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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

STRUCTURAL AND MAGNETIC PROPERTIES OF $BaFe_{12-x}Al_xO_{19}$ HEXAGONAL FERRITES

Speciality: 2223.01 – Crystallography, crystal physics

Field of science: Physics

Applicant: **Ramiz Eldar oglu Huseynov**

Baku – 2021

The work was performed at the Institute of Physics of Azerbaijan National Academy of Sciences, laboratory "Non - standard control and quality".

Scientific supervisor:

Doctor of physical sciences, associate professor
Rafiga Zabil gizi Mehdiyeva

Official opponents:

Active member of ANAS,
Doctor of physics-mathematics sciences, professor
Chingiz Oveis oglu Gajar
Correspondent member of ANAS,
Doctor of physics-mathematics sciences, professor
Ogtay Kazım oglu Gasımov
Doctor of physics-mathematics sciences, professor
Tariyel Humbat oglu Ismailov

Dissertation council ED 1.14 of Supreme Attestation Commission under the President of Azerbaijan operating Institute of Physics of Azerbaijan National Academy of Sciences

Chairman of the dissertation council:

Active member of ANAS,
Doctor of physics-mathematics sciences, professor
Nazim Timur oglu Mammadov

Scientific secretary of the Dissertation council

Doctor of physical sciences, associate professor
Mahmud Hashim oglu Kazimov

Chairman of the scientific seminar:

Doctor of physics sciences, professor
Imamaddin Rajabali oglu Amiraslanov

GENERAL DESCRIPTION OF WORK

The actuality of work. In this dissertation work focused on the synthesis of physically curious M type hexagonal structured ferromagnetic materials and analyze their crystal structure, microstructures, atoms dynamics also magnetic properties. Study of these physical properties is one of the main actual issues in condensed matter physics. As we know, ferroelectricity is a physical phenomenon that occurs as a result of spontaneous polarization by the fact that some of the crystalline structures have certain shifts in the atoms from their ideal positions or the regularity of the systems. On the other hand, it is known that the formation of distant magnetic fluctuations depends on atoms at certain distances within the compounds and the thermal vibrations of the atoms. Determining the interaction between the physical properties of the materials and the study of the microscopic mechanisms of physical phenomena in industrial technology is one of the main problems of material science, not just the condensed matter physics.

Investigation of magnetic properties under low temperatures and high magnetic fields is considered to be very important for studying the magnetic properties of compounds that have ferromagnetic properties. Simultaneously, the experiments with the effects of temperature and the external magnetic field are important for the study of magnetic properties of materials. It can be used for modelling systems for solid solutions based on barium hexaferrite ($BaFe_{12}O_{19}$) and magnetic properties for compounds with these external effects.

Recently, the hexagonal crystalline structure of barium hexaferrite is one of the most studied multiferroics. Barium hexaferrite is a material with ferrimagnetic properties at room temperature and normal conditions so it has a high-temperature ferrimagnetic-paramagnetic phase transition. ($T_C \approx 750K$). The previous structure studies have shown that the partial replacement of Fe^{3+} magnetic ions in the composition of barium hexaferrite with Ga^{3+}, In^{3+}, Sc^{3+} and other diamagnetic metal ions cause to the observation of fundamental changes in the crystalline structures of

the compounds and the atomic dynamics. As a result of the increased concentration of diamagnetic ions, a partial disturbance of magnetic order arises, thereby weakening the magnetic properties.

Hexaferrites and composite materials based on them are widely used in space technology and aerospace industries, such as electromagnetic absorbing materials. Therefore, under the conditions of keeping magnetic properties, the substitution of Fe atoms with Al is among the most important materials for aviation. It is important to note that the temperature variability is characteristic for the aviation, and the study of these materials are of particular importance in the wide temperature range.

Dissertation work fulfilled the scientific research plan of the Institute of Physics named after academician H.M.Abdullayev of Azerbaijan National Academy of Sciences.

Aims and purpose of the research:

The purpose of dissertation is to study the effect of replacement Fe^{+3} magnetic ions with Al^{+3} diamagnetic ions in $BaFe_{12-x}Al_xO_{19}$ hexaferrites to morphology, crystal structure and magnetic properties of solid solutions, also to determine the dependence mechanism in crystal structure and magnetic properties (x = 0.1 - 1.2) from Al atom's concentration as a result of this replacement.

The following issues have been solved to achieve the goal:

- Investigation of the structural aspects of the formation of atomic levels, polyhedrons (octahedron, bipyramid and tetrahedron) systems in $BaFe_{12-x}Al_xO_{19}$ (x = 0.1, 0.3, 0.6, 0.9 and 1.2) solid solutions. Studying the dependence of the concentration of Al atoms on morphology and atomic dynamics in these solid solutions.
- Study of thermal properties and weight loss of $BaFe_{12-x}Al_xO_{19}$ compounds in the high temperature (300-1200 K) region. Partially replacement of iron atoms with aluminium atoms in the high-temperature region is the study of the effect of the Al atoms on the thermal properties and weight loss of compounds in the concentration range x = 0.1-1.2.
- The determination of the magnetic moments of Fe atoms in

different crystallographic positions in $BaFe_{12-x}Al_xO_{19}$ solid solutions when partially substitutions of Fe^{3+} magnetic ions with Al^{3+} diamagnetic ions in the ferrimagnetic barium hexaferrite in the low-temperature range (5 - 300 K) and the study of the mechanism of magnetic properties change under the influence of the external magnetic field.

