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ABSTRACT

of the dissertation for the degree of Doctor of Science

STRUCTURAL AND MAGNETIC PHASE TRANSITIONS IN PEROVSKITES AND HEXAFERRITES BY PRESSURE AND TEMPERATURE

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GENERAL DESCRIPTION OF WORK

The relevance of the topic. The presented dissertation work is dedicated to the synthesis of perovskite and hexaferrite compounds having ferroelectric and magnetic properties where several physical phenomena have observed and the investigation of the effect of high pressure, high and low temperature on the crystal and magnetic properties of obtained polycrystals. The compounds having perovskite structure are widely studied in the condensed matter physics as functional materials due to various physical properties. The perovskite combinations have the simple crystal structure, so they are used as model objects during the theoretical investigations. Although the hexaferrtis have a complex structure, they have sufficiently stable crystal structure. Besides, recently, these combinations attract the attention of the researchers as an interesting research object due to the ferroelectric and ferrimagnetic properties in the wide temperature range.

ABO_3 type perovskite compounds have sufficiently simple crystal structure, so, the perovskite ferroelectrics have been used as a suitable model object for the theoretical calculations of the physical parameters, in order to imagine the ferroelectric effect, to form the development model of the magnetoelectric effect, and for the explanation of other complex physical phenomena. Both the combinations ($BaTiO_3$, $PbTiO_3$, and etc.) with the ferroelectric properties and the combinations ($BaMnO_3$, $SrMnO_3$, and etc.) with the ferromagnetic properties are seen among the perovskites. The main reason for spontaneous polarization in perovskites is B metal atoms in the center of the BO_6 octahedra shifts from their ideal positions, and the reason for the formation of ferromagnetic properties is a long range magnetic-order of metal atoms in the centers of BO_6 octahedra. There are perovskites that, have both ferroelectric and ferromagnetic properties, called multiferroics. We can show bismut manganate compound as an example. Recently, the compounds with the ferromagnetic (or antiferromagnetic) properties are synthesized by substitution of the diamagnetic metal atoms with the magnetic atoms in the perovskites having the ferroelectric (or

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antiferroelectric) properties. The formation of different crystal structures in the combinations $BaTi_{1-x}Mn_xO_3$ and $BaTi_{1-x}Fe_xO_3$ obtained on the basis of $BaTiO_3$ and thestudy of the formation mechanism of long range magnetic-order is very important.

The cobalt containing compounds have a particular place among the combinations with magnetic properties. It is very significant the investigation of the structure and magnetic properties of $Ca_3Co_2O_6$ perovskite-like complex oxide in awide temperature and pressure ranges to study the formation mechanism of the long range magnetic order formed by Co atoms in different crystalline positions.

The hexaferrite multiferroics have sufficient sustainable crystal structure and stable physical properties in a wide temperature range, so, they are considered the unique materials for the different technological applications which possible to manage with their electrical and magnetic properties. Recently, the $BaFe_{12}O_{19}$ and the compounds obtained by partial substitutions of Fe atoms with diamagnetic metal atoms are themost widely studied materials. Barium hexaferrite have a ferrimagnetic feature in a wide temperature range ($T_C \sim 750$ K). The experimental investigations have shown that these combinations have the magnetic properties in a high temperature range by partial substitution of Fe atoms with Al, In, Ga, Sc, etc diamagnetic atoms. Barium hexaferrite and solid solutions obtained based on it are considered absorbing materials, therefore, they are widely applied as cover materials in the aviation technologies, space instrumentation engineering and especially in radar protection systems.

Multiferroics are considered the significant materials in the obtaining various transducers used for controlling the electrical properties under the influence of magnetic field, and conversely, for controlling the magnetic properties under the influence of electric field. These results gained during the investigation of these materials in the high pressures, low and high temperatures are very significant for the production of the transducers that are possible to use under the extreme operating conditions. It is necessary to study the crystal

structures of these combinations at atomic levels in order to study the dependence of their various properties on the crystal structure, and a comprehensive study of the physical properties . A precise study of the crystal structure, the determination of the lattice parameters, atomic coordinates, interatomic distances and interconnected angles helps toexplain different physical properties of these compounds. Because the physical properties of materials having spontaneous polarization (ferroelectrics) are explained by certain shifts of atoms from their ideal positions in the crystal structure, the precise study of atomic levels is needed more in these materials. The determination of the interaction between physical properties with crystal and magnetic structures, and the nature of chemical bonds, as well as the study of microscopic mechanisms of the physical phenomena for using in the industrial technology, is one of the main problems in the condensed matter physics, crystallophysics, and generally, in the material science. The conduction of the investigations in a wide range of the thermodynamic parameters as pressure and temperature is a perspective method for getting the new structure and magnetic phases, and the solution of the above-mentioned problems.

Aims and purpose of the research:

 The main purpose of the dissertation is determining the mechanisms of the observed structural transformations and phase transitions by studying crystal and magnetic structures, atomic dynamics of powdered polycrystals having ferroelectric and magnetic properties with perovskite and hexaferrite structure at high pressure, high and low temperature.

The following tasks have been solved to achieve the goal:

- Obtaining $BaTi_{1-x}Mn_xO_3$ ($0 \leq x \leq 0.5$) compounds by partial substitution of Mn atoms with Ti atoms in the $BaTiO_3$ compound, the study of the crystal structures, atomics dynamics and the structural aspects of the formation mechanism of magnetism in these systems.
- Exploring the structural phase transitions in the $BaTi_{0.99}Fe_{0.01}O_3$ compound at high temperature. The study of the change

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mechanisms of lattice parameters and vibration modes of the atoms of this compound in the different structure phases under the high pressure.

- The investigation of the structural and magnetic properties of $Ca_3Co_2O_6$ perovskite-like compound at high pressure and low temperature. Construction of the P-T phase diagram at low temperatures and high pressures. The determination of the change mechanism of Neel temperature depending on pressure.

- An investigation of crystal and magnetic structures of the $La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$ compound in the low temperature ranges. The study of the effect on the magnetic structure of the alternation of Mn and Fe atoms situated in different crystallographic positions in the double perovskites.

- The study of the crystal structures and atomic dynamics of $YMnO_3$ and $LuMnO_3$ and perovskite manganites under high pressure. The solution of Birch-Murnaghan equation for this compounds and determination of the bulk modulus and linear compression coefficients.

- The invetigation of the crystal structure and structural phase transitions of $BiMnO_3$ multiferroic compound in the high temperature ranges under the high pressure. Obtaining the pressure dependence of the phase transition temperature and construction of the P-T phase diagram.

- The study of crystal structure and atomic dynamics of the $BaFe_{12-x}Ga_xO_{19}$ compound gained in the result of partial substitution of Ga atoms with Fe atoms in the hexaferrite $BaFe_{12}O_{19}$. The investigation of the change mechanism of the structural properties depending on x concentration of Ga atoms.

- The study of crystal structure of $BaFe_{11.1}Ga_{0.9}O_{19}$ and $BaFe_{11.1}In_{0.9}O_{19}$ compounds in high pressure ranges. The determination of the bulk modulus and linear compression coefficients of the $BaFe_{11.1}Ga_{0.9}O_{19}$ and $BaFe_{11.1}In_{0.9}O_{19}$ hexaferrites.

Research methods:

The research objects are complex oxides with the perovskite

and hexaferrite crystal structure: $BaTi_{1-x}Me_xO_3$ (Me = Mn, Fe) compounds are the new multiferroic compounds gained on the basis of the barium titanate classical ferroelectric. Perovskite-like cobaltites, ferrites and manganites ($La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$, $Ca_3Co_2O_6$, $BiMnO_3$, $YMnO_3$, $LuMnO_3$) are the compounds having antiferromagnetic and ferrimagnetic properties with different crystal structures. The $BaFe_{12-x}Me_xO_{19}$ (Me = Ga, In) compounds have a hexagonal crystal structure and ferrimagnetic properties in a wide temperature range.

The traditional x-ray diffraction, synchrotron radiation and neutron diffraction methods have been used in order to phase analysis and determination the crystal structure of the samples. These methods are considered an important tool for the investigation of the phase transitions and various changes occured in the crystal structures of the solids as the reliable experimental methods in order to get information about crystal structure. Modern x-ray devices and synchrotrons offer opportunities in order to conduct experiments in high accuracy during the short period and wide x-ray spectral range.

The diffraction method is one of the most accurate method for the study of the crystal and magnetic structures. Neutron diffraction technique allows the study of crystal and magnetic structures of compounds that contain light element atoms and atoms with close row numbers, which in the most cases cannot be accurately determined through the x-ray diffraction analysis. Because, unlike x-rays, the neutrons are scattering from the nuclei of the atoms that formed the crystal structure. The neutrons have the spin magnetic moment, which allows them to study not only the crystal structures but also their magnetic properties when investigating the magnetic compounds while doing neutronographic studies.

The diffraction spectra gained through the x-ray and neutron diffraction methods were analyzed in the "MRIA", "VMRIA" and "FullProf" software packages using Rietveld method. The program DIAMOND 3.2 was used in the construction of the crystal structures, and the program Origin 9 in the study of the change

mechanism of the parameters.

The atomic dynamics of the research materials were investigated by Raman Spectroscopy method. Obtained results were analyzed using "Origin" software.

The most modern technologies have been used during the high-pressure investigations. The diamond anvil cells were used in the Raman spectroscopy and sapphire anvil cell were used in the neutron diffraction studies. Both diamond and tungsten carbide (WC) anvils were used during the X-ray diffraction studies by synchrotron radiation method. Each of these methods used to obtain high pressures are the most unique methods for minimizing the pressure gradient and obtaining hydrostatic pressure.

Main provisions to the defence:

1. The formation of new structural phase in the combinations $BaTi_{1-x}Mn_xO_3$ ($0 \leq x \leq 0.12$). The structural transition into the cubic (paraelectric) phase from the tetragonal (ferroelectric) phase in the $BaTi_{0.99}Mn_{0.01}O_3$ compound at $T \approx 400$ K temperature.

2. The formation of the antiferromagnetic phase in the combinations $BaMn_{1-x}Ti_xO_3$ ($0 \leq x \leq 0.25$). Antiferromagnetic to paramagnetic phase transition at low temperatures. Decrease in Neel temperature depending on the concentration of Ti atoms.

