

# THE INVESTIGATION OF CRYSTAL AND MAGNETIC STRUCTURES OF SOLID SOLUTIONS $BaFe_{12-x}D_xO_{19}$ (D= In AND Ga; x= 0.1 – 1.2)

Vitalii Turchenko<sup>1,2,\*</sup>, Alex V. Trukhanov<sup>3,4</sup>, Sergei V. Trukhanov<sup>3,5</sup>, and I.S. Kazakevich<sup>3</sup>

<sup>1</sup>Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research Joliot-Curie str., 6, 141980 Dubna, Russia

<sup>2</sup>Donetsk Institute of Physics and Technology named after O.O. Galkin of the NASU, 46 Nauki Ave, 03680, Kiev, Ukraine

<sup>3</sup>SSPA “Scientific and practical materials research centre of NAS of Belarus”, 19 P. Brovki str., 220072 Minsk, Beloruss

<sup>4</sup>South Ural State University, Lenin’s prospect 76, 454080, Chelyabinsk, Russia

<sup>5</sup>National University of Science and Technology MISiS, Leninsky Prospekt, 4, 119049, Moscow, Russia

**Abstract.** The influence of partially substituted of barium ferrites by diamagnetic In and Ga ions with neutron diffraction method was studied. The substitution of Fe by In ions leads to increase of volume of unit cell while replacing with Ga ions insignificantly change the lattice parameters. The concentration dependence of the  $T_c$  Curie temperature as well as the magnetization is constructed. The refinement of the magnetic structure was carried out within the framework of Gorter’s model. The microstructural parameters of solid solutions  $BaFe_{12-x}D_xO_{19}$  (D= In and Ga; x = 0.1–1.2) were determined by the high-resolution neutron diffraction method.

## 1 Introduction

The crystalline structure of barium ferrites and their solid solutions has a structure of magnetoplumbite  $PbFe_{12}O_{19}$  which was first studied by Adelskold [1] in 1938. As a rule, it is well described in the framework of the space group  $P6_3/mmc$  (No. 194) with a hexagonal unit cell  $a = b \approx 5.90 \text{ \AA}$ ,  $c \approx 23.30 \text{ \AA}$  containing two formula units. Iron ions are localized in five nonequivalent crystallographic positions:  $2a$ ,  $4f_{VI}$  and  $12k$  - with octahedral,  $2b$  - with trigonally bipyramidal and  $4f_{IV}$  - with a tetrahedral oxygen environment.

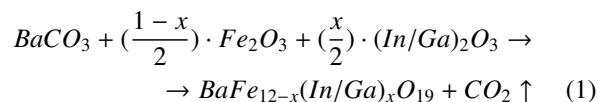
In order to improve functional properties of barium ferrites for their application use the substitution of iron ions with diamagnetic ions Al, Sc, Ga, etc. [2, 3], which change the number of bonds between magnetoactive ions. The replacement of iron ions in certain crystallographic positions influences on valence angles and interatomic distances in Fe–O–Fe [4] bonds, and consequently, affects to the pair exchange integral and the magnitude of the sublattice exchange [5].

In this paper, the effect of partial replacement of magnetoactive Fe ions by diamagnetic In and Ga ions on the crystal and magnetic structures of  $BaFe_{12-x}D_xO_{19}$  in a wide range of concentrations (D= In and Ga; x = 0.1–1.2) was studied by neutron diffraction method. The substitution of solid solutions  $BaFe_{12-x}D_xO_{19}$  by diamagnetic ions D= In and Ga allows research the influence of appearing chemical pressure on distortions of unit cell parameters and on the value of bond length Fe/In/Ga-O and determine the influence to magnetic properties (temperature

of magnetic phase transition, value of magnetic moments, etc). Concentration range of diamagnetic substitution (x= 0.1–1.2) was determined due to the preservation of optimal magnetic characteristics in doped Ba-hexaferrites. For concentration more than 10 at.% is high risk of observation some magnetic anomalous like frustration of magnetic structure [6] instead of collinear ferrimagnetic structure. Another feature of the work is the use of a high-resolution diffractometer for the measurement of neutron diffraction patterns  $BaFe_{12-x}D_xO_{19}$  (D= In and Ga; x = 0.1–1.2), which made it possible to obtain information about both the crystalline and magnetic structures and the microstructure of the samples studied.

