ABSTRACT

of the dissertation for the degree of doctor of philosophy (PhD) on the specialty 6D060600 – Chemistry

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Synthesis and study of the electrophysical properties of new inorganic compounds based on mixed oxides of rare-earth elements, transition, alkaline, alkaline-earth metals

The thesis is devoted to the synthesis and investigation of the electrophysical properties of new materials such as complex oxides of cobalt, iron, rare-earth elements, alkaline and alkaline-earth metals.

Complex oxides were obtained by the solid-phase synthesis with the help of ceramic technology. The phase composition was established by the X-ray diffraction method. The parameters of the crystal lattice and the expected phase composition were determined taking into account the parameter shift. The measurements of the temperature dependence of the conductivity were carried out by the method of electrochemical impedance under temperature variation.

X-ray phase and X-ray analysis, electrochemical impedance method, and methods for measuring the temperature dependence of electrical conductivity were used in the study as the main physicochemical methods of research.

Actuality of the research topic. One of the primary tasks of chemistry, chemical technology and materials science is the search for new compounds and the study of their chemical and physicochemical properties suitable for use in the field of microelectronics and science-intensive technology.

Complex oxide compounds based on transition metal oxides and rare-earth elements of the ABX3 type with perovskite structure or any similar structure might be considered as prospective objects in the theoretical and practical terms. Ferrites and cobaltites and their solid solutions with oxides of alkaline-earth elements are referred to them. Currently, such compounds have found wide application in various fields due to the presence of a wide range of interesting properties, namely, high melting points, high electrical conductivity over a wide temperature range, electronic conductivity, magnetic and superconducting properties as well as compatibility with solid electrolytes.

Lanthanum cobaltites have been used as a small polarizable electrode in high-temperature fuel cells based on zirconia, and as a catalyst that is a substitute for platinum in the oxidation of CO in car exhaust gases. Ferrites with cylindrical magnetic domains are promising materials used in memory devices and magneto-optical devices. In addition, ferrites of barium, strontium, etc. are used as magnetically hard materials, i.e. permanent magnets.

Scientists of the chemical faculty of KSU named after Ye.A. Buketov accumulated a certain experimental data on the synthesis of complex oxides and the study of structure by X-ray diffraction methods and the study of their

thermodynamic and electrophysical properties. This study was the logical continuation of a number of works aimed at the synthesis of new complex oxides with a given crystalline and defect structure, preprogrammed properties for their application in a variety of technical devices.

The aim of the research is to synthesize and study the electrophysical properties of new materials, namely, complex oxides of cobalt, iron, rare-earth elements, alkaline and alkaline-earth metals.

In connection with the goal, the following tasks were solved in the work:

- development of technology for the synthesis of new compounds;
- establishment of phase composition by X-ray diffraction and crystal structure, indication of powder diffraction patterns, determination of translational symmetry, parameters of the crystal lattice;
- measurement of the temperature dependence of electrical conductivity of new compounds;
- study of the electrical conductivity of new compounds by the electrochemical impedance method.

The objects of the study: complex oxides of the composition $LnM^{II}CoO_{3,5}$ (Ln – La, Gd, Tb, Er, Yb, Me^{II} – Mg, Ca, Sr, Ba) and $Ln_2M^{I}_3Fe_5O_{12}$ (Ln – La, Gd, Tb, Er, Yb, M^{I} – Li, Na, K).

The subject of the study is the crystal structure of complex oxides of the composition $LnM^{II}CoO_{3,5}$ (Ln – La, Gd, Tb, Er, Yb, Me^{II} – Mg, Ca, Sr, Ba) and $Ln_2M^{I}_3Fe_5O_{12}$ (Ln – La, Gd, Tb, Er, Yb, M^{I} – Li, Na, K) as well as their defect structure and electrical conductivity.

Scientific novelty of the study. In the research for the first time:

- complex oxides of the composition $LnM^{II}CoO_{3,5}$ (Ln – La, Gd, Tb, Er, Yb, Me^{II} – Mg, Ca, Sr, Ba) and $Ln_2M^{I}_3Fe_5O_{12}$ (Ln – La, Gd, Tb, Er, Yb, M^{I} – Li, Na, K) have been synthesized;
- the symmetry and parameters of the crystal lattices of new compounds have been established;
- the thermal dependence of the electrical conductivity of new compounds has been investigated;
- the activation energies of electrical conductivity have been determined.

The connection of the thesis with the research plan and state programs. Research was carried out in the laboratory with the area of expertise in engineering "Physical and chemical methods of research" of KSU named after Ye.A. Buketov and within the framework of the scientific project financed by the grant of the Ministry of Education and Science of the Republic of Kazakhstan on the topic "Development of synthesis technology and physico-chemical research of new materials promising as solid oxide fuel cells used in hydrogen energy" (State Register No. 0115RK00932) for 2015-2017.