3. The formation of the long range magnetic order in the $BaFe_{1-x}Ti_xO_3$ ($0.05 \leq x \leq 0.2$) compounds. Ferromagnetic-paramagnetic phase transition at low temperatures.

4. Ferroelectric-paraelectric phase transition from tetragonal to cubic structure in the $BaTi_{0.99}Fe_{0.01}O_3$ compound under the $P \approx 19$ GPa pressure.

5. P-T phase diagram of the combination $Ca_3Co_2O_6$. Antiferromagnetic-paramagnetic phase transition at low temperatures. Increase of the Neel temperature with the coefficient of $dT_N/dP = 3.04$ K/GPa under the high pressure.

6. P-T phase diagram in the multiferroic $GaFeO_3$ for the first time. Structural phase transition from the polar orthorhombic phase into the nonpolar orthorhombic phase under $P \approx 21$ GPa pressure.

7. The magnetic structure of the combination

La$_{0.7}$Ca$_{0.3}$Mn$_{0.5}$Fe$_{0.5}$O$_3$. Ferromagnetic-paramagnetic phase transition at $T_N \approx 346$ K Neel temperature.

8. The crystal structures and atom dynamics of the manganites YMnO$_3$, LuMnO$_3$ in the pressure range $P \approx 0\text{-}30$ GPa. Solution of Birch-Murnaghan equation for these compounds.

9. The dependence of the structural properties of BaFe$_{12-x}$Ga$_x$O$_{19}$ ($0.1 \leq x \leq 1.2$) compounds on the concentration of Ga atoms. Dependence of the lattice parameters and vibration modes of atoms on the concentration of Ga atoms.

10. The crystal structures of BaFe$_{11.1}$Ga$_{0.9}$O$_{19}$ ($P = 0\text{-}5.3$ GPa) and BaFe$_{11.1}$In$_{0.9}$O$_{19}$ ($P = 0\text{-}5.5$ GPa) compounds in the high pressure range. The solution of Birch-Murnaghan equation, the bulk modulus and linear compression coefficient of these combinations.

The scientific novelty of the research:

1. Ti atoms were partially substituted for Mn atoms in the classical perovskite structure ferroelectric BaTiO$_3$ compound, and BaTi$_{1-x}$Mn$_x$O$_3$ ($0 \leq x \leq 0.12$) compounds have been synthesized. New structure phases depending on the concentration of Mn atoms, as well as atomic coordinates and inter-atomic distances for each compound have been investigated. The tetragonal-cubic phase transition at the temperature $T \approx 400$ K was found in the BaTi$_{0.99}$Mn$_{0.01}$O$_3$.

2. The partial substitutions of Mn atoms in BaMnO$_3$ antiferromagnetic compounds with hexagonal crystal structure have been realized, and the formation mechanisms of the long range magnetic-orderin the BaMn$_{1-x}$Ti$_x$O$_3$ ($0 \leq x \leq 0.25$) compound have been studied. The dependence of decreasing of Neel temperature has been determined depending on concentration of Ti atoms.

3. The structural aspects of the long range magnetic-order formation have been determined in the BaFe$_{1-x}$Ti$_x$O$_3$ compounds obtained in the $0.05 \leq x \leq 0.2$ concentration range of Ti atoms. It was observed that the Curie temperature decrease from $T_K = 133$ K to 70 K with increasing the concentration of Ti atoms.

4. The crystal structure and atomic dynamics of the BaTi$_{0.99}$Fe$_{0.01}$O$_3$ compound obtained by partial substitution of Fe atoms with Ti

atoms in the $BaTiO_3$ compound have been investigated under the high pressure at room temperature. It has been determined that the ferroelectric-paraelectric phase transition from tetragonal to cubic structure occurs at $P \approx 20$ GPa pressure. The changing mechanisms of the lattice parameters have been determined for each phase. Birch-Murnaghan equation of state has been solved for the different phases and the bulk modulus have been determined.

5. P-T phase diagram of the $Ca_3Co_2O_6$ complex oxide has been constructed in a wide temperature and pressure range for the first time. Antiferrmagnetic-paramagnetic phase transition temperature has been determined as $T_N \approx 25$ K in the low temperature range and the pressure dependence mechanism of Neel temperature has been studied. The value of the temperature of phase transition increase under the influence of high pressure.

6. The phase transition from polar orthorhombic phase to nonpolar orthorhombic phase at $P \approx 21$ GPa has been revealed in the $GaFeO_3$ multiferroic for the first time. The temperature of ferrimagnite-paramagnetic phase transition was determined $T_N \approx 292$ K in the low temperature range.

7. The long range magnetic-order has been determined at the room temperature with the equal concentration of Mn and Fe atoms in the $La_{0.7}Ca_{0.3}MeO_3$ (Me = Mn, Fe) compound. The complex magnetic structure consisting of both antiferromagnetic and ferromagnetic clusters has been observed in the low-temperature area. The antiferromagnetic-paramagnetic phase transition has been detected at $T_N \approx 346$ K.

8. P-T phase diagram has been constructed in a wide temperature and pressure range, as well as, a new intermediate phase which both orthorhombic and monoclinic phase has been observed. It was defined that the temperature interval where the intermediate phase is available is expanded with increasing the pressure.

9. The crystal structures and atomic dynamics of perovskite-like manganites $YMnO_3$, $LuMnO_3$ with high hexagonal crystal structure have been investigated at high pressures ($P \approx 0$-30 Gpa). It was determined that the phase transition is absent in the given pressure

range. Birch-Murnaghan equation of state has been solved for each combiantion and the bulk modulus have been determined.

10. The changes occurred in the crystal structure of the $BaFe_{12-x}Ga_xO_{19}$ ($0.1 \leq x \leq 1.2$) compounds synthesized through the partial substitution of Fe atoms with Ga atoms have been studied depending on the concentration of Ga atoms. It was determined that the $BaFe_{12-x}Ga_xO_{19}$ compounds in the $0.1 \leq x \leq 1.2$ range of Ga atoms have a stable hexagonal crystal structure. The changes in the lattice parameters and vibrations modes of inter-atomic connections are explained by the difference in the ionic radii of three valence Ga and Fe atoms.

11. The crystal structures of barium hexaferrits have been studied under high pressures for the first time. The crystal structure of the $BaFe_{11.1}Ga_{0.9}O_{19}$ compound has been studied in a wide pressure range (P = 0-5.3 Gpa) at room temperature. It was determined that any phase transition is absent in the crystal structure of this compound in the mentioned pressure range. Birch-Murnaghan equation for the $BaFe_{11.1}Ga_{0.9}O_{19}$ hexaferrite has been solved and the bulk modulus has been determined. The linear compression coefficient of the lattice parameters has been calculated from experimental results.

12. The crystal structure of the $BaFe_{11.1}In_{0.9}O_{19}$ hexaferrite has been investigated in the high pressure range (P = 0-5.5 GPa) at room temperature for the first time. It has been determined that, the structural phase transition do not occur in this compound in the mentioned pressure range. Birch-Murnaghan equation for the $BaFe_{11.1}Ga_{0.9}O_{19}$ hexaferrite has been solved, as well as the bulk modulus and linear compression coefficient of the lattice parameters have been calculated.

The theoretical and practical significance of the research:

The structural parameters of the compounds having different electrical and magnetic properties at the high pressures, high and low temperatures, the lattice parameters, as well as the information obtained about the interaction between magnetic properties and

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structural parameters have great importance in the crystallophysics, solid state physics, condensed matter physics, material science and chemistry – for the development of obtaining the different ferroelectrics and multiferroics with the given properties, for the development of the modern ideas about the mechanisms of formation of the physical properties in the atomic level. There are the several technical applications of perovskite ferroelectric (antiferroelectric) and ferromagnetic (antiferromagnetic) materials in some directions. We can show particularly some of them: the preparation of the small, low-frequency and high-capacity condensers, the use of large nonlinear polarization materials for the dielectric amplifiers, modulators and other control mechanisms, memory elements in the computational technology, transducers for laser irradiation, ferroelectric and antiferroelectric materials for modulation, the preparation of piezoelectric and pyroelectric transducers.

Barium hexaferrite and its solid solutions are used in the modern electronics and spintronics as magnetic-electric (or electric-magnetic) converters in devices working under extreme conditions, due to high stability of crystal structure and having magnetic properties in a wide range of temperature and pressure.These compounds are widely used in the aviation technologies, space devices and radar protection systems due to absorption properties of electromagnetic waves.

Approbation and implementation:

The results obtained in the dissertation work were discussed at the following national and international events:

XXII Международное совещание и Международная молодежная конференция «Использование рассеяния нейтронов в исследованиях конденсированного состояния» РНИКС-2012, 15–19 октября 2012, Санкт-Петербург, Россия; Birləşmiş Nüvə Tədqiqatları İnstitutunun İ.M. Frank adına Neytron Fizikası Laboratoriyasının elmi-texniki semiarı, 13 aprel 2012-ci il, Dubna, Rusiya; International Conference on Nanoscale Magnetism (ICNM2013), 02-06 September 2013, Istanbul, Turkey; Birləşmiş

Nüvə Tədqiqatları İnstitutunun İ.M. Frank adına Neytron Fizikası Laboratoriyasının elmi-texniki semiarı, 5 dekabr 2013-cü il, Dubna, Rusiya; 1st International Scientific conference of young scientist and specialist, The role of multidisciplinary approach in solution of actual problems of fundamental and applied sciences (earch, technical and chemical), 15-16 October 2014, Baku, Azerbaijan; International Conference Condensed Matter Research at the IBR-2, 11-15 October 2015, Dubna, Russia; International Workshop on Nanoscience and Nanotechnology Joint 4th Asia-Pacific Chemical and Biological Microfluidics Conference, 2-4 November 2015, Da nang, Vietnam; High Pressure Science and Technology, 54th EHPRG Meeting, 4-9 September 2016, Bayreuth, Germany; The Third International Conference On Advanced Materials And Nanotechnology (ICAMN 2016), 2-5 October, 2016, Hanoi, Vietnam; Azərbaycan Dövlət Pedaqoji Universitetinin Fizika və texnologiya fakültəsinin elmi seminarı, 3 mart 2017-ci il, Bakı, Azərbaycan; International Conference Condensed Matter Research at the IBR-2, 9-12 October 2017, Dubna, Russia; "LI Зимняя школа ПИЯФ по физике конденсированного состояния", ПИЯФ, 11-16 марта 2017, Гатчина, Россия; IV Международная конференция «Многомасштабное моделирование структур, Строение вещества, Наноматериалы и нанотехнологии», 18-21 сентября 2017 г. Тула, Россия; XVIII Всероссийская школа-семинар по проблемам физики конденсированного состояния вещества, 16-23 ноября 2017 Екатеринбург, Россия; Конференция «Молодежь в науке - 2.0'17», 30 октября – 2 ноября 2017 г. Минск, Беларусь; "52-ая Зимняя школа ПИЯФ по физике конденсированного состояния", ПИЯФ, 12-17 марта 2018, Санкт-Петербург, Россия; Ümummilli lider Heydər Əliyevin anadan olmasının 95-ci ildönümünə həsr olunmuş Gənc Tədqiqatçıların II Beynəlxalq Elmi Konfransı, 27-28 Aprel 2018-ci il, Bakı, Azərbaycan; "Modern trends in condensed matter physics, MTCMP-2018"Akademik H.B. Abdullayevin 100 illiyinə həsr olunmuş beynəlxalq konfrans və məktəb, 24-26 Sentyabr 2018-ci il, Bakı, Azərbaycan; Конференция

«Молодежь в науке - 2018», 29 октября – 1 ноября 2018 г. Минск, Беларусь.

