The influence of high pressure to crystalline and magnetic structure of $Ba_2FeMoO_6$

V A Turchenko$^{1,2}$, N A Kalanda$^3$, L V Kovalev$^3$, M V Yarmolich$^3$, A V Petrov$^3$, Ye V Lukin$^1$, A S Doroshkevich$^{1,2}$, M Balasoiu$^{1,4}$, N Lupu$^5$ and B N Savenko$^1$

$^1$ Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 6 Joliot-Curie str., 141980 Dubna, Russia
$^2$ Donetsk Institute of Physics and Technology named after O.O. Galkin of the NASU, 46 Nauki Ave, 03680, Kiev, Ukraine
$^3$ SSPA Scientific and practical materials research centre of NAS of Belarus, 19 P. Brovki str., 220072 Minsk, Belorussia
$^4$ Horia Hulubei National Institute for Physics and Nuclear Engineering, Bucharest, Romania
$^5$ National Institute of Research and Development for Technical Physics, Iasi, Romania

E-mail: turchenko@jinr.ru

Abstract. The behavior of the crystalline and magnetic structure of $Ba_2FeMoO_6$ compound in a wide pressure range from 0 to 4.7 GPa was studied. The crystal structure of ceramic sample was described in the framework of SG I4/mmm (No 139) and contains less 10% of anti-site defects. The change of tetragonal structure (I4/mmm) was not observed in all measured pressure range. It was shown multidirectional influence of ambient pressure onto the average interionic distances of metal-ligand in oxygen octahedrons of $FeO_6$ and $MoO_6$. For tetragonal structure of $Ba_2FeMoO_6$ were determined coefficients of the linear and all-round compressibility. The influence of ambient pressure on the value of magnetic moment of iron sublattice was shown.

1. Introduction

Oxides of double perovskites $A_2MM'O_6$ (where $A$ = Ba, Sr, Ca ...; $M$ = Fe, Cr ...; $M'$ = Mo, W, Re ...) and their solid solutions attract the attention of researchers due to variety of physical properties associated with chemical composition and ordering of cations in crystalline structure. In general, cations $M$ and $M'$ can be distributed randomly in their sublattices, however, if there are a large difference in charges or ionic radii between them, they can arranged ordered. In this case, the crystal structure of these materials contains arranged in staggered order oxygen octahedrons $MO_6$ and $M'O_6$, where $M$ and $M'$ are cations of different chemical elements [1]. However, an appearance of anti-site defects (ASD) in crystal structures of these materials is able significantly influence onto their functional properties. This sort of structural disorder occurs when $M$ ions are located at $M'$ sites and vice versa. Several earlier theoretical and experimental studies have shown clear connection between the magnetic properties of SFMO and the anti-site disorder. The saturation magnetization [2, 3, 4, 5] and the Curie temperature [3, 6] has been seen to decrease with increasing amount of ASD. In addition to the $T_C$ and $M_s$ ASD reduces the band gap in the majority spin channel and this effect is large enough that the half metallic feature of SFMO is lost [7, 8, 9]. Double perovskites have higher values of the Curie
temperature [10, 11, 12] and their tunnel type magnetoresistive properties appear in a weak range of magnetic fields near the room temperature [12, 13], as opposed to ordinary manganite-lanthanum perovskites. Another feature of this materials is the ferromagnetic half metallic properties, which have a potential for application in electronic devices of spintronics [12, 14]. The spin polarization of carriers controlled by the magnetic field will determine the double perovskite as a conductor for electrons with spin oriented upwards (or down), or as an insulator for the other charge carriers with an oppositely directed spin orientation. It is possible to influence onto the spin polarization of carriers of double perovskites by controlling the concentration of antisites defects or creating "chemical presse", for example the incommensurate substitution of ions in the $A$– sublattice influences to bond-lengths and angles among ions of metal and oxygen and, consequently, onto the orbital overlap of ions located at $M$ and $M'$ sites. Another way to control the spin polarization of charge carriers of these materials is the external action, for example an ambient temperature and pressure. The main aim of this work is ascertain regularities of influence of high pressure (up to 4.7 GPa) on the features of the crystalline and magnetic structure of the double perovskite $\text{Ba}_2\text{FeMoO}_6$. A main feature of this work is application of the neutron diffraction method that allowed one to collect information about both the crystalline and magnetic structure of the sample during one experiment and over a wide pressure range (from 0 to 4.7 GPa).