Research methods:

The research objects are $BaFe_{12-x}Al_xO_{19}$ (x = 0.1, 0.3, 0.6, 0.9 and 1.2) solid solutions with M-type hexagonal group. X-ray diffraction, neutron diffraction, scanned electron microscopy, Raman spectroscopy, infrared spectroscopy, differential thermal analysis, thermogravimetric analysis and vibrational magnetometry were used in the study of crystal structures and magnetic properties of these compounds.

Main provisions to the defence:

1. Stability of crystal structures of $BaFe_{12-x}Al_xO_{19}$ solid solutions in the range of x = 0.1 to 1.2 concentrations of aluminium atoms.
2. Determination of magnetic moments of Fe atoms at various positions in crystal structures of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1 - 1.2) at room temperature.
3. Decrease of the specific magnetic moment of polycrystals $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) from σ = 49.6 A m^2/kg (x = 0.1) to σ = 32 A m^2/kg (x = 1.2).
4. Increasing the special magnetic moment in the $BaFe_{12-x}Al_xO_{19}$ system under the effect of the external magnetic field in the low-temperature ranges.
5. Monotonic absorption of the supplied thermal energy to the system at T = 300-1220 K temperature range in $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) solid solutions and ~ 0.5% change in the weight.
6. Determination of the mechanism depending on the concentration of change of the atomic vibrations and the change coefficients k in the $BaFe_{12-x}Al_xO_{19}$ systems
7. Determination of the change mechanisms of thermal vibrations depending on the concentration and $k_v=-(1/\nu_0)\ (d\nu/dx)_{T,\ P}$ change coefficients in the $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) systems.

The scientific novelty of the research:

1. The crystal and magnetic structures of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1, 0.3, 0.6, 0.9 and 1.2) hexaferrites were investigated and magnetic moments of Fe^{3+} magnetic ions based on different crystallographic positions were determined. The changes mechanisms of lattice parameters and volume are given depending on the concentration of Al atoms.
2. Atomic dynamics of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) hexaferrite were studied for the first time and the frequency of vibrational modes observed at room temperature was determined by the compatibility of octahedron, bipyramids and tetrahedrons to thermal vibrations formed by Fe (Al) and O atoms. The vibrational modes depend on the concentration of Al atoms were obtained.
3. For the first time, the thermal properties of the $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) solid solutions were investigated in the high-temperature range (300-1220 K) and the changes in the weight depending on the temperature. The thermal energy supplied to the system and the change mechanism of the weight of the samples were studied in a wide temperature range (T = 300 - 1220 K).
4. The magnetic properties of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1 - 1.2) hexaferrite was investigated in the low temperature (5 - 300 K) range under the influence of the external magnetic field. The changes in the specific magnetic moment were determined when substituting magnetic iron ions with diamagnetic aluminium ions.

The theoretical and practical significance of the research:

The study of crystal and magnetic structures in solids, investigating their changes mechanism under the external influences, identification of the configurations formed by atoms as well as the study of their atomic dynamics are important in the condensed matter physics and material science.

Hexagonal ferrites have many applications in which they can be considered important: preparing low dimensional, low-frequency and high-capacity condensers, use of large non-linear

polarization materials for dielectric amplifiers, modulators and other control mechanisms, the use of magnetic elements as a memory element in computing technique, the preparation of information carriers, the use of ferroelectric and ferromagnetic crystals for converters in laser irradiation and modulation, converters in radar protection systems such as electromagnetic absorbing materials and so on.

Approbation and implementation:

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

- International scientific school for young researchers: Modern Neutronography, October 28 - November 1, 2013, Dubna, Russian Federation;
- "III International Scientific Conference of Young Researchers dedicated to the 92nd anniversary of National Leader Heydar Aliyev", April 17-18, 2015, Baku, Azerbaijan;
- Petersburg Nuclear Physics Institute 53rd School on Condensed State Physics, 16-21 March 2015, Petersburg, Russian Federation
- "The IV International Scientific Conference of Young Researchers dedicated to the 94th anniversary of national leader Heydar Aliyev", April 29-30, 2016, Baku, Azerbaijan;
- XLIX school for condensed environments of the Petersburg Institute of Nuclear Physics, March 16-21, 2015, Saint-Petersburg, Russian Federation;
- 2nd International Scientific Conference of Young Researchers dedicated to the 95th anniversary of National Leader Heydar Aliyev, April 27-28, 2018, Baku, Azerbaijan
- 14th international conference "Technical and physical problems of electrical engineering", 15-17 October 2018, Nakhchivan State University, Nakhchivan, Azerbaijan.
- III International Scientific Conference of Young Researchers dedicated to the 96th anniversary of National Leader Heydar Aliyev, April 29-30, 2019, Baku, Azerbaijan

Publications: The main materials of the dissertation were published in 14 publications, of which 6 articles (including 3 foreign scientific journals with impact factor) and 8 are theses of the conference. Acquired results have been published in 4 reports in the Institute of Physics of the Azerbaijan National Academy of Sciences named after academician H.M.Abdullayev.

Name of the organization the Dissertation has been performed:

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

Volume, structure and main content of the dissertation:

The dissertation consists of the introduction, 5 chapters, results and list of 132 used literature. The study consists of 234558 symbols - 17 tables and 28 pictures.