Publications: The main results of the dissertation were published in 50 publications, of which 27 articles (including 17 foreign scientific journals with impact factor) and 23 are abstracts of the conference. Acquired results have been published in reports in the Institute of Physics of the Azerbaijan National Academy of Sciences named after academician H.M. Abdullayev.

Name of the organization where the dissertation has been performed:

Dissertation work, completed in the laboratory of "Non-standard control and diagnostic systems" of the Institute of Physics named after Academician H.M. Abdullayev.

Volume, structure and the main content of the dissertation:

The dissertation consists of the introduction, 7 chapter, results and list of 278 used literature. The study consists of 416267 symbols, 50 tables and 81 figures.

CONTENT OF WORK

Introduction covers the relevance of the topic of dissertation work, main purpose, scientific novelty, scientific and practical significance, main provisions to the defence.

Chapter I isdedicated to the literature review of the wide investigations carried out on the compounds with the perovskite and hexagonal structure. The crystal structure, structural phase transitions occurred at low and high temperatures, as well as at high pressures were investigated in the classical $BaTiO_3$ perovskite structure, and the structural parameters of each phase have been presented. The formation mechanisms of the long range magnetic-order during the partial substitutions of the diamagnetic atoms with the magnetic ions in the classical ferroelectrics have been analyzed. The structural transformations are occurring in the barium titanate by substitutions of Ti atoms with the magnetic Mn and Fe atoms.

There are some perovskites unlike the classical ferroelectrics that, they have the magnetic properties along with the spontoneus

polarization. Wide information has been reported about the multiferroics having these properties. The magnetic phenomena ocurred in the manganites, cobaltites and ferritites: the antiferromagnetism and ferrimagnetism were analyzed. It was determined that, the enhancement of the ferroelectric properties in the materials is arising in the result of the slidings of atoms from their ideal positions. At this time, the violation of the long range magnetic order occurs. During the formation of the long range magnetic-order, the regular arrangement of the magnetic ions in the direction of the certain axis of symmertry, and at this time, the atoms containing the crystal structure become to return their ideal position. In this case, the value of the spontaneous polarization decrease. Simultaneously, the ferroelectric and the structural aspects of the perovskites having magnetic properties have been revealed. The results gained on structure and magnetic properties of the $AMnO_3$[1], $ACoO_3$[2] and $AFeO_3$[3] compounds have been widely explained in the previous investigations.

The structural and magnetic properties of the barium hexaferrite and compounds synthesized onits basis were investigated. The difference of the diamagnetic metallic atoms entering the combinations from the ionic radiuses, the crystal structures of the combinations gained during the partly substitution with the metallic atoms of Fe atom sin the combinations $BaFe_{12}O_{19}$. It has been determined that the structural and magnetic properties of the $BaFe_{12-x}Me_xO_{19}$ compounds, as well as the atomic dynamics strongly depends on x concentration of these atoms and ionic radiuses of the metallic atoms included in the solutions. The stable crystal structure

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[1] Kozlenko, D.P. Antipolar phase in multiferroic $BiMnO_3$ at high pressure / D.P.Kozlenko, A.A.Belik, A.V. Belushkin [et al.] // Phys. Rev. B, -2011. v.84, -p.094108.

[2] Rutkauskas, A.V. Suppression of the antiferromagnetic state in $La_{0.82}Ba_{0.18}CoO_3$ cobaltite at high pressure / A.V.Rutkauskas, D.P. kozlenko, I.O.Troyanchuk [et al.] // JETP letters, -2015. v.101, -p.820-824.

[3] Kozlenko, D.P. Antipolar phase in multiferroic $BiFeO_3$ at high pressure / D.P.Kozlenko, A.A.Belik, A.V.Belushkin [et al.] // Phys. Rev. B, -2011. v.84, -p.094108.

is observed in the compounds synthesized on its basis as in the barium hexaferrite. The change mechanism of the lattice parameters under the high pressure has been determined.

Chapter II is dedicated to the experimental methods used to perform of the dissertation work. The methods used for the analysis of the results and the experimental devices used to conducting investigations are described. All investigations were performed using the latest generation of modern devices and equipments.

The powdered samples of the perovskite and hexaferrite compounds were synthesized and the crystal structures of these samples were investigated by x-ray diffraction method using D8 Advance (Bruker) powder diffractometer – with 40 kV, 40 mA, CuK α - X-rays ($\lambda = 1.5406$ Å) parameters at room temperature and normal condition.

The x-ray diffraction experiments through the synchrotron irradiation method were performed in the P02.2 channel of PETRA-III (DESY, Hamburg, Germany) source. The diamond anvils with d= 250 mkm were used in order to obtain the high pressures during the investigations carried out in the source of PETRA-III. The Re gasket have been used in order to place the sample among the diamond anvils. The sample with $h = 30$-40 mkm were placed in $h = 125$-130 mkm part of the gasket. The ruby crystal with $d = 10$-15 mkm was placed near the sample in order to determine the value of pressure. The value of pressure was determined with $\Delta P = 0.005$ Gpa accuracy in according to luminescence lines of the ruby. Mainly two methods are used in order to reduce the pressure gradient and to ensure the hydrostatics in the pressure chambers consisting of the ruby anvils. If the experiments are carried out under high pressures up to $P = 10$ GPa, the methanol/ethanol are used in the 4:1 ratio. The inert He and Ne gases were used under the pressure higher than $P = 10$ GPa.

The structural investigations by energy-dispersive x-ray diffraction method was carried out in the MAX80 high pressure hydraulic press (DESY, Hamburg, Germany) installed in the channel F2.1 of the DORIS-III source. WC (volfram carbide) anvils

were used in order to obtain high pressures in MAX80 device. The 6 sided compression was used to minimize the pressure gradient. The graphite furnaces placed in the special chamber were used in order to obtain a high temperature. MAX80 device has the abilitytoconduct measurements in the range T = 300-1200 K temperature and P = 0-10 GPa pressure.

The neutron diffraction experiments in high pressures were carried out in DN-12 neutron diffractometer located in the 12th channel of the "ИБР-2" impulse reactor and in DN-6 neutron diffractometer located in the 6th channel (FLNP, JINR, Dubna, Russia). DN-12 neutron diffractometer gives an opportunity to research at high pressures. The high pressure chambers containing sapphire anvils are used to obtaining high pressure that it is possible to obtain the pressure up to 10 GPa using these anvils. The neutron flux falls on the sample from distance between anvils (this distance varies by pressure). The values of the pressure, volume and temperature are determined by changes in the obtained diffraction lines. The sample is irradiated by the neutron flux, neutrons scattered from the sample are recorded with a He based gas detector. Braag angle of the detector is 90°. The spectra are recorded within 12 hours. The volume of the sample is V ~ 2.5 mm^3. The pressure gradient is about 10%. The helium cooling system is used in order to study the crystal structures and magnetic properties at low temperatures. It is possible to obtain the low temperature to 10 K in the research sample through this system. The design of the cooling system permits to place the high pressure chamber inside it. Therefore, it allows to conduct investigations at high pressures and low temperatures, simultaneously. DN-6 neutron diffractometer has been created in the DN-12 diffractometer base. It is possible to conduct experiments with both sapphire and diamond anvils in this diffractometer.

Raman spectra were measured in LabRam spectrometers (NeHe laser with the wavelength of 632 nm). The pressure chambers consisting of the diamond anvils were used in the x-ray diffraction experiments through the synchrotron irradiation method

in the P02.2 channel of the PETRA-III source to obtaining the high pressure during Raman investigations.

X-ray and neutron diffraction spectra were analyzed by Ritveld method. The crystal structures were studied using "FullProf", "MRIA", "VMRIA" and "Fit2D" programs and the magnetic structures using "FullProf" program. Raman spectra were analyzed using Guass and Lorentz functions at "Origin" software. The "Diamond 3.2" software was used to calculation of the angles between connections and lengths of interatomic bonds in the crystal structures.

The crystal and magnetic properties of the multiferroics obtained on the basis of the classical ferroelectrics were investigated in **chapter III**. The structural investigations of the powdered $BaTi_{1-x}Mn_xO_3$ compounds shown that the crystal structure of the samples in $x \leq 0.01$ concentration interval of Mn atoms are corresponds to P4mm tetragonal crystal structure at room temperature. The lattice parameters, atomic coordinates and interatomic distances of the $BaTi_{0.99}Mn_{0.01}O_3$ compound at room temperature are presented in Table 1.

Table 1. The lattice parameters, atomic coordinates and interatomic distances of the $BaTi_{0.99}Mn_{0.01}O_3$ compound at room temperature.

