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Magnetic study of interatomic interactions, synthesis, structural and mass spectroscopy investigations of lanthanum gallate doped with cobalt and magnesium

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ABSTRACT

For the first time by X-ray method two phases of the solid solutions $LaCo_xGa_{1-1.2x}Mg_{0.2x}O_{3-\delta}$ and $LaCo_xGa_{1-1.5x}Mg_{0.5x}O_{3-\delta}$ ($x = 0.01–0.10$) with different structure were found – rhombohedral and orthorhombic phases. On the basis of the data on evaporation of the components a synthetic procedure was advanced allowing the losses of cobalt to be minimized. The study of magnetic characteristics of obtained solid solutions showed the formation of high nuclearity clusters containing cobalt atoms, and also magnesium and associated vacancies even in diluted solid solutions. Clusters are characterized by a competition between ferro- and antiferromagnetic exchange interactions, whereas the long order exchange is antiferromagnetic.

1. Introduction

Solid electrolytes, ionic, electron–ionic conductors based on oxide matrices are of great practical importance in the technologies of solid oxide fuel cells (SOFC). Doped lanthanum gallate is one of the well-accepted subjects used in SOFC owing to a high mobility of oxygen ions and low coefficients of thermal expansion [1].

A number of works is devoted to the study of the structure and conducting properties of doped lanthanum gallate [2–5], to the search for the compositions providing a maximal ionic conductivity. Introduction of strontium and/or magnesium into lanthanum gallate often gives rise to secondary phases of the $LaSrGa_3O_7$, $LaSrGaO_4$ and $La_4Ga_2O_9$ oxides, which decreases the conductivity and life spans of the material. At the same time the introduction of transition metal cations along with strontium and magnesium was noted to result in single phase samples, i.e. is in aid to the stabilization of the structure of doped lanthanum gallate. Moreover, the concentration and nature of the dopants drastically affect the conductivity. Nickel and cobalt containing systems are considered to be the best conductors and chromium and manganese containing systems – the worst [2,6–18]. The reasons of the influence of the dopants, as a rule, are not discussed. The influence of the nature and concentration of inserted strontium and magnesium on the valence state of a transition element and interatomic interactions remains an enigma.

Lanthanum gallate doped with bivalent elements and cobalt is much investigated owing to a sufficiently high ionic conductivity [9,10,14,16–18]. In this case the data on conductivity appear to differ significantly, strongly depend on the content of diamagnetic additions and cobalt, and are badly reproduced. The authors of [16,17] specify with good reason that only a thoroughly selected concentration of a transition element can provide for a high conductivity and the transport number of oxygen ions close to a unit. We can state with assurance that the same is valid for diamagnetic additions.

It is obvious that the fundamental role in the formation and migration of vacancies in the doped lanthanum gallate belongs to its electronic structure – the state of transition element atoms and interatomic interactions. Systematic study of magnetic properties of the systems containing strontium, magnesium, and *d*-elements as dopants [19–23] showed that a simultaneous doping with a paramagnetic and a diamagnetic element results in an essential clustering in the structure, clusters incorporating transition element atoms, strontium and magnesium, and also the vacancies in the oxygen sublattice. In the case of doping with cobalt and strontium two problems aroused requiring to be solved.

The first problem is associated with the stoichiometry of the solid solution being obtained. The ceramic procedure of the synthesis of complex oxide materials is conventional on obtaining any kinds of construction and functional ceramics. However it has a number of substantial drawbacks associated with the duration of thermal treatment resulting in the batch depletion in volatile

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components and in the composition of the final product differing from the composition of the batch. In particular, in [24] the concentration of cobalt in the system was found to decrease substantially during high-temperature sintering compared to the equation of the solid state reaction. We emphasize that in all the works devoted to the study of cobalt containing systems [9,10,14,16–18] the analysis of the cobalt content after sintering was not carried out, which, to some extent cast some doubt on the quantitative data on optimizing the composition of electron–ionic conductors. Gallium oxide is known to be characterized by a sufficiently high volatility under vacuum [25], which can result in its selective evaporation from the batch and in substantial discrepancies between the composition specified for the synthesis and the obtained composition, and also in the emergence of additional phases.

The second problem is associated with the possibility of various spin states for trivalent cobalt, which must influence interatomic interactions and, consequently, the conductivity of the ceramics.

This work is devoted to a complex study of lanthanum gallate doped with cobalt and magnesium with the ratio Co:Mg = 5:1 and 2:1 ($LaCo_xMg_{0.2x}Ga_{1-1.2x}O_{3-\delta}$ and $LaCo_xMg_{0.5x}Ga_{1-1.5x}O_{3-\delta}$, $x = 0.01 \div 0.10$). On the basis of mass spectroscopy data a synthetic procedure was developed minimizing the losses of cobalt and gallium oxides during high-temperature sintering. The main aim of the work was to study the states of cobalt atoms and interatomic interactions in the structure and also to reveal their dependence on the relationship between cobalt and magnesium in the systems under study.

2. Experimental

Solid solutions of composition $LaCo_xMg_{0.2x}Ga_{1-1.2x}O_{3-\delta}$ and $LaCo_xMg_{0.5x}Ga_{1-1.5x}O_{3-\delta}$ ($x = 0.01 \div 0.10$) were synthesized by ceramic procedure. As starting substances we used special pure grade La_2O_3 (99,999%), MgO (99,995%), Ga_2O_3 (99,999%), and analytical pure grade CoO (9999%). During the high-temperature sintering (1723 K) of the samples containing strontium and cobalt, as was found in [24], an essential decrease in the concentration of cobalt was observed. This can result from a rapid, during about 2 h increase in temperature to 1723 K. A selective evaporation of cobalt oxide seems to occur during the high-temperature synthesis.