## 2 Experimental Details

Solid solutions of  $BaFe_{12-x}D_xO_{19}$  (D= In and Ga; x = 0.1–1.2) have been prepared from high purity  $Fe_2O_3$  and  $In_2O_3$  and  $Ga_2O_3$  oxides and carbonate  $BaCO_3$  using ‘two-steps’ topotactic reactions (conventional solid reaction method). Oxides and carbonate have been mixed with design ratio and synthesized at  $1200^\circ C$  (6 h) and at  $1300^\circ C$  (6 h) in air. After synthesis the sample has been slowly cooled ( $100^\circ C/h$ ).



The powder neutron investigations of sample was performed by neutron time-of-flight method at High Resolution Fourier Diffractometer (HRFD, Dubna) at room temperature. The refining of crystal and magnetic structures

\*e-mail: turchenko@jinr.ru

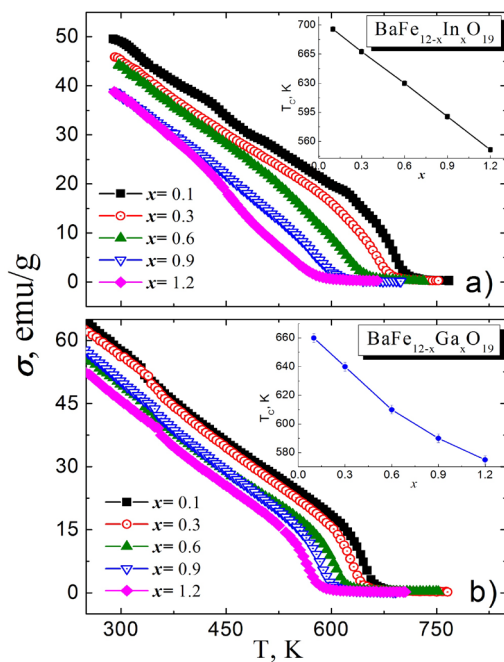
was performed by Rietveld analysis [7], using the FullProf [8] software program. The resolution of diffractometer is  $\Delta d/d_0 \approx 0.001\%$  and lattice parameters were defined more exactly at standard  $Al_2O_3$  powder (standard SRM-676 of NIST, USA).

Field dependences of specific magnetization were measured at 10–730 K by Liquid Helium Free High Field Measurement System (VSM) [9]. The "ferrimagnet-paramagnet" phase transition temperature for the  $BaFe_{12-x}D_xO_{19}$  (D= In and Ga;  $x = 0.1-1.2$ ) has been defined as the inflection point in the temperature dependence of the specific magnetization.

### 3 Results and discussion

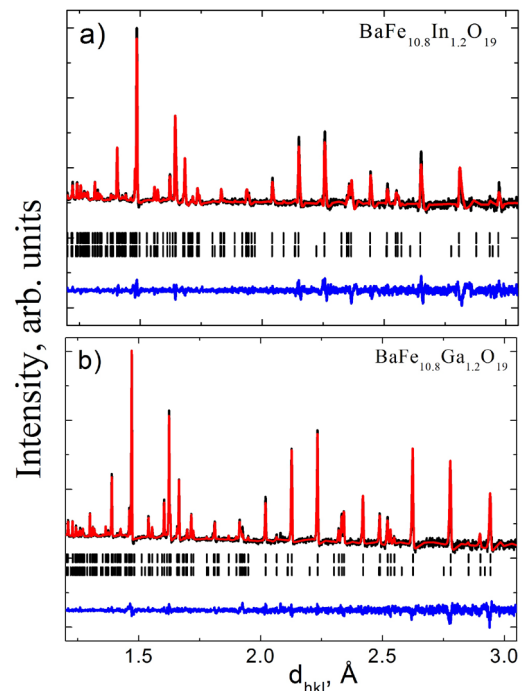
#### 3.1 Magnetic properties

Fig. 1 demonstrates temperature dependences of the specific magnetization for the  $BaFe_{12-x}D_xO_{19}$  (D= In and Ga;  $x = 0.1-1.2$ ) obtained by VSM. The concentration dependence of the Curie temperature determined as the inflection point in the temperature dependence of the specific magnetization are shown on the inset in Fig. 1. It nec-