2. Methods and methodology

The ceramic sample of $\text{Ba}_2\text{FeMoO}_6$ has been fabricated by solid state method from a mixture of $\text{Fe}_2\text{O}_3$ and $\text{MoO}_3$ oxides of analytical grade purity and $\text{BaCO}_3$ carbonate taken in appropriate ratios. The initial mixture was synthesized at 900°C (4 h) in air and then was annealed at 1200°C (10 h) under $\text{H}_2$/Ar stream. After annealing, the sample was slowly cooled (∼ 100 °C/h). The phase composition was determined by X-ray diffraction method using an Empyrean diffractometer (firm PANalytical) in Cu-K$_\alpha$ radiation at room temperature. Structural studies at high pressures (up to 4.7 GPa) have been performed using a high-pressure chamber with sapphire anvils on a DN-6 neutron diffractometer [15] (Dubna, Russia). An 1 mm$^3$ sample was placed in an anvil hole drilled in the center, that allowed to create a quasi-hydrostatic pressure distribution on the sample. The unevenness of pressure distribution across the surface of the test sample in the anvils with the holes usually does not exceed 15%. The magnitude of the applied pressure was measured from the shift of the ruby fluorescence line [16] (doublet 6942 and 6927 Å) to within 0.05 GPa. The neutron diffraction spectra were measured at scattering angles $2\Theta = 90^\circ$ and $45^\circ$. For these scattering angles, the resolution of the diffractometer at wave length $\lambda = 2$ Å was $\Delta d/d_0 = 0.02$ and 0.025, respectively. A typical measurement time of one spectrum was 12 hours. Analysis of neutron diffraction patterns with the Rietveld method has been carried out by the software package FullProf [17] using the built-in tables for coherent scattering lengths and magnetic form factors. Measurements of the magnetization of the $\text{Ba}_2\text{FeMoO}_6$ sample in the temperature range 77 – 900 K and in a magnetic field of 0.86 T were carried out using an universal automated appliance.

3. Results and discussions

3.1. Magnetic properties

The behavior of the specific magnetization shown in Fig.1 characterizes the response of magnetic properties of $\text{Ba}_2\text{FeMoO}_6$ onto a change of ambient temperature. The perovskite sample is in a saturated state at low temperatures. A gradual increase the ambient temperature leads to a violation of the long-range magnetic ordering in the sample because of the increasing of thermal motion of ions and the magnetization is decreased. When the temperature reaches $T_C \sim 317$ K the energy of thermal motion becomes comparable with the energy of the exchange interaction, as a consequence the magnetic order is destroyed and the sample of $\text{Ba}_2\text{FeMoO}_6$ passes from
the magnetically ordered to the paramagnetic state. The Curie temperature was determined as the inflection point in the temperature dependence of specific magnetization.

![Magnetization vs. Temperature](image)

**Figure 1.** The temperature dependence of specific magnetization of the $\text{Ba}_2\text{FeMoO}_6$ compound.

### 3.2. Crystal structure

According to X-ray diffraction data, the sample $\text{Ba}_2\text{FeMoO}_6$ is homogeneous. An analysis of the crystal structure of $\text{Ba}_2\text{FeMoO}_6$ has been carried out by the Rietveld method. The results of the analysis are shown in Fig. 2. At room temperature, $\text{Ba}_2\text{FeMoO}_6$ has a tetragonal structure with the sp. gr. I4/mmm (No. 139). The scheme of the unit cell of the tetragonal structure is shown in Fig. 3, a.

An important characteristic that determines the functional properties of double perovskites is the concentration of ASD which can be determined from the ratio of integrated intensities of the diffraction peaks: $I_{(101)}/(I_{(200)} + I_{(112)})$ [18]. It should be noted that the diffraction peak (101) in the double perovskite structure is superstructural and it is associated with the Fe/Mo alternative ordering. In completely disordered structure when a half of iron ions occupy positions in the molybdenum sublattice and vice versa, the diffraction peak (101) is absent. Examples of X-ray patterns corresponding to fully ordered and disordered structures were simulated in the FullProf program and they are shown in the inset of Fig. 2. The degree of structural disorder was determined, similarly to the procedure described in [19]:

$$R = 0.000271 \cdot (\text{ASD})^2 + 0.000684 \cdot (\text{ASD}) - 0.0035$$  \hspace{1cm} (1)

According to Eq. 1, the concentration of anti-site defects (ASD) in $\text{Ba}_2\text{FeMoO}_6$ is less 10%.