Space group **P4mm**, $a = b$ = 3.9930(4) Å , c = 4.0209(5) Å			
Atom	x	y	z
Ba	0	0	0
M (Ti/Mn)	0.5	0.5	0.4823(2)
O1	0.5	0.5	0.0185(3)
O2	0.5	0	0.5221(3)
Interatomic distances			
M-O1 2.177(2) Å×1			
M-O1 1.856(2) Å×1			
M-O2 2.000(2) Å×4			

It has been determined that new hexagonal crystal structure with $P6_3/mm$ space group is formed when the concentration of Mn atoms is $x = 0.04$ in the $BaTi_{1-x}Mn_xO_3$ compound. The further increase in the concentration of Mn atoms shown that the intensity of diffraction peaks corresponding to hexagonal symmetry became stronger than the intensity of diffraction peaks corresponding to tetragonal symmetry. In case of $x = 0.09$, the tetragonal phase was disappeared completely, and the hexagonal phase was obtained for the $BaTi_{1-x}Mn_xO_3$ compounds in the concentration range of $0.09 \leq x \leq 0.12$. The dependence of Mn atoms on concentration have been determined. The lattice parameters, atomic coordinates and interatomic distances in 6H type hexagonal phase of $BaTi_{0.9}Mn_{0.1}O_3$ compound at room temperature are shown in Table 2.

Table 2. The lattice parameters, atomic coordinates and interatomic distances in 6H type hexagonal phase of $BaTi_{0.99}Mn_{0.01}O_3$ at room temperature.

Space group $P6_3/mmc$, $a = b = 5.7062(4)$ Å , $c = 13.9297(5)$ Å			
Atom	x	y	z
Ba1	0	0	0.25
Ba2	1/3	2/3	0.0988(2)
M1 (Ti/Mn)	0	0	0
M2 (Ti/Mn)	1/3	2/3	0.8416(2)
O1	0.5166(2)	-0.5166(2)	0.25
O2	0.8320(3)	-0.8320(3)	0.0795(3)
Interatomic distances			
M1-O2 1.996(2) Å×6			
M2-O1 1.957(2) Å×2			
M2-O2 1.970(2) Å×4			
M1-M2 3.965(1) Å×1			
M2-M2 2.552(1) Å×1			

6H type hexagonal crystal structure consists of the connections of dimers of M_2O_9 octahedra located along the c axis

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with MO_6 octahedra standing on the corners of the crystal lattice. Two independent crystallographic M1 and M2 transition metals surrounded by octahedrons exist in this structure. M2 metal atoms are located inside the dimers, and M1 metal atoms are located within the octahedrons that standing on the nodes of the crystal lattice. The distances betweenM2 metal atoms located in the dimers are close to 2.552 (4) Å. M2 ions are displaced from the centers of the oxygen octahedra as a result of the reduction of the electrostatic repulsion of metal ions in the dimers, resulting in the distortion of the octahedrons in the dimers and leads to three of the M-O bonds smaller than the other three. The distances between the atoms M1-M2, O2-O1 and M2-O2 in the $BaTi_{0.9}Mn_{0.1}O_3$ compound are corresponds to 1.996(1) Å, 1.956(2) Å and 1.970(1) Å, respectively. It should be notethat, the distortion of the octaheder symmetry in 6H type hexagonal phase is less than the tetragonal phase. While the average distortion value of the length of M-O bonds in the tetragonal $BaTi_{0.99}Mn_{0.01}O_3$ compound is 0.058 Å, the average distortion of the length of same bonds in the $BaTi_{0.9}Mn_{0.1}O_3$ compound with 6H type hexagonal phase is approximately four times less and is equal to $\Delta l \approx 0.015$ Å.

The crystal structure of the $BaTi_{0.99}Mn_{0.01}O_3$ compound was investigated by neutron diffraction method under the influence of temperature in order to study the influence of Mn atoms to Kuri temperature of $BaTi_{1-x}Mn_xO_3$ ferroelectrics. The anomaly was observed in the temperature dependence of the latttice parameters at $T_C = 400$ K Curie temperature. This anomaly correpomds to the phase transition from the tetragonal phase with P4mm space group having ferroelectric properties to the cubic phase with Pm3m space group having paraelectric properties. It was found that the Curie temperature slightly decrease in comparison with $BaTiO_3$ ($T_K = 403$ K) as a result of the substitutions of Ti atom with Mn atoms.

The neutron diffraction investigations revealed that new phase began to be formed in the $BaTi_{1-x}Mn_xO_3$ ($0.12 \leq x \leq 0.5$) compounds in case of $x \geq 0.2$. New structural phase corresponds to the rhombohedral crystal structure with R-3m space group. Further increase in the concentration of Mn atoms leads to stronger

diffraction peaks corresponding to the rhombohedral phase in relatively to diffraction peaks corresponding to the hexagonal phase. The existence of these phases was observed to $x = 0.5$ value of the concentration of Mn atoms. The percentage of the hexagonal and rhombohedral phases in the $BaTi_{0.5}Mn_{0.5}O_3$ combination was 31:69 (Figure 1).
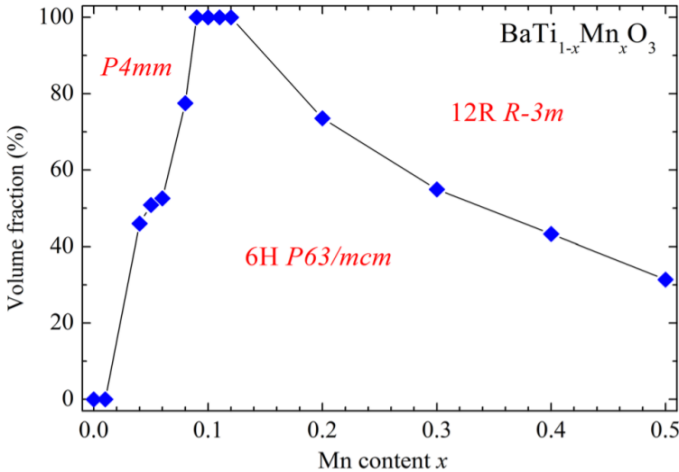

Figure 1. Dependence of the phase percentages on the concentration of Mn atoms for $BaTi_{1-x}Mn_xO_3$ compounds.

The neutron diffraction experiments were shown that the magnetic properties can not be formed under the terms of $0 \leq x \leq 0.5$ in the $BaTi_{1-x}Mn_xO_3$ crystals. The substitutions of Mn ions with Ti ions were carried out in the antiferromagnetic $BaMnO_3$ in order to formation magnetic properties in these compounds. The crystal structures of the powdered $BaMn_{1-x}Ti_xO_3$ ($0 \leq x \leq 0.25$) have been investigated by x-ray diffraction method. The crystal structure of the $BaMnO_3$ compounds corresponds to the rhombhoedral crystal structure with R-3m space group. The formation of new maximums was observed in the x-ray diffraction spectra of the $BaMn_{0.95}Ti_{0.05}O_3$ compound obtained with the partial substitutions of Mn atoms with Ti atoms in $BaMnO_3$ polycrystals. The analysis of the obtained

results shown that these maximums corresponds to the hexagonal symmetry with P6 3/mmc space group. The crystal structure of the $BaMn_{0.9}Ti_{0.1}O_3$ compound consisted of the rhombohedral and hexagonal phases. This rhombohedral phase was observed to $x = 0.25$ value of the concentration of Ti atoms.

The neutron diffraction experiments were carried out in the low temperature ranges (to $T = 10$ K) in order to study long range magnetic-order in the $BaMn_{1-x}Ti_xMnO_3$ ($0 \leq x \leq 0.25$) compounds. The new magnetic maximums were observed in all samples in the low temperature ranges. The analysis of the spectra by Rietveld method shown that the magnetic properties in the compounds corresponds to the antiferromagnetic order. The magnetic structures have been determined for hexagonal and rhombohedral phases.

The study of the crystal and magnetic properties of the multiferroics obtained on the basis of the classical ferroelectric $BaTiO_3$ was carried out in the **Chapter IV**. The powdered $BaTi_{1-x}Fe_xO_3$ ($0 \leq x \leq 0.1$) polycrystals were synthesized and the crystal structures were investigated by neutron diffraction method at room temperature. It has been determined that $BaTiO_3$ has tetragonal symmetry with P4mm space group. The crystal structures of the synthesized compounds correspond to the hexagonal symmetry with $P6_3$/mmc space group in the $x = 0.08$, 0.09, 0.1 values of concentration. The structural changes in the crystal structures of the obtained compounds were explained with the difference in the ionic radiuses of Ti and Fe atoms. The analysis of the spectra shown that the crystal structure of the $BaTi_{0.92}Fe_{0.08}O_3$ compounds correspond to the hexagonal symmetry with $P6_3$/mmc phase group. The crystal structures of the $BaTi_{0.91}Fe_{0.09}O_3$ and $BaTi_{0.9}Fe_{0.1}O_3$ compounds have the hexagonal symmetry with $P6_3$/mmc space group. The atoms are located in the hexagonal $BaTi_{1-x}Fe_xO_3$ compounds as following positions: Ba1 – (2b) (0, 0, 0.25); Ba2 – (4f) (1/3, 2/3, z); Ti/Fe1 – (2a) (0, 0, 0); Ti/Fe2 – (4f) (1/3, 2/3, z); O1 - (6h) (x, $-x$, 0.25) and O2 - (12k) (x, $-x$, z). The value of the lattice parameters and atomic coordinates calculated for these compounds are given in the Table 3.

Table 3. The lattice parameters and atomic coordinates in P6₃/mmc hexagonal phase of the $BaTi_{1-x}Fe_xO_3$ (x = 0.08, 0.09 and 0.1) comopunds.

x	0.08	0.09	0.10
a (Å)	5.714(4)	5.713(3)	5.713(3)
c (Å)	13.940(3)	13.947(2)	13.929(3)
Ba2: z	0.097(3)	0.093(4)	0.093(3)
Ti/Fe2: z	0.843(4)	0.847(2)	0.846(2)
O1: x	0.513(4)	0.513(4)	0.510(3)
O2: x	0.831(2)	0.831(3)	0.831(3)
z	0.080(4)	0.081(4)	0.081(4)

The main changes occurring in the crystal structures of the compounds in the result of the increasing x concentrations of Fe atoms is related to the difference ionic radiuses between titan and iron atoms: the ionic radius of Fe atoms R_{Fe} = 0.54 Å and the ionic radius of Ti atoms R_{Ti} = 0.65 Å differs sufficiently from each other. As we know, the difference in the ionic radiuses directly influences the length of the interatomic bonds that forms the crystal structure. Therefore, while Fe atoms concentration increases in the $BaTi_{1-x}Fe_xO_3$, the compounds are formed in higher symmetry structure.

