the sample. It indicates that despite a two-hour exposure of a charge at 1400 K, the synthesis of the $La_{1.3}Sr_{0.7}CoO_4$ mixed oxide was not completed, and the value of cobalt oxide activity in the charge was higher than in the mixed oxide. Apparently, the complete synthesis of the sample requires a longer time, and in this case cobalt oxide losses can take place. Then temperature was raised up to the temperature of the sample synthesis 1705–1735 K. As before, the vapor contained only atomic cobalt and oxygen. Peaks of Sr^+ ions and of atomic strontium have appeared in the mass spectrum and in the vapor, respectively, starting from the temperature of ~1800 K. The experiment was stopped when the partial pressure of atomic cobalt has largely decreased, that, undoubtedly, has led to a change in the sample composition. The resulting values of partial pressures of the molecular vapor forms depending on vaporization time and temperatures are presented in the table.

To determine the vaporization rate and the weight of possible losses during the sample synthesis, the Hertz-Knudsen equation (4) in form (5) can be used.

$$p_i = \frac{q_i}{StL}\sqrt{\frac{2\pi RT}{M_i}}, \tag{4}$$

$$\frac{m}{St} = \frac{pL}{2285\sqrt{T/M_i}}. \tag{5}$$

Here p is a partial pressure; q is a weight of substance evaporated in time t through the effusion aperture with an area S and Klauzing coefficient L; R is the universal gas constant; T is temperature, K; M_i is a molecular weight of component i in vapor. The value 2285 is connected with measuring a partial pressure, Pa.

The left-hand part of Eq. (5) represents the rate of the *i*th component vaporization. We can calculate the rate of cobalt oxide vaporization from a known vaporization area equal to the effusion aperture area. The value found by Eq. (5) was scaled to the vaporization area of 1 cm^2 and vaporization time of 1 h.

When CoO is vaporized in a vacuum at 1625 K, the rate of vaporization of atomic cobalt from preliminary calcined charge is 0.658 g cm^{-2} h^{-1}. As cobalt oxide passes in vapor according to Eq. (2), the initial vaporization rate of cobalt oxide in a vacuum is 0.836 g cm^{-2} h^{-1} or 1.11 mol cm^{-2} h^{-1}. As to the sample, in this case at 1625 K the initial vaporization rate of CoO is 6.06×10^{-3} mol cm^{-2} h^{-1}.

At a higher temperature (1735 K) the vaporization rate of atomic cobalt from the charge is 3.17 g cm^{-2} h^{-1}. The initial vaporization rate of cobalt oxide at this temperature is 4.02 g cm^{-2} h^{-1} or 5.37×10^{-2} mol cm^{-2} h^{-1}. For the sample this value is 2.55×10^{-2} mol cm^{-2} h^{-1}.

As all calculations refer to the conditions of vaporization in a vacuum, and the sample synthesis from a charge is carried out at atmospheric pressure, we have converted the calculated values in view of the fact that the partial pressure of oxygen in air is 21275 Pa. The conversion was carried out as follows. The equilibrium constant of reaction (2) was presented in form (6), where *a*(CoO) is the activity of cobalt oxide in a condensed phase.

$$K_p = \frac{p(\mathrm{Co})p^{0.5}(\mathrm{O}_2)}{a(\mathrm{CoO})}. \tag{6}$$

As this value is constant for a sample of certain composition at a constant temperature, the product of the activity and the constant is also constant. Hence it follows that the product $p(\mathrm{Co})p^{0.5}(\mathrm{O}_2)$ is also a constant. In the case of the charge or sample vaporization this value was determined from Eqs. (1) and (3). Having replaced the value of the oxygen partial pressure in a vacuum by the value characteristic for air atmosphere, we have found a partial pressure of atomic cobalt for the sample or charge vaporization in air.

At 1625 K the initial vaporization rate of cobalt oxide in air from a charge was 5.45×10^{-6} mol cm^{-2} h^{-1}, and from a sample, 2.96 mol cm^{-2} h^{-1}. At 1735 K these values were 5.85×10^{-5} and 2.78×10^{-5} mol cm^{-2} h^{-1} for the charge and the sample, respectively.

Thus, the results of the mass-spectrometry study have shown that the cobalt oxide vaporization from a charge and a sample begins at a rather high temperature close to the final temperature of the synthesis. Losses of CoO even at a long-term exposure at the synthesis temperatures are insignificant, whereas the removal of strontium oxide begins at a higher temperature. The data obtained point to the fact that the appearance of a microstructure in a sample (the local change of the ratio of elements in oxide) is not connected with selective vaporization of oxides during the synthesis, but apparently is connected with morphological distinctive features of homogeneous mixed oxides.

Partial pressures of molecular forms of vapor above a charge and $La_{1.3}Sr_{0.7}CoO_4$ sample depending on vaporization time temperature

Vaporization time, min	*T*, K	$p(\mathrm{Co})\times10^2$, Pa		$p(\mathrm{Sr})\times10^2$, Pa	
		charge	sample	charge	sample
0	1625	1.38	0.75		
3	1620	1.31	0.72		
6	1612	0.89	0.61		
10	1608	0.89	0.60		
12	1696	4.32	2.61		
15	1705	3.14	2.62		
20	1708	3.14	3.15		
30	1728	4.16	4.14		
40	1735	6.87	3.26		
45	1735	6.14	3.26		
50	1753	8.43	3.52		
60	1760	6.72	3.61		
62	1834	20.00	15.61	1.29	1.59
67	1840	23.24	16.10	1.85	1.60
70	1834	24.21	15.61	2.07	1.58
80	1834	2.00	2.79	1.71	1.51

EXPERIMENTAL

The mixed oxides were synthesized by the ceramic method. The following reagents were used to obtain the mixed oxides $La_{2-x}Sr_xCoO_4$: special-purity lanthanum oxide; special-purity strontium carbonate; analytical grade cobalt(III) oxide. Initial lanthanum oxide and strontium carbonate were preliminary calcinated at 1073 K to remove adsorbed water and carbon dioxide. Relative contents of cobalt and lanthanum oxides and also of strontium carbonate in a charge prepared for the synthesis of samples were calculated from the reaction equation.

$$(2-x)La_2O_3 + 2xSrCO_3 + Co_2O_3$$
$$= 2La_{2-x}Sr_xCoO_4 + 2xCO_2 + [(1+x)/2]O_2.$$

A series of the mixed oxides $La_{2-x}Sr_xCoO_4$ ($0 \le x \le 1.5$) synthesized at 1200–1700 K was studied by the methods of X-ray phase analysis and scanning electron microscopy with microanalysis of composition and possible coexisting phases.

The mass-spectrometry study was fulfilled by the high-temperature mass-spectrometry method on an MS-1301 mass-spectrometer intended for studying processes of vaporization of low-volatile substances. Samples were evaporated from a dual tungsten one-temperature cell heated by electronic bombardment. Temperature was measured by an EOP-66 optical pyrometer accurate to ±5 K in the temperatures range 1400–2000 K. A charge was placed in one of effusion chamber cells, and the mixed oxide $La_{1.3}Sr_{0.7}CoO_4$ synthesized by the ceramic method was placed in another cell, a comparison cell. Gold was used as the interior pressure standard, which was loaded in both cells of the chamber.

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