ANNOTATION
to the thesis for the degree of Doctor of Philosophy (PhD) in the specialty 6D060600-chemistry

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“Directional synthesis, structure and electrophysical properties of complex oxide manganites”

General characteristics of the thesis paper:

The dissertation is contributing to the understanding of the method for producing solid solutions based on dysprosium manganite doped with bismuth, their specific design and characteristics. The results of the work can be used with a suitable choice of perovskite manganites and electrical conductivity in the magnetic properties of the memory, depending on the magnetic energy. In addition, the research results make it easy to use heterostructures containing magnetically active layers, significantly expanding the functionality of low-dimensional structures, since in this case, along with the charge, the electron spin is an active element. The dissertation is intended for the synthesis of previously unknown compounds, including complex manganitors, by several methods and their x-ray, electron-diffraction, and physical properties, including their magnetic properties.

Oxides of Bi_2O_3, Dy_2O_3, Mn_2O_3 grades ("ch. c.") and distilled water, citric acid were used as starting materials. Triatomic alcohol glycerin - in Sol-gel method, concentrated nitric acid-in citrate-nitrate method, and urea-in Pechini method were used as gel-forming agents. The initial substances obtained from stoichiometric calculation are weighed on analytical scales with maximum accuracy, mixed, ground in agate mortar and placed in an alund crucible.

The thermal properties of compounds between 298-1000 K. the separation of compounds according to thermal characteristics completely coincides with the construction system were studied using a differential scanning calorimeter.

The practical determination of the thermodynamic properties of inorganic substances requires expensive, complex equipment and requires many complex experiments. In practice, there are difficulties, such as instability of objects, aggressiveness, the need for valuables, etc.

Therefore, to determine the thermodynamic properties of inorganic substances, it is advisable to use a variety of calculations. There are methods of calculation and practical methods. Currently, various methods for calculating thermochemical and thermodynamic stability are given. Thermodynamic properties of manganites synthesized by the effective method are calculated by semi-empirical methods.

Based on the results of thermochemical analyzes, the conditions for the synthesis of complex mixed manganites were determined, new polycrystalline manganites were synthesized, and a phase analysis of the compositions was carried out. By means of an X-ray diffraction study, the syngonies of the crystal lattices of

polycrystals were determined, and the relationship between the pycnometric and X-ray densities was determined by the cell parameters.

The intrinsic heat capacity is determined and the thermodynamic functions of manganites are calculated. In addition, phase transitions in layered structures were detected, surface morphology was studied, and particle size in manganite powder was measured.

The method of magnetometry was used to study the temperature dependence of the magnetic properties of complex oxides and determine the temperature dependence of the magnetic moment of complex magnesium. The temperature dependences of magnesium on dispersions of bismuth manganites in ZFC and FC modes in a magnetic field of 10, 100, 1000 kOe are studied.

Relevance of research

In connection with the urgent problems of microelectronics, the task of creating systems with large isotropic negative magnetoresistance operating at room temperature was very urgent. In particular, they are needed for creating magnetic recording heads, for reliable storage of information, etc. In recent years, the main work in this area has been carried out in the direction of creating multilayer magnetic films and granular magnetic systems.

Goals and objectives of the thesis paper

The aim of the work is to develop methods for the synthesis of complex manganites doped with bismuth dysprosium and to study their structure and functional properties, as well as the relationship between the structure, magnetic and dielectric properties of the synthesis of the obtained materials.

To achieve this goal, the following tasks were achieved:

1. determination of an effective method for the synthesis of complex dysprosium manganites doped with bismuth;
2. determine the influence of synthesis technology on the process, structure, surface morphology of complex manganites;
3. determination of phase transitions and surface morphology in layered structures, measurement of particle size;
4. determination of intrinsic heat capacity and calculation of thermodynamic functions of manganites;
5. study of the temperature dependence of magnetism of bismuth manganite;
6. study of the dependence on temperature and frequency of the dielectric constant of an effective method of synthesized manganite.
7. The previously unexplored complex perovskite manganite $Bi_xR_{1-x}MnO_3$ (0.1 - 0.8) dysprosium was chosen as the object of the study.

Scientific novelty:

1. For the first time, $Bi_xR_{1-x}MnO_3$ manganite (0.1-0.8) was synthesized by four different methods (solid-phase method, sol-gel method, citrate-nitrate method, Pechini method);

2. For the first time, the Pechini method is the best method for the synthesis of $Bi_xR_{1-x}MnO_3$ manganite (0.1-0.8) .;

3. X-ray phase analysis was carried out to determine the synthesized complex oxides and to control the phase composition, x-ray and phnometric densities were

calculated comparatively; For the first time, simple cell parameters, syngnic types, and structures of synthesized compounds were determined;

4. An electron microscope showed that the proportion of elements in manganite obtained by the Pechini method corresponded to $Bi_xR_{1-x}MnO_3$ (0.1 - 0.8);

5. and also investigated the surface layer of the obtained manganites;

6. According to the results of thermal analysis, an exothermic effect was observed in the range of 400-600°C due to the mismatch of electrons in the manganite structure.;

7. The volume of manganite powders was determined by precipitation;

8. The intrinsic heat capacity of $Bi_{0.2}Dy_{0.8}MnO_3$ manganite was determined for the first time at high temperature;

9. For the first time, the thermodynamic properties of manganites $Bi_{0.2}Dy_{0.8}MnO_3$ were calculated;

10. The temperature dependence of magnetism was determined for the first time in ZFC and FC modes in a magnetic field of 10, 100, 1000 kOe for $Bi_xR_{1-x}MnO_3$ (x = 0.1; 0.4; 0.5).