CONTENT OF WORK

In the introduction, the relevance of the topic of the dissertation, the main purpose of the work, the scientific novelty, practical significance, the objectives and the main provisions to the defence are justified.

Chapter I of the dissertation is dedicated to the literature review of investigations carried out with the solid solution of barium hexaferrite and similar compounds.

Chapter II is devoted to the experimental methods used in the dissertation work, analysis methods used to processing of results, and the devices in which the research is being carried out.

The ceramic powder samples of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1, 0.3, 0.6, 0.9 and 1.2) solid solutions were synthesized by the standard method in high - temperature furnace using high purity Fe_2O_3, Al_2O_3 and $BaCO_3$. The $BaFe_{12-x}Al_xO_{19}$ hexaferrite is synthesized and the crystal structures of the powder samples were investigated at D8 Advance (Bruker) powder diffractometer at room temperature under the condition of 40 kV, 40 mA, CuKα - radiation (λ = 1.5406 Å). The obtained x-ray diffraction spectra were first detected in the

multichannel analyzer, then analyzed by the Rietveld method through the FullProf and Origin software packages.

In **Chapter III,** the crystal structures of powdered $BaFe_{12-x}Al_xO_{19}$ (x = 0.1, 0.3, 0.6, 0.9 and 1.2) solid solutions, atomic dynamics have been studied extensively with modern research methods. Structural studies were performed by X-ray diffraction and atomic dynamics studies using Raman spectroscopy and infrared spectroscopy at room temperature.

The crystal structures of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1, 0.3, 0.6, 0.9 and 1.2) solid solutions were studied by X-ray diffraction method at room temperature and normal conditions to investigate the effects of the substitution of the trivalent iron atoms with diamagnetic metal atoms on the crystalline structures of $BaFe_{12-x}Me_xO_{19}$ hexaferrites. It has been determined that $BaFe_{12-x}Al_xO_{19}$ compounds in the range of $0.1 \leq x \leq 1.2$ concentrations of Al atoms are partly replaced by Fe atoms with Al atoms, and in normal conditions, they have a hexagonal symmetry crystal structure with a P63mmc (194) space group. The lattice parameters of the x = 0.1 concentration $BaFe_{11.9}Al_{0.1}O_{19}$ are: a = 5.889 (2) Å, c = 23.186 (6), which corresponds to previous investigation results. Since Z = 2, the elementary lattice of $BaFe_{12-x}Al_xO_{19}$ consists of 2 barium, 24 iron or aluminium, 38 oxygen atoms. It has been established that the lattice parameters decrease as a result of the chemical pressure by increasing Al atoms in the $BaFe_{12-x}Al_xO_{19}$ compounds. This decrease is due to the fact that Fe^{3+} ions (R_{Fe} = 0.645 Å) have larger ionic radii than Al^{3+} ions (R_{Al} = 0.535 Å). Corresponding lattice parameters are given in Table 1.

Table 1. Lattice parameters and volume of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1, 0.3, 0.6, 0.9 and 1.2) of solid solutions at room temperature.

Compounds	*a*, Å	*c*, Å	*V*, Å^3
$BaFe_{11.9}Al_{0.1}O_{19}$	5.889(2)	23.186(7)	696.43295
$BaFe_{11.7}Al_{0.3}O_{19}$	5.885(3)	23.163(8)	694.83184
$BaFe_{11.4}Al_{0.6}O_{19}$	5.883(5)	23.160(8)	694.31598
$BaFe_{11.1}Al_{0.9}O_{19}$	5.881(4)	23.146(2)	693.39213
$BaFe_{10.8}Al_{1.2}O_{19}$	5.879(7)	23.117(7)	692.13241

Figure 1 shows the dependence of the distances between Fe(Al) and O atoms on the x concentration. From dependencies, it seems that the interatomic is linearly reduced, and the reduction occurs by $k_i = -(1/l_0)(dl/dx)_{T,P}$'s law. The values for k_i are as follows: $k_{Fe(Al)-O}$=0.00185(9), k_{Ba-O}=0.00192(1), $k_{Ba-Fe(Al)}$=0.00194(8) due to the distances between Ba, Fe and Al atoms. It's clear from dependencies in Figure 1, the octahedrons, bipyramids and tetrahedrons formed by Fe (Al) and O atoms relatively more stable than the distances between Fe (Al) and Ba atoms when partially substitutions of Fe atoms with Al atoms. While the distances between the Ba-O and Ba-Fe(Al) atoms are almost reduced by the same mechanism, the length of the Fe(Al)-O bonds decreases with a smaller speed. From here it is possible to conclude that oxygen atoms are more resistant to other atoms. Taking into consideration the reason for distant magnetic order is the order of Fe atoms along the c axis. It is possible to conclude that an irregularity appears in the atomic linearity and the magnetic order decreases when Fe atoms are replaced by Al atoms.