The neutron diffraction experiments of the $BaTi_{1-x}Fe_xO_3$ compounds shown that the magnetic properties are not observed in the x = 0-0.1 concentration range of the Fe atoms. The metal atoms shifts towards the center of Ti(Fe)O₆ octahedra by partial substitutions of Ti atoms with Fe atoms. Consequently, the ferroelectric properties decrease with increasing the concentration of Fe atoms.

The magnetic properties are not observed in the $BaTi_{1-x}Fe_xO_3$ (x = 0.08, 0.09, 0.1) compounds, therefore, the $BaFe_{1-x}Ti_xO_3$ (x = 0.05, 0.1, 0.15, 0.2) compounds were synthesized to observing the formation mechanism of long range magnetic-order. It has been determined that, these compounds have the hexagonal symmetry crystal structure with P6₃/mmc space group. The crystal structure

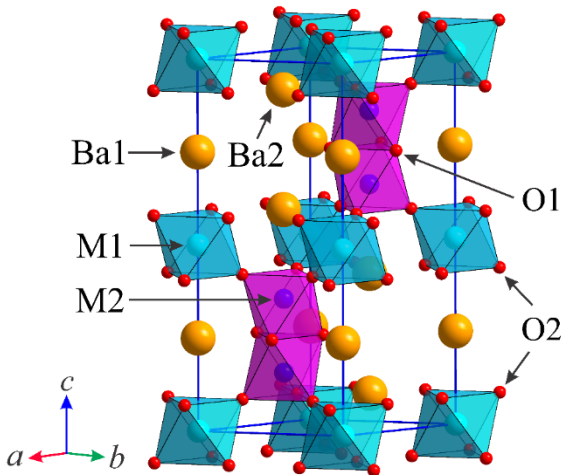obtained under normal condition and room temperature are given in figure 2.

Figure 2. The crystal structure of the $BaFe_{1-x}Ti_xO_3$ ($0.05 \geq x \geq 0.2$) compound at normal condition and room temperature.

The different changes have been observed in the values of the lattice parameters, length of the interatomic bonds and interbond angles with increasing the concentration of Ti atoms in the compounds. Obtained results have shown that these changes corresponds to approaches to the tetragonal crystal structure and have the ferromagnetic properties in the low temperature ranges. The study of the structural aspects of long range magnetic-order shown that the octahedra formed by oxygen atoms in the unit cell are joined to forms a dimers. Curie temperature of the $BaFe_{1-x}Ti_xO_3$ compounds in the $0.05 \geq x \geq 0.2$ concentration of Ti atoms decrease from $T_C = 133$ K to 70 K. The attenuation of the magnetic properties depending on the Ti atoms has been observed not only in the decrease in Curie temperature, but also in the values of the magnetic moments of Fe atoms located in the different crystallographic positions.

The crystal structure and atomic dynamics of the $BaTi_{0.99}Fe_{0.01}O_3$ compounds were investigated by neutron diffraction, x-ray diffraction and Raman spectroscopy methods under the

influence of high pressure. It was determined that the ferroelectric-paraelectric phase transition occurs from tetragonal to cubic structure at $P \approx 19$ GPa pressure. The change mechanisms of the lattice parameters for each phase were defined. The pressure dependence of unit-cell parameters was obtained for tetragonal and cubic phases and Birch-Murnaghan equation has been solved. Bulk modulus and linear compression coefficients were determined. According to the results obtained from experiments, the tetragonal phase corresponds to $B_0 = 121(3)$ GPa and $B' = 4.0(5)$, the cubic phase corresponds to $B_0 = 147(8)$ GPa and $B' = 4.0(5)$ values.

X-ray diffraction investigations were confirmed by Raman spectroscopy experiments. The analysis of Raman spectra obtained in the pressure range of $P = 0\text{-}36.49$ GPa shown that there are significant changes in the vibration modes at $P \approx 19$ GPa.

In **Chapter V**, the phase transitions and the structural properties of these phases in the perovskite-like manganites having different structure and magnetic properties in a wide range of temperature and pressure are investigated under the influence of pressure and temperature.

The crystal structure of $BiMnO_3$ multiferroic has been investigated using the energy dispersive x-ray diffraction method. Simultaneously, P-T phase diagrams have been constructed based on the structural studies at high pressures ($P = 0\text{-}4$ GPa) and high temperatures ($T = 300\text{-}900$ K). It has been determined from high-temperature experiments that phase transition occurs from monoclinic symmetry with C2/c space group to orthorhombic phase with Pnma space group at $T \approx 773$ K temperature. At the same time, the crystal structure of the $BiMnO_3$ multiferroic along with the reduction in the transition temperature of the monocline-orthorhombic phase has been formed under the influence of pressure and temperature, as well as the intermediate phase of each these structures. At $P < 1.6$ GPa pressures, at first monoclinic phase with C2/c space group (M1), followed by II monoclinic phases with C2/c space group (M2) and after all orthorhombic phase (O) with Pnma space group were observed in the high temperature ranges. Phase

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transition temperatures are obtained $T_{M1-M2} = 490$ K and $T_{M2-O} = 773$ K under the normal conditions ($P = 0$ GPa pressure). The intermediate phase width increase with increasing the pressure. The lattice parameter a sharply increased and parameters b and c decreased when the structural transformation occurred in the monoclinic phase, resulting in the unit cell volume reduced by 0.2%.

The Birch-Murnaghan equation has been solved and bulk modulus have been determined. According to the obtained results, the values for the $BiMnO_3$ corresponds to $B_0 = 125(5)$ GPa and $B' = 4(1)$.

X-ray diffraction investigations were performed to study the crystal structure of $BiMnO_3$ compound in a wide pressure range. A new struvtural phase transition was observed at $P = 20$ GPa pressure. A new structure phase in $BiMnO_3$ crystals corresponding to the orthorhombic crystal structure with Imma space group was detected when analysing the obtained spectra by Rietveld method. Cubic-like $a_p\sqrt{2} \times 2a_p \times a_p\sqrt{2}$ perovskite model was used for orthorhombic Pnma and Imma phases. The main difference between these structures is a location at different angles of MnO_6 octahedrons which formed them. In Pnma structure phase, MnO_6 octahedra rotate by certain angle around the axes of (010) and (101), but in the Imma structure phase, MnO_6 octahedrons only rotate at a certain angle around the axis of (010). It has been determined that Jahn-Teller distortion occurs in Pnma phase but do not occur in the Imma phase.

The structure and magnetic properties of the polycrystals of powdered $BiMn_2O_5$ double perovskite compounds were investigated in the range of $P = 0$-5.7 GPa pressure and $T = 10$-60 K temperature, pressure dependence of Neel temperature has been obtained and P-T phase diagram has been constructed. It has been determined that this compound has antiferromagnetic properties at normal condition in the low temperature range and antiferromagnetic-paramagnetic phase transition are observed at $T_N \approx 41$ K temperature. There are observed an increase in Neel temperature by $dT_N/dP = 3.04$ K/GPa coefficient under the influence of high pressure. The atomic coordinates, interatomic distances and the interbond angles are determined

determined for the antiferromagnetic and paramagnetic phases. Crystal structure is presented in figure 3.

The magnetic moments of Mn atoms in the crystal lattice have been determined, as well as pressure and temperature dependence of magnetic moments have been constructed The crystal and magnetic structure have been constructed from $Mn^{3+}O_5$ octahedra and $Mn^{3+}O_5$ bipyramids (Figure 3).
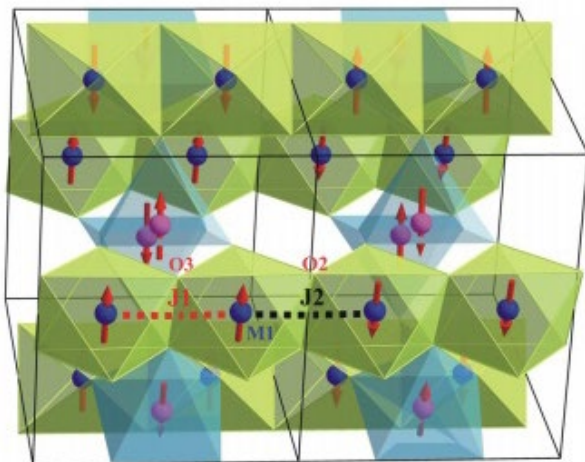

Figure 3. The crystal and magnetic structure of the $BiMn_2O_5$ compound.

It has been determined in the result of the analysis of the neutron diffraction spectra obtained in $T = 10\text{-}60$ K temperature range that the crystal structure of this compound has orthorhombic symmetry with Pbam space group in the low temperature ranges. The lattice parameters, atomic coordinates, interatomc distances and interbond angles in the $BiMn_2O_5$ compound obtained at 60 K temperature are given in table 4.

The crystal structure and atomic dynamics of the YMn_2O_5 compound were studied by neutron diffraction, X-ray diffraction and Raman spectroscopy in the high-pressure ranges. It has been determined that the YMn_2O_5 compound has orthorhombic symmetry

with Pbam space group under normal condition. P-T phase diagram has been constructed in the range of $P = 0$-6.5 GPa pressure and $T = 10$-290 K temperature. The phase diagram reveals the anomaly is observed in the pressure dependence of the Neel temperature and there was a decrease. It has been found that the YMn_2O_5 compound has antiferromagnetic properties in the low temperature ranges and normal condition. Antiferromagnetic-paramagnetic phase transition is observed at $T_N \approx 45$ K of Neel temperature. The magnetic moments of three-valence and four-valence Mn atoms were determined, as well as the pressure and temperature dependencies, were established.

Table 4. Lattice parameters, atomic coordinates, interatomic distances, and interbond angles of $BiMn_2O_5$ compound at 60 K.