Theoretical and practical significance of the work

The results obtained from the phase-guiding, structural stability of the complex oxide, the compatibility of materials and the electrochemical characteristics of the cells can be used as data for the methods of synthesis, processing and quality control used in applying bulk samples and films of manganite perovskites, as well as in chemical composition, structure and the properties of a substance in the physical chemistry of oxidized compounds. Value increases the theoretical concept. The results of thermal analysis, volumetric quantities of manganite powders, values of construction parameters and other measured and calculated values can be used as an overview for preparing material for products and electrochemical devices in accordance with this topic. In general, manganites can be considered promising in the following new areas:

- for the manufacture of magnetic field sensors;
- a spin transistor (controlled by a magnetic field) and other devices based on the strong polarization effects of current carriers;
- for the manufacture of magneto-optical converters using strong magnetopositive effects.

The results of the work can be used with a suitable choice of perovskite manganites and electrical conductivity in the magnetic properties of the memory, depending on the magnetic energy. In addition, the research results make it easy to use heterostructures containing magnetically active layers, significantly expanding the functionality of low-dimensional structures, since in this case, along with the charge, the electron spin is an active element.

Objects of research

The synthesis, phase certification, and construction of complex bismuth doped dysprosium manganites and X-ray diffraction were performed at the Integrated Chemical Biological Research Center (KazNatWTTU). The high-temperature regime of the samples was studied using an optical microscope to

study the surface layer of the surface of manganite by the method of thermogravimetric analysis, scanning electron microscope in the National Open-type Nanotechnology Laboratory (Al-Farabi Kazakh National University). The volumetric values of the synthesized compounds were determined by sedimentation at the Institute of Radio Electronics and Engineering Physics (SFU, Russia). The temperature dependence of the magnetization, the temperature dependence of the complex dielectric constant, and the temperature dependence of the magnetization in magnetic fields of 500 and 50 Oe were studied at the Institute of Physics. L.V.Kirensky (Siberian Federal University, Russia). Thermodynamics and thermochemistry of polymerization and polycondensation processes in the engineering laboratory Laboratory "Physicochemical Research Methods" (Karaganda University named after Buketov, Karaganda) were investigated by the method of thermodynamics of bismuth manganites. Magnetic resonance imaging in ZFC mode in the temperature range 10K between the -50 and 50 kOe magnet was carried out in the laboratory of Cavendish (University of Cambridge, UK).

Connection of the topic of the dissertation with priority areas of science

1. GF4/38 "Synthesis and physicochemical studies of multifunctional magnetic materials of a new generation" 2015 – 2017y.
2. AR05130165 "Development and physical foundations of new crystalline systems in the class of multiferroics" 2018 – 2020y.

Key Results:

1) For the First time manganite $Bi_xR_{1-x}MnO_3$ (0.1-0.8) was synthesized by four different methods (solid-phase method, sol-gel method, citrate-nitrate method, Pechini method), the scheme of effective method of synthesis of manganites-Pechini method was developed;

2) It is established that manganites synthesized by the Pechini method crystallize in orthorhombic singony at x =1, 2, crystallize in tetragonal singony at x =3, crystallize in cubic singony at x =8, and the number of units in the formula changes in accordance with the singony.

3) As a result of the analysis on the electron microscope skanirovanii found that powders mannitol, synthesized by the Sol-gel and citrate – nitrate methods, distributed in microrasbora, and as a method Pechyny have microrasbora if x=1 and increasing values of x have nano-scale.

4) According to the results of thermal analysis, the manifestation of the exothermic effect of manganite from 400 to 600C is manifested as a result of the oxidation of manganite.

5) The High values observed at low frequencies can be explained by the shear polarization of the spatial charge generated by inhomogeneous dielectric structures such as porosity, granulation, and combinations of two different conductive materials.

6) The heat capacity of bismuth dispersive mandanite is investigated, the thermodynamic characteristics are calculated with respect to several methods and the average values are derived.

7) Manganites synthesized at low temperatures indicate ferromagnetic properties, and at a temperature of 40-45K a small magnetic excitation is formed,

which is considered a residual magnetic excitation, manganite in this case refers to a permanent paramagnetic.

Testing of experimental results

The main conclusions on the topic of the dissertation are presented in reports presented at international conferences and forums: “XVIII International Scientific and Practical Conference of Students and Young Scientists named after Professor L.P. Kulev” (Tomsk, Russia, 2017), 70th International Scientific and practical conference “Youth and science: reality and future” (Almaty, 2017), International scientific conference “Theoretical and experimental chemistry”, dedicated to EXPO-2017 (Karaganda, 2017), “Modern trends in the development of education and science in chemistry b of Ecology, and Geography”(Almaty, 2017), the International Scientific and Practical Event of the Society of Science and Creativity“ The Sphere of Knowledge: Structural Transformations and Promising Directions for the Development of Scientific Thought ”(Kazan, Russia, 2018), International scientific-practical conference 5th International Conference on Innovations and Development Patterns in Technical and Natural Sciences (New York, USA, 2018).

The publication of the main materials of the thesis

As a result of the dissertation, 12 scientific papers were published, including 1 article in international peer-reviewed journals, 4 articles in journals recommended by the Committee for Control of Education and Science, 6 articles at international and domestic scientific and practical conferences, 1 innovative patent of the Republic of Kazakhstan.

Structure and scope of work

The dissertation consists of 127 pages of printed text. The dissertation contains a list of abbreviations and definitions, introduction, 3 chapters, general conclusions, 136 special list of literature. The work has 76 figures and 10 tables.