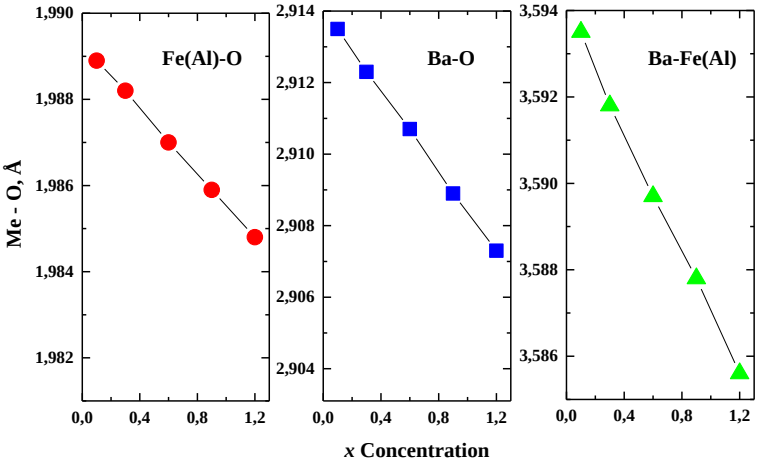

Figure 1. The dependence of interatomic distances between Fe (Al), Ba and O atoms on the x concentration in the $BaFe_{12-x}Al_xO19$ (x = 0.1, 0.3, 0.6, 0.9 and 1.2)

Atomic dynamics of compounds were investigated by Raman spectroscopy at room temperature and normal conditions (Figure 2). The peaks observed in the Raman spectrum of $BaFe_{11.9}Al_{0.1}O_{19}$ are mainly in the range of ν = 200 to 800 cm^{-1} frequencies. In this frequency range, the most suitable 8 peaks of vibration modes were observed: ν_1 = 289 cm^{-1}, ν_2 = 337 cm^{-1}, ν_3 = 413 cm^{-1}, ν_4 = 469 cm^{-1}, ν_5 = 525 cm^{-1}, ν_6 = 617 cm^{-1}, ν_7 = 684 cm^{-1} , and ν_8 = 717 cm^{-1} (Figure 2). These vibration modes are interpreted corresponding to vibration modes of barium hexaferrite and other solid solutions as follows:

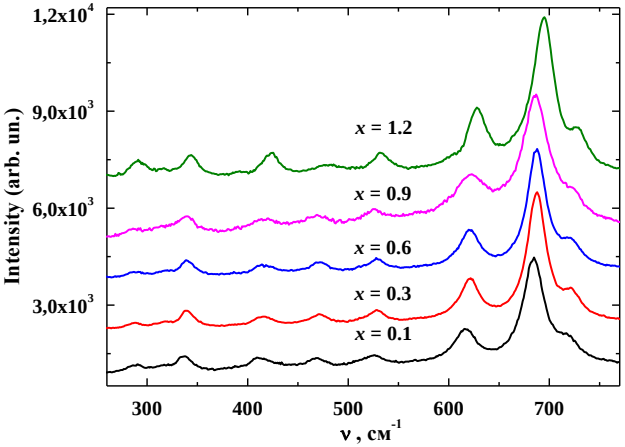

Figure 2. Raman spectra of $BaFe_{12-x}Al_xO_{19}$ solid solutions

- ν_1 = 289.11 cm^{-1} mode: compatible to the vibrations of O-Fe-O bonds;
- ν_2 = 337.19 cm^{-1} mode: compatible to the vibrations of O-Fe-O bonds;
- ν_3 = 413.56 cm^{-1} mode: corresponds to the vibrations of Fe(12*k*)/Al(12*k*)O_6 octahedron;
- ν_4 = 469.42 cm^{-1} mode: corresponds to the vibrations of Fe(2*a*)/Al(2*a*)O_6 and Fe(12*k*)/Al(12*k*)O_6 octahedrons;

- ν_5 = 525.34 cm^{-1} vibration mode: corresponds to the vibrations of Fe(2*a*)/Al(2*a*)O_6 and Fe (12*k*)/Al(12*k*)O_6;
- ν_6 = 617.65 cm^{-1} mode: corresponds to the vibrations of Fe(2*a*)/Al(2*a*)O_6, Fe(12*k*)/Al(12*k*)O_6 and Fe ($4f_2$)/Al($4f_2$)O_6 octahedrons;
- ν_7 = 684.24 cm^{-1} mode: corresponds to the vibrations of bipiramide Fe (2*b*)/Al(2*b*)O_5;
- ν_8 = 717.54 cm^{-1} mode: corresponds to the vibration frequencies of Fe($4f_1$)/Al($4f_1$)O_4 tetrahedron.

It clearly seems from Raman spectra of $BaFe_{12-x}Al_xO_{19}$ solid solutions in the concentration range of $0.3 \leq x \leq 1.2$ of Al atoms, the values of vibration modes increased to high-frequency ranges with increasing of the concentration. This phenomenon is explained by the reduction of length of the covalent bonds formed between the atoms due to the smaller ion radius of the Al atoms, compared to the Fe atoms. The frequencies of Raman modes depending on the concentration of the Al atoms has been studied by $k_\nu = -(1/\nu_0)(d\nu/dx)_{T,P}$ relation at the room temperature and normal conditions. Vibration modes and concentration dependences of vibration modes of $BaFe_{12-x}Al_xO_{19}$ solid solutions are given in Table 2.

Table 2. Modification coefficients depending on vibration modes and vibration modes obtained by Raman spectroscopy of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) solid solutions.