Space group: Pbam, $a = 7.5574(8)$ Å, $b = 8.5543(9)$ Å, $a = 5.7704(7)$ Å

Atom	Position	x	y	z
Bi	4g	0.1624(5)	0.1669(5)	0
Mn1	4f	0	0.5	0.2558(6)
Mn2	4h	0.4097(8)	0.3501(9)	0.5
O1	4e	0.5	0.5	0.2945(7)
O2	4g	0.1586(9)	0.4410(7)	0
O3	4h	0.1430(8)	0.4281(7)	0.5
O4	8i	0.3873(7)	0.1992(6)	0.2498(9)

Mn-O (Å)		Mn-Mn (Å)		Mn-O-Mn (°)	
Mn1-O2×2	1.967(5)	Mn1-Mn1	2.818(5)	Mn1-O2-Mn1	99.2(2)
Mn1-O3×2	1.879(5)	Mn1-Mn1	2.952(5)	Mn1-O3-Mn1	97.2(2)
Mn1-O4×2	1.905(5)	Mn2-Mn2	2.910(2)	Mn1-O3-Mn2	130.5(2)
Mn2-O1×1	1.875(6)			Mn1-O4-Mn2	122.8(2)
Mn2-O3×2	2.123(9)			Mn2-O1-Mn2	101.0(2)
Mn2-O4×2	1.944(8)				

X-ray diffraction investigations have shown that the phase transition occurs observing with an anomaly on the change

mechanism of the lattice parameters of the orthorhombic phase in the compound at $P \approx 16$ GPa of pressure. This phase transition has also been observed during Raman spectroscopy studies in the changing mechanism of the vibration modes. Birch-Murnaghan equation has been solved for YMn_2O_5 crystals. According to the experimental results: $B_0 = 192(5)$ GPa and $B' = 3.0(5)$ values of the coefficients have been determined.

The crystal structures of powdered samples of $YMnO_3$ and $LuMnO_3$ perovskite-like manganites with hexagonal crystal structure were studied at room temperature and wide pressure range ($P \approx 0$-30 GPa) by x-ray diffraction method. It has been determined that, any structural phase transition is absent at the indicated pressure range and these compounds have a stable crystal structure. It has been determined that, no any structural phase transition occurs under the pressure interval stated and these combinations have a stable crystal structure.

Atomic coordinates obtained for $YMnO_3$ compound at room temperature and normal conditions by x-ray diffraction method are given in the Table 5.

Table 5. Atomic coordinates of the $YMnO_3$ compound.

Atom	x	y	z
Y1	0	0	0.2726(6)
Y2	1/3	2/3	0.2388(5)
Mn	0.3516(10)	0	0
O1	0.3127(7)	0	0.1647(6)
O2	0.6549(6)	0	0.3367(6)
O3	0	0	0.4974(8)
O4	1/3	2/3	0.0197(5)

The pressure dependence of volume of the unit cell of $YMnO_3$ compound at room temperature reveals the lattice parameters decrease by $k_i = (1/l_0)(dl/dP)_T$ law with increasing the pressure. The values of $k_a = 0.0014(6)$ GPa^{-1}, $k_c = 0.0006(2)$ GPa^{-1} were determined for the change in the parameters of a and c, respectively.

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The reduction of the volume was studied by Birch-Murnaghan equation, and $B_0 = V(dP/dV)_T$ bulk modulus, as well as its $B' = (dB_0/dP)_T$ first-order pressure derivative values were calculated for YMnO$_3$. According to the results obtained from the experiments: $B_0 = 214(7)$ GPa and $B' = 4(1)$.

The x-ray structure investigations were carried out also for the LuMnO$_3$ compounds. Atomic coordinates gained at room temperature and under normal conditions are given in table 6.

Table 6. Atomic coordinates of LuMnO$_3$.

Atom	x	y	Z
Lu1	0	0	0.2854(3)
Lu2	1/3	2/3	0.2371(2)
Mn	0.3387(1)	0	0
O1	0.3172(7)	0	0.1736(5)
O2	0.6387(6)	0	0.3447(9)
O3	0	0	0.4740(5)
O4	1/3	2/3	0.0237(8)

The analysis of x-ray diffraction spectra obtained at high pressures confirmed that the phase transition was not observed in LuMnO$_3$ compound in the $P = 0$ - 31.2 GPa pressure range similar to the YMnO$_3$ compound. The reduction in the lattice parameters and the volume of the unit cell under the influence of pressure is associated with a decrease in the lengths of interatomic bonds at high pressures. Hexagonal syngony is sufficiently high symmetry crystal structure. The row number of the C$_{6v}$ P6$_3$cm space group observed in RMnO$_3$ compounds is sufficiently high (185) among the hexagonal syngony space groups. Pressure dependence of volume of the LuMnO$_3$ unit cell revealed that the lattice parameters decrease according to $k_l = (1/l_0)(dl/dP)_T$ law with increasing the pressure. Linear compression coefficients of the lattice parameters a and c depending on the pressure are $k_a = 0.0012(1)$ GPa^{-1}, $k_c = 0.0006(9)$ GPa^{-1}, respectively. The empirical parameters

obtained from Birch-Murnaghan equation corresponded to $B_0 = 237(7)$ GPa and $B' = 4(1)$.

Atomic dynamics of $YMnO_3$ and $LuMnO_3$ compounds were investigated by Raman spectroscopy method at room temperature and in the range of $P = 0\text{-}30$ Gpa pressure. Obtained results shown that the phase transition do not occur which also confirmed by x-ray study. Raman spectra have been obtained at different pressures for each compound in the frequency range of $v = 250\text{-}900$ cm^{-1}. The values of the vibration modes were determined analyzing spectra by Gaussian function and pressure dependence has been obtained.

Neutron diffraction experiments on the YMn_2O_5 compound were carried out in the low temperature ranges to study of magnetic properties, the effect of high-pressure on the antiferromagnetic-paramagnetic phase transition. Moreover, neutron diffraction investigations were conducted to constructing P-T phase diagram in the range of $T = 10\text{-}290$ K temperature and $P = 0\text{-}6.5$ GPa pressure. High pressures on the powdered YMn_2O_5 polycrystals were obtained using sapphire anvils cell. Low temperatures were obtained by helium in the system where a high pressure chamber could be placed in. During the analysis of neutron diffraction spectra obtained under normal conditions and at low temperatures for YMn_2O_5 combination, the crystal structure of the YMn_2O_5 compound at room temperature underlies the crystal structure of $BiMn_2O_5$ compound. It can be seen from the spectrum that the phase transformation did not occurred in the temperature range $T = 10\text{-}290$ K. New magnetic peaks were formed at $T = 40$K when $d_{hkl} \approx 6.90$ Å, 5.20 Å and 3.98 Å. Analysis of the spectra reveals these changes is due to the formation oof antiferromagnetic structure. Magnetic moment values of Mn^{3+} and Mn^{4+} ions were determined from neutron diffraction spectra of the YMn_2O_5 compound. The average value of the magnetic moment for Mn^{3+}/Mn^{4+} ions at $T = 10$ K and under normal condition is $\mu = 3.30(5)$ µB, which is significantly higher than the $BiMn_2O_5$ compound. Temperature dependence of average value of the magnetic moment for Figure 5.20 shows the temperature dependence of the average values of the magnetic moment for the Mn^{3+}/Mn^{4+}

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ions at different pressures in the YMn$_2$O$_5$ compound. As it is seen, there has been decrease in the values of magnetic moments due to high pressure. About $\mu = 1.40(7)$ μ_B at $P = 5.4$ GPa pressure and $\mu = 0.70(5)$ μ_B at $P = 6.5$ GPa pressure decreased at $T = 10$ K temperature. Apparently, the magnetic properties of YMn$_2$O$_5$ multiferroic compound weakened under high pressure. It is known that, the effect of high pressure on the structure and magnetic properties of compounds with magnetic properties can be different. In some cases, the spin-spin interaction is enhanced by the convergence of the magnetic properties forming the crystal structure under pressure. However, in some compounds, there is a partial disruption of the long range magnetic-orderdue to the increased fluctuations during the atomic vibrations in the crystal structure at high pressures. Neutron diffraction studies show that, as with the BiMn$_2$O$_5$ compound, there are a decrease in the magnetic moment values of Mn^{3+}/Mn^{4+} ions also in the YMn$_2$O$_5$ compound. The value of the Neel temperature has been determined $T_N \approx 45$ K. The curves obtained at pressures of $P = 1.2$ and $P = 5.4$ GPa reveals there was a decrease in the Neel temperature due to the high pressure, which is explained by the increased fluctuations of the atoms under high pressure. P-T phase diagram of the YMn$_2$O$_5$ multiferroic compound determined at low temperature and high pressure is given in figure 5. The pressure dependence of the Neel temperature is interpolated by the linear function. It has been established that Neel temperature is reduced by the $dT_N/dP = -1.1$ K/GPa coefficient under the influence of high pressure.

In **Chapter VI**, The crystal structures and magnetic properties of the Ca$_3$Co$_2$O$_6$, GaFeO$_3$ and La$_{0.7}$Ca$_{0.3}$Mn$_{0.5}$Fe$_{0.5}$O$_3$ compounds are investigated to study of structural and magnetic properties of perovskite-like cobaltites and ferrites**.**

The crystal and magnetic structures of the Ca$_3$Co$_2$O$_6$ compound have been widely investigated by neutron diffraction and x-ray diffraction methods. Neutron diffraction method has been determined that this conpound has rhombohedral symmetry with R-3c space group. The magnetic moments of Co atoms in different

positions were determined and temperature dependences were obtained. P-T phase diagram has been constructed in the range of P = 0-6.8 GPa pressure and T = 4-290 K temperature. Phase diagram revealed that Neel temperature increase depending on the pressure. It was found that $Ca_3Co_2O_6$ has antiferromagnetic properties in the low-temperature area and under normal condition. Antiferromagnetic-paramagnetic phase transition occurs at $T_N \approx 25$ K Neel temperature. As the pressure increased, the Neel temperature increased with the coefficient dT_N/dP = 0.65 K/GPa. Pressure dependences of Co-Co, Co-O and O-O interatomicdistances have been obtained, and the mechanism for changing the lengths of the bonds depending on the pressure has been determined.

The structural studies have been carried out in the high pressure range by x-ray diffraction method. The study states that structural transformation do not occurs in the $Ca_3Co_2O_6$ to $P \approx 32$ GPa value of pressure, and the rombohedric symmetry with R-3c space group is maintained. Pressure dependence of lattice parameters and unit cell volume has been obtained at room temperature and P = 0-32 GPa pressure range. Birch-Murnaghan equation was solved according to the change in the relative volume depending on the pressure. The coefficients are determined as B_0 = 154(5) GPa and B' = 4.0(5) based on the experimental results.