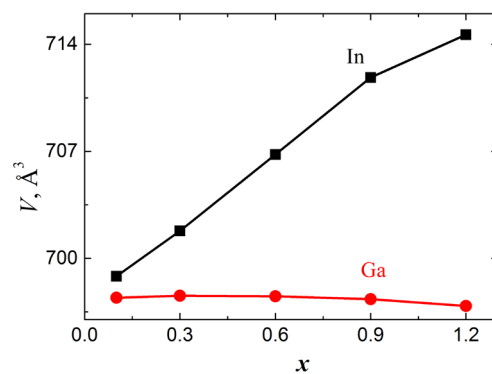


**Figure 1.** Temperature dependencies of the specific magnetization of  $BaFe_{12-x}D_xO_{19}$  (D= In – (a) and Ga – (b);  $x = 0.1-1.2$ ). In the inset, the concentration dependencies of the Curie temperature are shown.

essary to note that doping of diamagnetic ions In and Ga leads to reducing of the number of neighbors of magnetic iron cations and so that the magnetic order is destroyed at lower temperatures [10]. Therefore the Curie temperature decreases as the doping of In or Ga ions is increased whereas for the un-doped  $BaFe_{12}O_{19}$  the Curie temperature is equal 740 K [11].



**Figure 2.** Neutron diffraction patterns of  $BaFe_{10.8}D_{1.2}O_{19}$  (D= In – (a) and Ga – (b)) obtained with the HRFD at room temperature and processed via the Rietveld method. Experimental points, calculated curves and difference functions normalized to steady state error are shown. For the crystalline and magnetic structures of barium hexaferrite vertical bars designate the calculated diffraction peak positions.



**Figure 3.** The concentration dependence of volume of unit cell of barium ferrites  $BaFe_{12-x}D_xO_{19}$  (D= In and Ga;  $x = 0.1-1.2$ ).

#### 3.2 Crystal structure

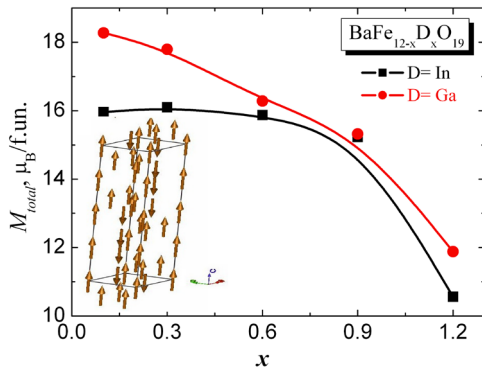
According to neutron data all investigated polycrystalline samples possesses a hexagonal structure with space group ( $P6_3/mmc$ ) with two formula units ( $Z = 2$ ). The powder neutron diffraction patterns for the  $BaFe_{10.8}D_{1.2}O_{19}$  (D= In and Ga) are presented in Fig. 2.

The high resolution of diffractometer and, correspondingly, the large number of well-separated peaks provided the good convergence of the minimization process. Fig-

ures of merit ( $R_{wp}$ ,  $R_{exp}$ ,  $\chi^2$ ) that quantify the quality of the refinement using the Rietveld method are in range:  $R_{wp}$  - from 14.8% to 16.9%,  $R_{exp}$  - from 10.0% to 11.9%,  $\chi^2$  - from 2.2 to 2.0. The dependencies of lattice parameters of unit cells versus temperature are shown in Fig. 3. Volumes of unit cells of solid solution of barium hexaferrite increase as the concentration of In ions is increased because of significant difference of ionic radii between  $In^{3+}$  ( $r = 0.94 \text{ \AA}$ ) and  $Fe^{3+}$  ( $r = 0.645 \text{ \AA}$ ) [12]. The increase of concentration of  $Ga^{3+}$  ( $r = 0.62 \text{ \AA}$ ) ions leads to insignificant decreasing of volume of unit cell.