X	**0.1**	**0.3**	**0.6**	**0.9**	**1.2**	k_ν
ν_1 **(cm^{-1})**	289.11	288.77	289.27	289.61	292.32	0.00908
ν_2 **(cm^{-1})**	337.19	339.23	340.11	340.88	343.26	0.01363
ν_3 **(cm^{-1})**	413.56	416.41	416.98	417.29	423.06	0.01816
ν_4 **(cm^{-1})**	469.42	471.85	472.44	472.44	482.19	0.02086
ν_5 **(cm^{-1})**	525.34	528.15	529.12	529.69	533.23	0.01141
ν_6 **(cm^{-1})**	617.65	621.33	621.64	621.78	629.11	0.01383
ν_7 **(cm^{-1})**	684.24	687.47	688.26	688.75	694.53	0.01092
ν_8 **(cm^{-1})**	717.54	721.31	721.96	722.52	727.35	0.01034

As can be seen in Table 2, the largest k_ν modification coefficient among the Raman modes was observed in ν_4 = 469.42 cm^{-1} mode. This vibration mode corresponds to the vibration of the octahedral Fe(2*a*)/Al(2*a*)O_6 and Fe(12*k*)/Al(12*k*)O_6, produced by iron (Al atoms when substitution) atoms in different crystallographic positions. The smallest k_ν coefficient was observed in ν_1 = 289.11 cm^{-1}, which is equivalent to the vibration of the O-Fe-O bonds. It follows from this that the main changes occur in the Fe(Al)O_6 octahedrons when partial substitution of Fe atoms with Al atoms in $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) compounds which confirms the results obtained with structural studies. Although the change mechanisms between vibration modes is quite different, the rate of change of all modes is in the same order and the average value of the change factor is k= 0.014.

In order to study of atomic dynamics of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1 - 1.2) multiferroics compounds also used infrared spectroscopy method.

In Chapter IV the surface morphology (measurement effects) and thermal properties of $BaFe_{12-x}Al_xO_{19}$ (x = 0,1 - 1,2) hexaferrites (Differential Thermal Analyzes and Thermogravimetric Analyzes) have been studied with modern research methods. Surface morphology studies at room temperature using a scanned electron microscope, thermal properties were investigated by differential thermal and thermogravimetric analysis methods in the range of *T* = 300 - 1220 K temperature.

The surface structure and size effects of the powdered $BaFe_{12-x}Al_xO_{19}$ (*x* = 0.1, 0.3, 0.6, 0.9 and 1.2) solid solutions were studied by modern scanning electron microscope which used to study the surface morphology of solid-state materials. The surface morphology which studied in SEM (Scanning Electron Microscope, ZEISS, ΣIGMA VP) is shown in Figure 3.

As it seems there are not only in crystalline structures but also considerable differences in the surface structures (morphology) and size effects are observed due to the differences between ionic radii of atoms when substitutions of magnetic iron atoms with diamagnetic aluminium atoms

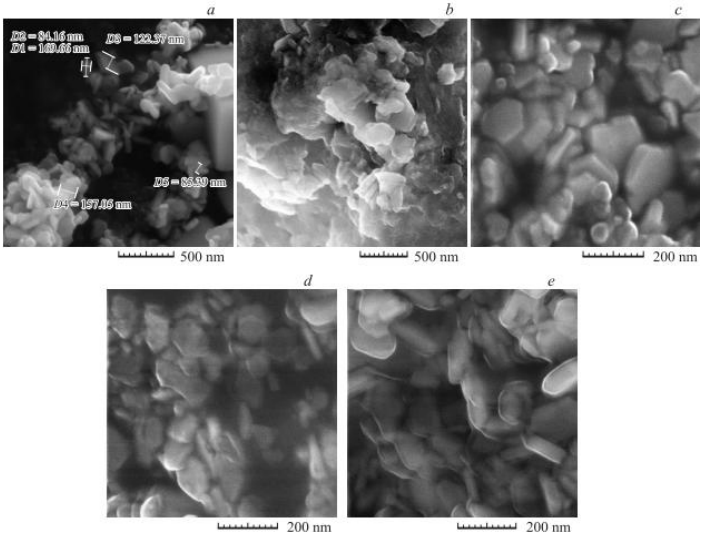

Figure 3. Surface morphology of $BaFe_{12-x}Al_xO_{19}$ solid solutions in the concentrations of x = 0.1 (*a*), 0.3 (*b*), 0.6 (*c*), 0.9 (*d*) and 1.2 (*e*) obtained by scanned electron microscope

Although the crystal structure and various physical properties of $BaFe_{12-x}Me_xO_{19}$ (x = 0.1-1.2) solid solutions have been widely studied in previous investigations, the thermal processes in these materials have not been studied in details. Differential thermal and thermogravimetric analyses of $BaFe_{12-x}Al_xO_{19}$ solid solutions synthesized in the range x = 0.1-1.2 concentrations of Al atoms were conducted in order to study thermal processes in $BaFe_{12-x}Me_xO_{19}$ (x = 0.1-1.2) systems (Figure 4).

Figure 4 shows that the thermal effect observed in the differential thermal analyzer, which is directly related to the absence of any effect (Endo and Exo) in the thermogravimetric analysis curve. The endo or exogenous effects that occur in the differential thermal analyzer must also be monitored (confirmed) in the absolute thermogravimetric analysis. The differential thermal analysis in the x = 0.1 concentration, was observed of monotonous decrease, which is because of the fact that the thermal energy flux to the system is

physically completely absorbed by the system and the heat energy does not reach the level where it can generate phase transition in that system. The heat energy given to the system has been completely absorbed by the system. There is a monotonous decrease in thermogravimetric analysis and differential thermal analysis curves, endo and echo effects have not been observed. These data indicate the thermal stability and the presence of the same structural phase in the wide temperature range of the synthesized compounds.