High-precision (R_p = 6.41% and R_{wp} = 8.52%) analysis of the angular dispersive x-ray diffraction spectra obtained at room temperature and high pressure for the $Ca_3Co_2O_6$ shown that the crystal structure of this compound corresponds to rhombohedric symmetry with R-3c space group. Lattice parameters are: a = 9.0663(3) Å and c = 10.372(4) Å. X-ray diffraction spectra in the high-pressure ranges shown that significant changes did not occurr such as the formation of new maximums or the disappearance of the maximum up to P = 31.62 GPa of pressure. It is connected with the absence of the phase transition. However, there was a shift in the spectrum to the higher values of Bragg angle, due to the decrease in the lattice parameters.

The pressure dependencies of lattice parameters and unit cell volume of the $Ca_3Co_2O_6$ compound are shown in Figure 4.

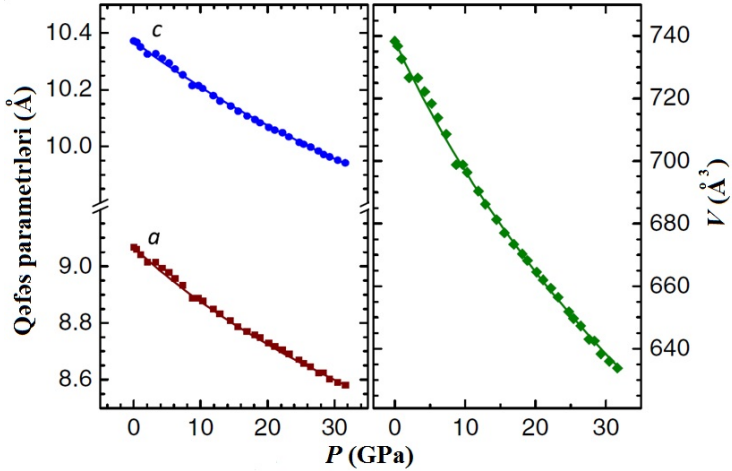**Figure 4. Pressure dependence of lattice parameters and unit cell volume of the $Ca_3Co_2O_6$ compound at room temperature.**

The linear compression $k_i = -(1/a_{i0})(d_{ai}/dP)_T$ of the cell parameters values are: $a_i = 0.0072$ GPa^{-1} for the cell parameter a, and $k_c = 0.0052$ GPa^{-1} for the parameter c. It seen from the compression coefficients values that the parameter a is compressed by 40% more than the parameter c. This is due to the fact that the crystal structure becomes anisotropic, and compression occurs mainly on the ab plane under the influence of high pressure. Therefore, $Ca_3Co_2O_6$ crystals are considered a chain structure.

Volumetric compression of calcium cobaltite was studied by the Birch-Murnaghan equation, $B_0 = V(dP/dV)_T$ bulk modulus and its $B' = (dB_0/dP)_T$ first-order pressure derivative was determined. It was obtained from experiments that these coefficients correspond to: $B_0 = 154(5)$ GPa and $B' = 4.0(5)$.

The crystal structure and magnetic properties of the $La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$ compound obtained with an equal concentration of Mn and Fe atoms were studied at low temperatures in order to study the magnetic properties of atoms having magnetic

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properties in complex oxides with their alternation in the crystal structure. It was determined that this compound has a crystal structure with Pnma space group and orthorhombic symmetry under normal conditions. Atomic coordinates, the length of the interatomic distances have been determined under normal conditions and at room temperature. Neutron diffraction studies revealed that the phase transition is absent in the temperature range to $T = 10$ K and the orthorhombic symmetry of the Pnma group is preserved. Temperature dependences of the cell parameters are obtained in the low temperature range and the change mechanisms of these parameters were determined depending on the temperature.

The long range magnetic-order was studied at low temperature by alternation of Mn^{3+} and Fe^{3+} magnetic ions in the Mn/Feu6 octaheder containing crystal structure of $La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$ compound. It was determined that this compound has antiferromagnetic properties under normal conditions and at room temperature. In the low-temperature region, there was an observed increase in the magnetic moments of Mn and Fe atoms, which is explained by the strengthening of the long-range magnetic-order due to the thermal extinction. The temperature dependence of the magnetic moments of the atoms has been obtained and determined that the antiferromagnetic-paramagnetic phase transition occurs at the $T_N \approx 346$ K Neel temperature.

As a result of neutron diffraction studies, it was determined that $GaFeO_3$ compound has ferrimagnetic properties in the low temperature range and ferrimagnetic-paramagnetic phase transition was observed at $T_N \approx 292$ K temperature. Neel temperature increased by the influence of the high pressure and acquired magnetic properties at $P \approx 2.5$ Gpa pressure and room temperature. P-T phase diagram of $GaFeO_3$ multiferronics is constructed at low temperatures and high pressure. Magnetic moments μ were determined for Fe1, Fe2, and Fe3 atoms located in different crystallic positions. It was determined that the F3 and Ga2 atoms are located at the same position in the crystal structure. Therefore, the crystal structure of the $GaFeO_3$ compound consists not only of Ga/FeO_6 octahedra but also

of Ga/FeO_4 tetrahedra. X-ray diffraction studies conducted at high pressures and room temperature shown that the transition from the polar orthorhombic phase to the non-polar orthorhombic phase occurs at $P \approx 21$ GPa pressure.

Lattice parameters obtained from x-ray diffraction spectra of the GaFeO3 compound under normal condition: $a = 8.754(3)$ Å, $b = 9.396(3)$ Å, and $c = 5.078(2)$ Å. It seen from analysis of the diffraction spectra that the lattice parameters decreased according to the $k_l = (1/l_0)(dl/dP)_T$ law with increasing the pressure: $k_a = 0.0015 GPa^{-1}$, $k_b = 0.0024 GPa^{-1}$, $k_c = 0.0012 GPa^{-1}$. The volumetric compression of gallium ferrite was studied by the Birch-Murnaghan equation, bulk modulus $B_0 = V(dP/dV)_T$ and the first-order pressure derivative $B' = (dB_0/dP)_T$ have been determined.

According to the results obtained from the experiments B_0 and B' are corresponds to 202.8(2.5) GPa and 4.0(5), respectively. There was a 7% decrease in the unit cell volume during the transition from the $Pc2_1n$ space group orthorhombic phase to the Pbmn space group orthorhombic phase. For the orthorobic pbnm phase of the $GaFeO_3$ combination, the equation of Birch-Murnaghan equation also solved for Pbmn orthorhombic phase of the GaFeO, as well as thebulk modulus is defined as $B_0 = 295(10)$ GPa. Lattice parameters of the Pbnm phase at $P = 30.5$ Gpa pressure are $a = 4.9900$ (9) Å, $b = 5.070$ (9) Å and $c = 7.000(15)$ Å.

Detected phase transition in the $GaFeO_3$ compound at high pressures is also confirmed by Raman spectroscopy studies conducted using diamond anvils.

In **chapter VII**, $BaFe_{12-x}Me_xO_{19}$ (Me = Ga; $x = 0.1, 0.3, 0.6, 0.9, 1.2$) compounds were obtained in order to study the structural changes that occur when partial substitutions of Fe atoms with diamagnetic metal atoms in barium hexaferrite, as well as crystal structures of samples and atomic dynamics were studied. X-ray diffraction study of $BaFe_{12-x}Ga_xO_{19}$ ($0.1 \leq x \leq 1.2$) samples were revealed that the crystal structures of these compounds correspond to hexagonal crystal structure with $P6_3mmc$ phase group at room temperature and normal condition. The coordinates of the atoms that

formed the crystal structures of compounds were determined, as well as the interatomic distances and interbond angles were calculated. It was found that the lattice parameters increase with increasing the concentration of Ga atoms in $BaFe_{12-x}Ga_xO_{19}$ compounds. This phenomenon is explained by the fact that Ga^{3+} ions have larger ionic radius than Fe^{3+} ions. Lattice parameters are presented in table 7.

Table 7. Lattice parameters and unit cell volume of $BaFe_{12-x}Ga_xO_{19}$ ($x = 0.1, 0.3, 0.6, 0.9$ and 1.2) compounds at room temperature.

Compound	Lattice parameters		
	a, Å	c, Å	V, Å³
$BaFe_{11.9}Ga_{0.1}O_{19}$	5.878(8)	23.154(3)	800.3
$BaFe_{11.7}Ga_{0.3}O_{19}$	5.875(2)	23.135(1)	798.6
$BaFe_{11.4}Ga_{0.6}O_{19}$	5.871(5)	23.114(9)	796.9
$BaFe_{11.1}Ga_{0.9}O_{19}$	5.866(8)	23.091(8)	794.8
$BaFe_{10.8}Ga_{1.2}O_{19}$	5.862(1)	23.065(1)	792.6

Changes in the crystal structure were also effect on the atomic dynamics. Raman spectroscopy method was revealed the shifts at the vibration modes of atoms when partial replacing of Fe atoms with Ga atoms in the $BaFe_{12-x}Ga_xO_{19}$. The dependence of the frequencies of vibration modes on the x concentration of Ga atoms has been determined. If we look at the lattice parameter values shown in table 7, the lattice parameter a decreased from $a_0 = 5.878(8)$ Å to $a = 5.862(1)$ Å i.e. 0.29% ($\Delta a = 0.016(7)$ Å) in the $0.1 \leq x \leq 1.2$ concentration range of the Ga atoms.. There is a further decrease in the lattice parameter c. It is from $c_0 = 23.154(3)$ Å to $c = 23.065(1)$ Å ($\Delta c = 0.089(2)$ Å), which is 0.38%. Atomic coordinates determined by x-ray diffraction are shown in table 8.

In the Diamond 3.2 program, it has been determined that following parameters are formed when partial substitutions of Fe atoms with Ga atoms: $Fe(5)/Ga(5)O_6$, $Fe(1)/Ga(1)O_6$, $Fe(5)/Ga(5)O_6$,

Fe(1)/Ga(1)O_6, Fe(4)/Ga(4)O_6 and Fe(5)/Ga(5)O_6 octahedra, Fe(2)/Ga(2)O_5 bipyramids and Fe(3)/Ga(3)O_4 tetrahedra.