Theoretical significance of the study. Presently advanced oxide materials with mixed electronic, oxygen and ionic conductivity play a very important role in many catalytic and magnetic systems, in energy conversion devices. Among these multifunctional materials, the most complex oxides are used with the perovskite structure ABO_3 containing lanthanide in the A sites, and the 3d atoms in the B

sites. The most promising materials in this class are complex oxides with a perovskite structure based on cobalt and lanthanum. These compounds represent absolute leaders, both in terms of scale of application, and attention to them from the part of researchers. Recently, double perovskites $ABaB_2O_{6-\delta}$, with A-lanthanide, B-Fe, Co have been studied with increasing intensity. Up to the present, attention has mainly been focused on perovskites, in which the rare-earth element is replaced by alkaline-earth metals, mainly strontium. Systematic studies of new perovskite-like phases in which a part of the ions of the sublattice A have been partially isomorphically replaced were practically not carried out. However, such isomorphous replacement leads to a significant change in almost all the target characteristics of these compounds, such as magnetic, electrical and catalytic properties. Such complex oxides have so far been investigated only in structural and applied aspects, therefore information on such fundamental properties as defect structure and electrical conductivity is extremely limited. In this connection, a comprehensive systematic study of perovskites doped with the A sublattice is a very urgent problem.

Practical significance of the study. Complex oxides with a perovskite-like structure attract the attention of a huge number of researchers around the world since they are considered as promising materials for the creation of electrochemical, catalytic and magnetic devices. Presently, many studies have been carried out on the interrelation between composition and properties of ABO_3 and $A_{n+1}B_nO_{3n+1}$ oxides, where A is rare-earth elements cation, Ca, Sr, Ba cations; and B is a transition metal cation. One promising field of application of such oxides is cathode materials in a solid oxide fuel cell (SOFC). However, materials with the best electrocatalytic characteristics, such as, for example, $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ ($0.4\leq x\leq 1$ and $0.5\leq y\leq 1$), have low chemical stability and an unacceptably high coefficient of thermal expansion (CTE), what makes their use as a cathode material for a solid oxide fuel cell impossible. The purpose of this work is the synthesis and investigation of new promising materials of cathodes of SOFC, namely, complex oxides of cobalt and iron.

Personal contribution of the author consists in the direct execution of experiments, analysis, generalization and interpretation of the results obtained and their theoretical justification.

Approbation of work. The main provisions of the thesis were presented at the international and regional conferences, symposia and congresses, including the International Scientific and Practical Conference dedicated to the 90th anniversary of Ye.A. Buketov (March 27-28, 2015, Karaganda); International scientific conference dedicated to the 90th anniversary of academician of the Academy of Sciences of Kazakh SSR, laureate of the USSR State Prize Ye.A. Buketov at the Chemical-Metallurgical Institute named after Zh. Abishev (2015, Karaganda); International scientific conference "Integration of Science, education and production - basis of the implementation of the Plan of the nation" (Saginov readings No. 7) dedicated to the 100th anniversary of the birth of Academician A. S. Saginov (December 10-11, 2015, Karaganda); Theoretical and experimental

chemistry: Abstracts of the VIth International scientific conference (June 15-17, 2017).

The reliability of the results and conclusions obtained in the research is confirmed by the use of a set of complementary methods (X-ray diffraction methods, the method of measuring the temperature dependence of electrical resistance and electrochemical impedance), a good correlation between the results of experimental studies obtained by different methods; using modern methods of digital processing of results, their internal consistency. The reliability and validity of the obtained results and conclusions is also confirmed by their comparative analysis with known results of research and development that are rare in the literature.

Publications. The main results of the research are described in co-authorship in 10 scientific papers, including 3 articles in the republican specialized journals recommended by the Committee for Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, 2 articles in the international scientific journal included in the Thomson Reuters database (Russian Journal of Physical Chemistry), as well as materials and theses of 6 reports at the republican and international scientific conferences, symposia and congresses, and the conclusion report on the grant of a patent for an invention. Application No. 2015 / 1262.1 "Method for obtaining complex perovskite-like oxides of rare-earth, alkaline earth and transition metals by the general formula $LnMeCoO_{3.5}$, where Ln is a rare-earth metal, Me is an alkaline earth metal".

The structure of the dissertation. The thesis is presented in 107 pages of typewritten text and includes an introduction, 3 sections, conclusion, 22 tables, 58 figures, a reference list of 101 titles and appendices.