With the aim to exclude or at least substantially decrease the loss of cobalt it is necessary to select the temperature and time conditions of the synthesis on the basis of the X-ray and quantitative analysis of the end product. The control over the ratio of the components in the solid solution may be carried out with the help of quantitative chemical analysis of both the batch and the obtained end product. This method takes a lot of time, though it is quite efficient. The method of mass spectroscopy control over the losses in the mass of a sample owing to a selective evaporation of the solid solution components that we advance makes possible the determination with a high accuracy: (1) the temperatures of the beginning of the transfer to vapor of all the components of the system under study; (2) the quantity of a component of the system transferred into vapor during a certain period of time.

Therefore, the high temperature mass spectroscopy appears to be the only direct method of analysis making possible the determination of the qualitative and quantitative composition of the vapor with a high accuracy.

The mass spectroscopy experiments were carried out using Knudsen effusion technique combined with mass spectrometric analysis of vapor composition, described in details elsewhere [26], on the mass spectrometer MS 1301 (Construction Bureau, Academy of Science, St. Petersburg). Testing the instrument was conducted by measuring the vapor pressure of calcium fluoride and subsequent comparing the values obtained with reference data [27].

X-ray diffraction experiment for the polycrystalline samples of investigated system have been performed in air at a temperature of 25 °C using a Bruker "D2 Phaser" diffractometer (Cu Kα radiation, Ni filter). The powder data were collected in the 2θ range of (10–130°) with a step size 0.01° 2θ and counting time 1 s per step, sample rotation rate of 30 rpm. The phase identification was carried out using the Powder Diffraction File database (PDF-2, 2011). Quantitative phase analysis has been performed by the Rietveld method using the TOPAS software complex and the structural data for each of the phases according to the Inorganic Crystal Structure Database (ICSD 2012). The chemical analysis of the content of cobalt and magnesium was carried out by the method of atomic emission spectroscopy on a SPECTRO CIROS, type ISP spectrometer. The error of the analysis did not exceed 4% from x in the solid solution formula. The preassigned Co:Mg ratio was shown to be preserved by and large as the result of the synthesis. The magnetic susceptibility was measured by Faraday method in the temperature range 77–400 K at 10 fixed values of magnetic field strength. The accuracy of measuring χ_g is 1%.

3. Discussion

3.1. X-ray study

The powders of sintered samples at 1723 K, were identified as single-phase with structure of orthorhombic $LaGaO_3$ (S.G. *Pbnm*) and rhombohedral $LaGaO_3$ (S.G. *R*-3*c*), which resulted from Rietveld refinement (the profile of the X-ray pattern are given in Fig. 1). As can be seen in Fig. 1 there is a line in the region of $2\theta \sim 29°$, which is a K_β line. It appears due to the special features of the experiment upon using Ni filter; a shoulder in the most intensive line at $2\theta \sim 32°$ is an edge of the absorption line of Ni filter. K_β lines were taken into account automatically on treating the patterns in TOPAS software. It

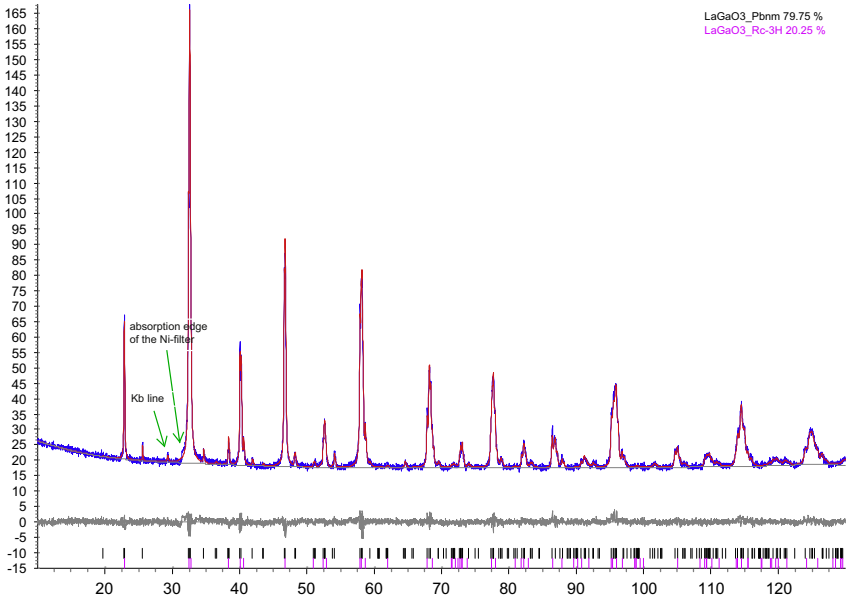

Fig. 1. Result of the Rietveld refinement for the pattern recorded at room temperature for the system $LaGa_{1-1.2x}Co_xMg_{0.2x}O_3$, x(Co) = 0.0845, y(Mg) = 0.0197. R_{wp} = 5.02% R_p = 3.95%, GOF = 1.23%, R-Bragg = 1.74.