Table 8. Atomic coordinates of the $BaFe_{11.9}Ga_{0.1}O_{19}$ compounds at room temperature.

Atom	x	y	z
Ba	2/3	1/3	1/4
Fe1(Ga1)	0.00000	0.00000	0.00000
Fe2(Ga2)	0.00000	0.00000	0.2573(1)
Fe2(Ga2)	0.00000	0.00000	1/4
Fe3(Ga3)	1/3	2/3	0.0274(1)
Fe4(Ga4)	1/3	2/3	0.1889(8)
Fe5(Ga5)	0.1668(9)	0.3374(1)	-0.1082(9)
O1	0.00000	0.00000	0.1501(6)
O2	1/3	2/3	-0.0551(2)
O3	0.1887(5)	0.3643(1)	1/4
O4	0.1555(9)	0.3129(1)	0.0518(2)
O5	0.5033(9)	0.0052(1)	0.1490(8)

When the concentration of Ga atoms increases in the $BaFe_{12-x}Ga_xO_{19}$ compounds (in the range of $0.1 \leq x \leq 1.2$), the chemical pressure results in more compression in the direction of the $\vec{c}$ axis relative to the $\vec{a}$ and $\vec{b}$ axes. Hexagonal crystal structure is more stable in the $\vec{a}\vec{b}$ plane.

X-ray studies shown that the crystal structures of hexagonal ferrites and their compounds consist of different polyhedra: Fe(Me)O_6 octahedra, Fe(Me)O_5 bipyramids, and Fe(Me)O_4 tetrahedra. The reason for the formation of long range magnetic-order is the regular arrangement of Fe^{3+} magnetic ions located in the centers of these polyhedra in the direction of a certain axis.

The crystal structures of the synthesized $BaFe_{11.1}Ga_{0.9}O_{19}$ and $BaFe_{11.1}In_{0.9}O_{19}$ as a result of partial replacement of Fe atoms with Ga and In atoms in $BaFe_{12}O_{19}$ crystals were investigated by neutron

diffraction method in the pressure ranges of $P = 0$-5.3 GPa and $P = 0$-5.5 Gpa, respectively. It was determined that the crystal structure of these compounds correspond to hexagonal structure with $P6_3mmc$ space group under normal condition. This structure is preserved up to $P \approx 5$ GPa of pressure at room temperature. The pressure dependence of the unit cell volume and lattice parameters, as well as the linear compression coefficients of the lattice parameters, were determined. The volumetric compression of $BaFe_{11.1}Ga_{0.9}O_{19}$ and $BaFe_{11.1}In_{0.9}O_{19}$ compounds has been studied by the Berch-Murnaghan equation. Bulk modulus was determined for each compound based on the experimental results.

CONCLUSION

1. $BaTi_{1-x}Mn_xO_3$ compounds were synthesized in the $0 \leq x \leq 0.12$ concentration range by partial substitutions of Ti atoms with Mn atoms in the classical ferroelectric $BaTiO_3$ compound having a perovskite crystal structure. Regularities of the formation of tetragonal, hexagonal, and rhombohedral structural phases of Mn atoms depending on the concentration of x have been determined. For the first time, atomic coordinates and interatomic distances were determined for these structural phases. It was determined that the $BaTi_{0.99}Mn_{0.01}O_3$ compound has a tetragonal-cubic structure phase transition at $T_C \approx 400$ K Curie temperature.

2. Partial replacements of Mn atoms with Ti atoms in the antiferromagnetic $BaMnO_3$ compound with a hexagonal crystal structure were performed and the formation mechanisms of the long range magnetic-order in the $BaMn_{1-x}Ti_xO_3$ ($0 \leq x \leq 0.25$) compounds were studied. The structural and magnetic properties of rhombohedral and hexagonal phases were determined. It was defined that while the Neel temperature of $BaMnO_3$ is equal to $T_N = 230$ K, for $BaMn_{0.75}Ti_{0.25}O_3$ is equal to $T_N = 100$ K. The reduction mechanism of the Neel temperature depending on the x concentration of Ti atoms in the $BaMn_{1-x}Ti_xO_3$ system are determined.

3. The crystal structure and atomic dynamics of the $BaTi_{0.99}Fe_{0.01}O_3$ compound were studied under the influence of high pressure at room temperature. It was determined that the phase transition occurs from P4mm tetragonal structure to Pm-3m cubic structure at $P \approx 20$ GPa pressure and room temperature. The change mechanisms of the lattice parameters for each phase were determined. The Birch-Murnaghan equation for different phases was solved and obtained values are $B_0 = 121(3)$ GPa and $B_0 = 147(8)$ GPa for tetragonal and cubic phases, respectively.

4. The crystal structure and atomic dynamics of perovskite-like $YMnO_3$ having a hexagonal crystal structure in the pressure range of $P = 0\text{-}25.75$ GPa were studied. It has been shown that the hexagonal symmetry with $P6_3cm$ space group is preserved in the given pressure range, and the structural phase transition is absent. Birch-Murnaghan state equation for $YMnO_3$ has been solved and defined that the value of the bulk modulus is $B_0 = 214(7)$ Gpa.

5. The crystal structure and atomic dynamics of the $LuMnO_3$ multiferroics were studied at room temperature and high pressure ($P = 0\text{-}31.2$ GPa). It was determined that the hexagonal symmetry with $P6_3cm$ space group is preserved in the specified pressure range, and the structural phase transition is absent. Birch-Murnaghan equation has been solved and defined that the value of the bulk modulus is $B_0 = 237(7)$ GPa.

6. The crystal and magnetic structures of the $Ca_3Co_2O_6$ compound were studied at low temperatures ($T = 4\text{-}290$ K) and high pressures ($P = 0\text{-}6.8$ GPa). It was determined that the $Ca_3Co_2O_6$ compound has antiferromagnetic properties in the low temperature range under normal conditions, and antiferromagnetic-paramagnetic phase transition occurs at $T_N \approx 25$ K of Neel temperature. Neel temperature increase by $dT_N/dP = 0.65$ K/GPa coefficient with increasing pressure.

7. The crystal structure of $Ca_3Co_2O_6$ compound was studied in the $P = 0\text{-}32$ GPa pressure range at room temperature and found that structural transformation in the mentioned pressure range does not occur and rhombohedral symmetry with R-3c space group is

preserved. The Birch-Murnaghan equation was solved according to the change in relative volume depending on the pressure and the coefficients were determined as $B_0 = 154(5)$ GPa and $B' = 4.0(5)$ based on the experimental results.

8. P-T phase diagram is constructed for $GaFeO_3$ multiferroic in a wide range of temperatures and pressures. The structural phase transition from polar orthorhombic to non-polar orthorhombic phase was detected at about $P \approx 21$ GPa pressure. The temperature of the ferrimagnetic-paramagnetic phase transition was determined about $T_N \approx 292$ K, and the mechanism of the pressure dependence of the Neel temperature is given.

9. The long range magnetic-order was detected in the $La_{0.7}Ca_{0.3}MeO_3$ (Me = Mn, Fe) compound when the equal concentration of Mn and Fe atoms at room temperature. A complex magnetic structure consisting of both antiferromagnetic and ferromagnetic clusters was observed in the low temperature range. Antiferromagnetic-paramagnetic phase transition was detected at $T_N \approx 346$ K temperature. It was shown that the magnetic moments of Mn/Fe atoms increases from $\mu_{Mn/Fe} = 0.8(4)$ μ_B to $\mu_{Mn/Fe} = 1.3(1)$ μ_B when cooled from room temperature to $T = 4$ K. The thermal expansion coefficient $\alpha = 6.89 \cdot 10^{-6}$ K^{-1} was determined for the unit cell volume.

10. The changes occurring in the crystal structures of $BaFe_{12-x}Ga_xO_{19}$ ($0.1 \leq x \leq 1.2$) compounds synthesized with partial substitutions of Fe atoms with Ga atoms were studied depending on the x concentration of Ga atoms. It was determined that the $BaFe_{12-x}Ga_xO_{19}$ compounds have a stable hexagonal crystal structure in the $0.1 \leq x \leq 1.2$ concentration range of Ga atoms. The frequency of the vibration modes is changed with $k_{vor} = 0.0155(8)$ coefficient when Fe atoms are partially replaced by Ga atoms.

11. The crystal structure of the $BaFe_{11.1}Ga_{0.9}O_{19}$ compound was studied in the high pressure range ($P = 0-5.3$ GPa) at room temperature. It was determined that there is no phase transition in the crystal structure of this compound in the specified pressure range. Birch–Murnaghan equation was solved for $BaFe_{11.1}Ga_{0.9}O_{19}$ hexaferrite, and the value of the bulk modulus is determined $B_0 =$

134(7) GPa. It was determined that the magnetic moments of the Fe atoms standing on the different crystallographic positions in the $BaFe_{11.1}Ga_{0.9}O_{19}$ compound varies from $\mu_{min} = 3.11$ µB to $\mu_{max} = 3.72$ µB.

12. The crystal structure of the $BaFe_{11.1}In_{0.9}O_{19}$ compound was studied in the high pressure range ($P = 0$-5.5 GPa) at room temperature. It was determined that there is no phase transition in the crystal structure of this compound in the specified pressure range. Birch-Murnaghan state equation was solved for $BaFe_{11.1}In_{0.9}O_{19}$ hexaferrite, and the value of the bulk modulus is determined $B_0 = 128(6)$ GPa. It was determined that the magnetic moments of Fe atoms standing in different crystallographic positions in the $BaFe_{11.1}In_{0.9}O_{19}$ compound varies from $\mu_{min} = 3.13$ µB to $\mu_{max} = 3.74$ µB.

13. It was determined the symmetries of the crystal structures increases in the complex oxides like perovskites and hexaferrites that under the influence of high pressure. Monoclinic-orthorhombic, orthorhombic-tetragonal, tetragonal-hexagonal, tetragonal-cubic structural phase transitions are observed. However, in hexaferrites having high symmetry and perovskites having hexagonal symmetry, the structural phase transition is absent, and the hexagonal structure is preserved. Only lattice parameters and unit cell volume decreased under the influence of pressure.

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