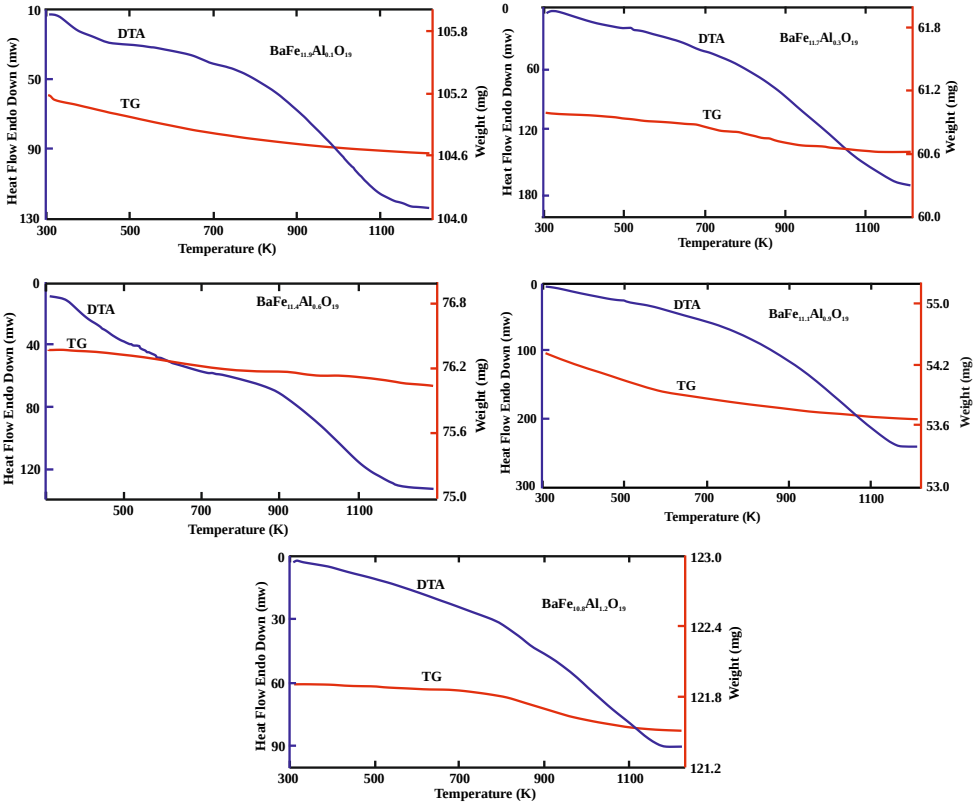

Figure 4. DTA and TG analysis of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) solid solutions.

Differential thermal analysis curves show the change occurs that after temperature T ~ 770 K. It is known from previous studies conducted on the study of magnetic properties that the ferromagnetic

phase transition occurs to the paramagnetic phase at temperatures of $T > 770$ K in $BaFe_{12-x}Me_xO_{19}$ (x = 0.1-1.2) as well as $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) solid solutions. As can be seen from the results obtained from the differential thermal analysis curves described in Figure 3, the thermal energy absorption in the paramagnetic phase is more rapidly than the ferrimagnetic phase in these compounds.

Therefore, in the $BaFe_{12-x}Al_xO_{19}$ (x = 0.1 - 1.2) systems, the regular arrangements of atoms in the paramagnetic phase are partially violated relative to the ferrimagnetic phase. It's known from thermodynamics and solid-state physics that the absorption of energy in irregular systems should be more than in regular systems.1

In chapter V, the magnetic properties of solid solutions of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) have been investigated. Magnetic moments of the Fe atoms and the final magnetic moment for the elementary lattice located in different crystallographic positions were determined by neutron diffraction method. The reduction mechanism of the values of magnetic moments was determined when partially substitution of Fe atoms with Al atoms. The magnetic properties of the investigated samples were determined by the vibrational magnetometry method from room temperature to T = 5 K under the influence of the ± 2 Tl external magnetic field.

The results obtained with the neutron diffraction method are fully compatible with the results obtained by the X-ray diffraction method. The results obtained by Raman spectroscopy and infrared spectroscopy methods in atomic dynamics studies have shown that the results of almost all experimental methods used in structural studies have been the same, as the concentrations of Al atoms show a decrease in the length of inter-atomic bonds as the concentration increases.

The neutron diffraction spectra obtained at room temperature and under normal conditions for the $BaFe_{11.9}Al_{0.1}O_{19}$ and $BaFe_{11.1}Al_{0.9}O_{19}$ compounds are shown in Figure 5. The vertical lines show the diffraction maxima of magnetic and crystal structure.

[1] Л.Д.Ландау, Е.М.Лифшиц. Статистическая физика / – М.: Наука, 1964. - 568 с.

Table 4 shows the magnetic moments of iron magnetic ions located in different crystallographic positions (2a, 2b, 4fIV, 4fVI and 12k) at $BaFe_{12-x}Al_xO_{19}$ (x = 0.1 - 1.2) in different concentration of Al atoms.