### 3.3 Magnetic structure

In hexaferrites the magnetic  $Fe^{3+}$  ions are located in positions which have octahedral (Fe1-2a, Fe4-4 $f_{VI}$  and Fe5-12k), tetrahedral (Fe3-4 $f_{IV}$ ) and bipyramidal (Fe2-2b) oxygen environment. Therefore, partially replacement of iron ions by diamagnetic In or Ga ions that are distributed statistically equivalent for all positions of the magnetic lattice are able to change in the values of the magnetic moments in corresponding positions.



**Figure 4.** The dependence of the total magnetic moment of ferrite  $BaFe_{12-x}D_xO_{19}$  (D= In and Ga;  $x = 0.1-1.2$ ) versus concentration of diamagnetic ions.

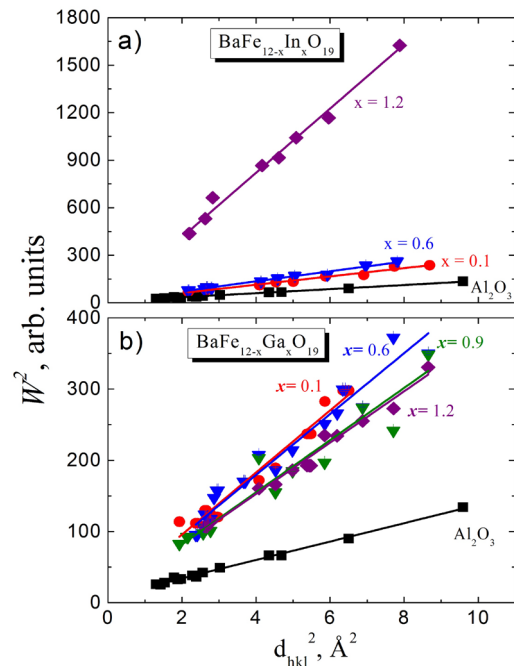
The absence at powder neutron diffraction patterns Fig.2 of the additional magnetic peaks allows to determine the wave vector of the ferromagnetic structure as  $\mathbf{k} = [0,0,0]$ . The magnetic structure for all compositions fully satisfies the model proposed by Gorter [13], according to which, all magnetic moments of the  $Fe^{3+}$  cations are oriented along the easy magnetization axis which coincides with the hexagonal c axis. The schema of magnetic structure of  $BaFe_{12-x}D_xO_{19}$  (D= In and Ga;  $x = 0.1-1.2$ ) is shown on the inset in Fig.4. The substitution of iron by diamagnetic cation breaks the exchange interactions between the magnetic positions and sublattices that leads to a decrease in the value of their magnetic moments, as it was previously shown in Ref. [14]. The total magnetic moment  $M_{total}$  per formula unit for the barium hexaferrite ( $BaFe_{12}O_{19}$ ) at T temperature can be calculated according to the formula [15]:

$$M_{total}(T) = 1[m_{2a}(T)] + 1[m_{2b}(T)] - 2[m_{4f_{IV}}(T)] - 2[m_{4f_{VI}}(T)] + 6[m_{12k}(T)] \quad (2)$$

where  $m_i$  is the magnetic moment of  $Fe^{3+}$  ion in the  $i$ -th sublattice. If the magnetic moment of  $Fe^{3+}$  ion at 0 K is equal  $5\mu_B$  then magnetic moment of pure  $BaFe_{12}O_{19}$  ferrite will be equal to  $20\mu_B$  per formula unit. Less values of magnetic moments are explained by influence of diamagnetic ions and thermal factor causing the disorientation of the magnetic moments in space due to the increase of the thermal fluctuations of the ions forming the crystal lattice. The dependencies of total magnetic moment per formula unit for the barium hexaferrite versus temperature are shown in Fig. 4.