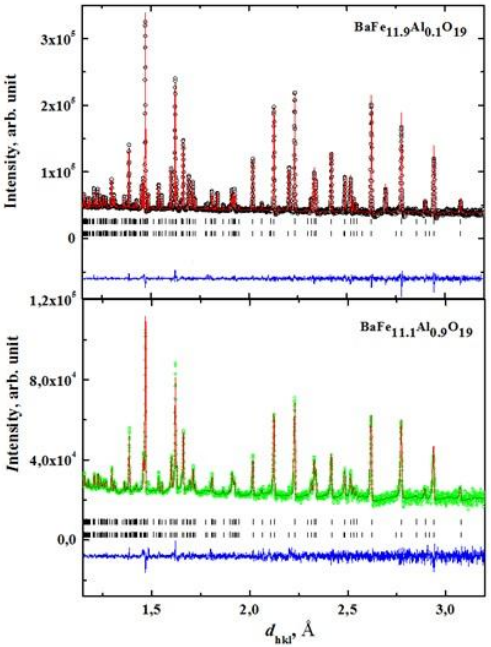

Figure 5. Neutron diffraction spectra measured at room temperature of $BaFe_{11,9}Al_{0,1}O_{19}$ and $BaFe_{11,1}Al_{0,9}O_{19}$ samples and analyzed by Ritveld method.

Iron and aluminium atoms stand in the same position at the crystalline structure. Therefore, if there are several Al atoms in the direction of the c-axis, a substantial decrease in the magnetic moments can be observed. However, on the contrary, if several atoms of Fe are consistent, then the magnitude of the magnetic moment is close to the values of the magnetic moment values obtained for Fe atoms in the barium hexaferrite compound.

We have to use a following simple formula to calculate total magnetic moment of the elementary crystal lattice of $BaFe_{12}O_{19}$ hexaferrite at T temperature:

$$\mu_{sum}(T) = 1[\mu_{2a}(T)] + 1[\mu_{2b}(T)] - 2[\mu_{4fIV}(T)] - 2[\mu_{4fIV}(T)] + 6[\mu_{12k}(T)]$$

where T - is the temperature at which magnetic moments are calculated, μ is the magnetic moment of each Fe^{3+} ions.

Table 4. Magnetic moments of Fe atoms located in various crystallographic positions of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) compounds determined by the FullProf program.

Concentration					
X	0.1	0.3	0.6	0.9	1.2
Magnetic moments of iron atoms (μ_B)					
Fe1 (2*a*)	3.82	3.77	3.25	3.36	2.16
Fe2 (2*b*)	4.08	4.11	3.09	3.74	2.18
Fe3 ($4f_{IV}$)	3.65	3.68	3.25	3.60	1.47
Fe4($4f_{VI}$)	4.09	4.15	3.75	3.57	1.25
Fe5 (12*k*)	3.59	3.55	3.25	3.12	2.07

If we calculate the general magnetic moment for $BaFe_{12-x}Al_xO_{19}$ solid solutions at room temperature, we will see that the $BaFe_{11.9}Al_{0.1}O_{19}$ compound has μ_{sum} = 13.96 μ_B and the $BaFe_{10.8}Al_{1.2}O_{19}$ compound has μ_{sum} = 11.32 μ_B. The values of generalized magnetic moments in the range of $0.1 \leq x \leq 1.2$ concentrations of al atoms are given in Table 5. As can be seen from the table, there are observed a decrease in the values of the magnetic moments when the number of diamagnetic Al^{3+} ions are increased in the crystal lattices of the compounds and this leads to the weakening of the distant magnetic order.

One of the most widely used methods for studying the magnetic properties of ferromagnetic, antiferromagnetic and ferrimagnetic properties materials is the vibrational magnetometry method. The vibrational magnetometry method was used for the complex study of magnetic properties of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) and re-confirmation of the result of neutron diffraction investigations. The dependence of the specific magnetic moments (hysteresis curves) of

[2] J.Smit, H.P.J. Wijn, Ferrites / Philips Technical Library, Eindhoven, - 1960. - 387 p.

the soluble $BaFe_{12-x}Al_xO_{19}$ solid solutions on the room temperature and T = 5 K (helium temperature) in the concentration of $0.1 \leq x \leq 1.2$ is shown in Figure 6.

Table 5. Generalized magnetic moments for $BaFe_{12-x}Al_xO_{19}$ ($0.1 \leq x \leq 1.2$) solid solutions.

Concentration	Compounds	Generalized magnetic moments
$x = 0.1$	$BaFe_{11.9}Al_{0.1}O_{19}$	13.96 μ_B
$x = 0.3$	$BaFe_{11.7}Al_{0.3}O_{19}$	13.52 μ_B
$x = 0.6$	$BaFe_{11.4}Al_{0.6}O_{19}$	11.84 μ_B
$x = 0.9$	$BaFe_{11.1}Al_{0.9}O_{19}$	11.48 μ_B
$x = 1.2$	$BaFe_{10.8}Al_{1.2}O_{19}$	11.32 μ_B

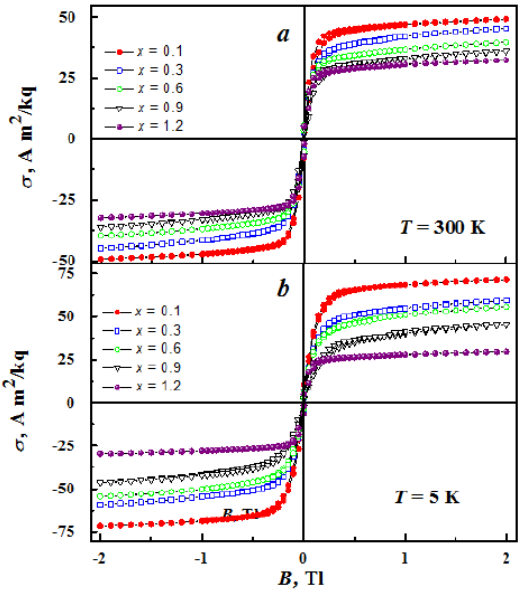

Figure 6. Dependence of special magnetic moments on the external magnetic field of the solid solutions of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1, 0.3, 0.6, 0.9 and 1.2) at room temperature (a) and T =5K.

The values of specific magnetic moments of $BaFe_{12-x}Al_xO_{19}$ compounds at room temperature (T = 300 K) decreases from σ = 49.6 A·m^2/kg (x = 0.1) to σ = 32 A·m^2/kq (x = 1.2) with increasing the concentration of Al atoms under the influence of the B = ± 2Tl external magnetic field which its due to the disturbance of the distant magnetic order with effect of Al^{3+} diamagnetic ions. Δσ = 17.6 A m^2/kg. Specific magnetic moment values for $BaFe_{12-x}Al_xO_{19}$ solid solutions in various concentrations of aluminium atoms are given in Table 6.

Table 6. Values of specific magnetic moments in $BaFe_{12-x}Al_xO_{19}$ solid solutions at different concentrations.

Concentration	Magnit moments, A·m^2/kg
x = 0.1	49.6
x = 0.3	45.3
x = 0.6	39.5
x = 0.9	36.1
x = 1.2	32.0

MAIN RESULT PRESENTED FOR DEFENCE

1. Crystal structures of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1- 1.2) hexaferrite were investigated and atomic coordinates were determined in solid solutions. It has been determined that the compression along c-axis occurs with increasing of the concentration of Al atoms in the crystal. The lattice parameter "a" decreased to 0.16% (Δa = 0.0095 Å), and c parameter to 0.29% (Δc = 0.0685 Å). This explained by the small ionic radii of aluminium atoms relative to iron atoms.

2. For the first time, the vibration modes of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1- 1.2) solid solutions at the room temperature have been determined to match the vibration of polyhedrons that form the crystal structure. The density of the vibration modes depends on the concentration of the Al atoms, and the greatest change is determined by the vibration of the $Fe(Al)O_6$ octahedral vibrations ν_4 = 469.42 cm^{-1}, and the smallest change corresponds to ν_4 = 289.11 cm^{-1}. The

average speed of vibration modes is the k_v. = 0.014 has been assigned.

3. Surface morphology of $BaFe_{12-x}Al_xO_{19}$ hexaferrite with the concentrations of x = 0.1, 0.3, 0.6, and 1,2 Al atoms and size effects for solid solutions have been determined. It has been discovered that the average value of the powder grains is $D \approx 120$ nm in case of the lowest concentration (x = 0.1). At the maximum value of the concentration (x = 1.2), the average value of the powder grains is $D \approx$ 70 nm, which is explained by the small ionic radii of aluminium atoms relative to iron atoms.

4. For the first time, the thermal properties of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1- 1.2) solid solutions were studied in the high-temperature range and the change in the sample mass and heat energy was determined at a wide temperature range (300-1220K). It has been established that the thermal energy absorption in the paramagnetic phase is greater than a ferrimagnetic phase, which is because the ferrimagnetic phase in crystalline structures is relatively more stable than the paramagnetic phase in these compounds. It has been established that 0.5% mass loss occurs in these compounds between 300 K and 1220 K temperature range.

5. Magnetic moments of Fe atoms of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1-1.2) solid solutions have been determined. It has been established that the magnetic moments of Fe atoms at various crystallographic positions are decreased from $\mu \approx 4.15\ \mu_B$ to $\mu \approx 1.25$ μB and generalized magnetic moment of the elementary lattice are decreased from $\mu_{sum} \approx 13.96$ μB to $\mu_{sum} \approx 11.32$ μB with increasing of the concentration of diamagnetic Al atoms.

6. Magnetic properties of $BaFe_{12-x}Al_xO_{19}$ (x = 0.1- 1.2) hexaferrite was investigated at the external magnetic fields and low-temperature range (5-300 K). It was determined that the value of the specific magnetic moment decreases from $\sigma = 49.6$ A m^2/kg (x = 0.1) to $\sigma = 32$ A m^2/kg (x = 1.2) when substitutions of Fe^{3+} magnetic ions with Al^{3+} diamagnetic ions at ± 2 Tl external magnetic field.

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The defence will be held on 31 March 2021 at 11:00 at the meeting of the Dissertation council ED 1.14 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating at Institute of Physics of Azerbaijan National Academy of Sciences.

Address: 131 H.Javid ave, AZ-1143, Baku

The dissertation is accessible at the Institute of Physics Azerbaijan National Academy of Sciences Library

Electronic versions of the dissertation and it's abstract are available on the official website of the Institute of Physics of Azerbaijan National Academy of Sciences.

Abstract was sent to the required addresses on 26 February 2021

Signed for print: 19.02.2021

Paper format: A5

Volume: 37005

Number of hard copies: 20