### 3.4 Microstructure

The high resolution of Fourier Diffractometer allowed making analysis of influence the concentration of diamagnetic ions to microstructural parameters, which were determined from broadening of powder neutron peaks.



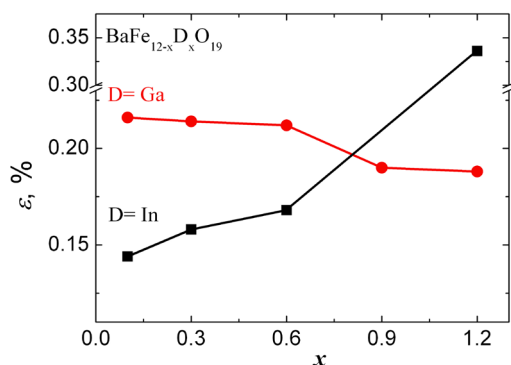
**Figure 5.** Dependencies of the square width of diffraction peak versus the square of interplanar spacing for  $BaFe_{12-x}D_xO_{19}$  (D= In – (a) and Ga – (b)). Experimental points lie on linear curves, i.e., there is no size effect (the coherent scattering region size is large). The lowest dependence corresponds to the diffractometeres solution function determined using the standard sample  $Al_2O_3$ .

The presence of microstresses and variation of average size of coherent blocks have different effect on the width of the diffraction peaks, which makes it possible to split their contributions. The widths of the diffraction peaks  $W_{hkl}$  of the tested samples have the following dependence from  $d_{hkl}$  [16]:

$$W^2 = C_1 + (C_2 + C_3) \cdot d^2 + C_4 \cdot d^4 \quad (3)$$

where  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$  – refining constants;  $W$  – full width at half maximum of diffraction peak;  $(C_1 + C_2 \cdot d^2)$  – resolution function of HRFD obtained from standard  $Al_2O_3$  (SRM-676 of NIST, USA);  $C_3 \cdot d^2$  – contribution determined by size effect;  $C_4 \cdot d^4$  – contribution determined by microstraine effect.

The contribution of true physical line broadening of powder neutron peaks for the  $BaFe_{12-x}D_xO_{19}$  (D= In and Ga;  $x = 0.1-1.2$ ) was determined by FullProf software calculated as difference of widths among experimental samples and standard  $Al_2O_3$ . In our case, the line broadening is connected with only microstresses factor. In ferrimagnetic crystals, the separate sublattices give different contributions to general deformation. Besides, the local environment symmetry of magnetic ions in ferrimagnetic crystals differs from macroscopic symmetry. This leads to increase of the microscopic parameters number in comparison with macroscopic. The slope of approximated function increases with temperature decreasing. This behavior indicates that the microstress increases in crystallites. It is shown in Fig. 5 the experimental points correspond to different combinations of Miller indices, which indicates the absence of explicit anisotropic effects in the broadening of diffraction peaks.



**Figure 6.** The dependencies of microstresses versus temperature in crystallites of  $BaFe_{12-x}D_xO_{19}$  (D = In and Ga).

The dependencies of microstress values versus temperature for the  $BaFe_{12-x}D_xO_{19}$  (D= In and Ga;  $x = 0.1-1.2$ ) are shown in Fig. 6. The calculation of microstresses has been carried out for isotropic approximation i.e. ( $L > 3000 \text{ \AA}$ ) size effect is absent. The increase in the microscopic microstress with the concentration of diamagnetic ions increasing is associated with rising of the system disorder, as a result of the statistical distribution of indium or gallium in magnetic sublattices, which can make different contributions to the total deformation.

## 4 Conclusions

The behavior of crystal and magnetic structures of barium ferrites doped by diamagnetic ions was investigated by neutron diffraction method with high resolution. The refinement of crystal structure of solid solutions of

$BaFe_{12-x}D_xO_{19}$  (D= In and Ga;  $x = 0.1 - 1.2$ ) has been performed in frames of space group  $P6_3/mmc$  (No. 194). Larger volume of unit cell of barium ferrites doped with In ions is explained by the larger value of ionic radii of  $In^{3+}$  unlike of  $Ga^{3+}$  ions. The magnetic structure of  $BaFe_{12-x}D_xO_{19}$  (D= In and Ga;  $x = 0.1 - 1.2$ ) is well described by the Gorter model: according to which the magnetic moments of the  $Fe^{3+}$  ions are oriented along the hexagonal axis that is the axis of easy magnetization. Microstresses in crystallites increase as the concentration of In ions is increased whereas the rising of concentration of Ga ions decreases microstresses. This behavior was explained by different distortion of crystal sublattices due to difference of ionic radii of indium and gallium ions at substitution of iron ions.

The work was supported by JINR (Grant 04-4-1121- 2015/2017) and BRF (Grant no. F17D- 003); Ministry of Education and Science of the Russian Federation (Grants of NUST «MISiS» K4-2017-041and K3-2017-059; in SUSU - 4.1346.2017/4.6 by Act 211 of the Government of the Russian Federation No. 02.A03.21.0011).

## References

- [1] V. Adelskold, Avk. Miner. A. **12**, 1 (1938).
- [2] D.A. Vinnik, D.A. Zhrebtsov, L.S. Mashkovtseva, S. Nemrava, M. Bischoff, N.S. Perov, A.S. Semisalova, I.V. Krivtsov, L.I. Isaenko, G.G. Mikhailov, R. Niewa, J. Alloys Compd., **615**, 1043 (2014).
- [3] 4) V. Kostishyn, V. Korovushkin, I. Isaev, A. Trukhanov, East-Europ. J. Ent. Techn., **1**(85), 10 (2017)
- [4] S. V. Trukhanov, A. V. Trukhanov, V. G. Kostishin, L. V. Panina, I. S. Kazakevich, V. A. Turchenko, V. V. Kochervinskii, JETP Letters, **103**, 100 (2016).
- [5] John B. Goodenough, *Magnetism and the chemical bond* (Interscience Publishers, New York-London, 1963) 393.
- [6] D.A. Vinnik, A.B. Ustinov, D.A. Zhrebtsov, V.V. Vitko, S.A. Gudkova, I. Zakharchuk, E. Lähderanta, R. Niewa, Ceram. Intern., **41**, 12728 (2015).
- [7] H. M. Rietveld, J. Appl. Crystallogr., **2**, 65 (1969).
- [8] J. Rodríguez-Carvajal, Physica B **192** 55 (1993).
- [9] S.V. Trukhanov, A.V. Trukhanov, A.N. Vasiliev, A.M. Balagurov, H. Szymczak, JETP, **113**, 820 (2011).
- [10] S.V. Trukhanov, JETP, **100**, 95 (2005).
- [11] T. Tsutaoka, N. Koga, J. Magn. Magn. Mater., **325**, 36 (2013).
- [12] R.D. Shannon, Acta Cryst. A. **32**, 751 (1976).
- [13] E.W. Gorter, Proc. IEEE Suppl., **104B**, 225 (1957).
- [14] S.V. Trukhanov, A.V. Trukhanov, V.G. Kostishyn, L.V. Panina, V.A. Turchenko, I.S. Kazakevich, An.V. Trukhanov, E.L. Trukhanova, V.O. Natarov, A.M. Balagurov, J. Magn. Magn. Mater., **426**, 554 (2017).
- [15] J. Smit, H. P. J. Wijn *Ferrites*, (Hume Press Ltd., Cleaver, 1959) 142.
- [16] M.V. Cabanas, P. Germi, J.M. Gonzalez-Calbet, M. Pernet, M. Vallet-Regi, J. Solid State Chem., **114**, 534 (1995).