### 3.3. Crystal structure under high pressure

The investigation of the atomic structure under the influence of high pressures allows ascertaining the relationship among changes of structural parameters, interatomic distances, magnetic structure and macroscopic properties that is necessary for understanding the nature and mechanisms of physical phenomena of double perovskites. Examples of neutron diffraction patterns $\text{Ba}_2\text{FeMoO}_6$ obtained at a temperature of 290 K in the range of applied pressures from 1 to 4.7 GPa are shown in Fig. 4. The presence of additional superstructural peaks on
Figure 2. X-ray diffraction pattern of $\text{Ba}_2\text{FeMoO}_6$, measured at 290 K and fitted by the Rietveld method. The experimental and calculated values (upper curves) and a difference curve (the bottom line) normalized to a statistical error are presented. Vertical bars are calculated positions of diffraction peaks corresponding to the crystal structure of $\text{Ba}_2\text{FeMoO}_6$ (sp. gr. $I4/mmm$) at 290 K. The inset shows X-ray patterns for completely ordered (upper curve) and disordered (lower curve) crystal structure of the $\text{Ba}_2\text{FeMoO}_6$ simulated in FullProf software.

Figure 3. Scheme of the tetragonal crystal structure of $\text{Ba}_2\text{FeMoO}_6$ at room temperature.

neutron patterns of $\text{Ba}_2\text{FeMoO}_6$ in the entire range of applied external pressures was not observed that indicates the absence of a change in the type of crystal and magnetic structure.

An increase of the external pressure leads to a monotonic decrease in the parameters of the unit cell (see Fig.5).

The results of refining by the Rietveld method of neutron diffraction patterns of $\text{Ba}_2\text{FeMoO}_6$ at different external pressures are shown in Table 1. The dependences of volume of unit cell
**Figure 4.** Neutron diffractograms of $\text{Ba}_2\text{FeMoO}_6$, measured at different pressures and processed by the Rietveld method. Experimental and calculated values (upper curves) and a difference curve (the bottom line) normalized to a statistical error are presented. Vertical bars are calculated positions of the diffraction peaks corresponding to the atomic and magnetic structures of $\text{Ba}_2\text{FeMoO}_6$ (sp. gr. $\text{I}4/\text{mmm}$).

versus pressure was interpolated by the Birch-Murnaghan equation [20] (Fig.6):  

$$P = \frac{3}{2} \cdot B_0 \cdot (x^{-\frac{7}{4}} - x^{-\frac{3}{4}}) \cdot [1 + \frac{3}{4} \cdot (B_x - 4) \cdot (x^{-\frac{3}{4}} - 1)]$$

where $x = (V/V_0)$ is the relative volume change, $V_0$ is the unit cell volume at $P = 0$, $B_0$ and $B'$ are empirical parameters that have the meaning of the modulus of comprehensive compression in the equilibrium state $(B_0 = -V \cdot (dP/dV)|_{V=V_0})$ and its first order derivative $(B' = dB_0/dP)$, respectively. In order to describe the equation of state of $\text{Ba}_2\text{FeMoO}_6$ was used a linear dependence corresponding to the Birch-Murnaghan equation for solids with low compressibility:  

$$V = \left(\frac{P}{B_0} - 1\right) \cdot V_0$$

Calculated values of $B_0$ and $B'$ for the equation of state of the $\text{Ba}_2\text{FeMoO}_6$ with tetragonal structure are 190 GPa and 4, respectively. The received value of modulus of the all-round compression is reasonable for perovskite structure and well agrees with the results of Ref.[21].
Figure 5. The dependence of crystal lattice parameters of the unit cell $Ba_2FeMoO_6$ versus external pressure.

Figure 6. $V/V_0 - P$ is relationship for $Ba_2FeMoO_6$. The filled squares are experimental data, the solid curve is calculated.

Table 1. Parameters of crystal lattice and atomic coordinates under the influence of ambient pressures at room temperature and figures of merit were refined by the Rietveld method in the framework of the space group: $I4/mmm$ (No. 139). Atoms are in positions: Ba (4d) $(0, 1/2, 1/4)$; Fe1 (2a) $(0, 0, 0)$; Mo2 (2b) $(0, 0, 1/2)$; O1 (4e) $(0, 0, z)$; O2 (8h) $(x, x, 0)$.

| Parameters of unit cell | P, GPa | 0  | 1  | 2.1 | 2.9 | 4.7 |
|-------------------------|--------|----|----|-----|-----|-----|
| a, (Å)                  |        | 5.7096(3) | 5.70(2) | 5.69(6) | 5.68(4) | 5.66(2) |
| c, (Å)                  |        | 8.0687(4) | 8.07(2) | 8.05(9) | 8.03(4) | 8.00(2) |
| V, ($Å^3$)              |        | 263.03(2) | 262(1) | 260.9(9) | 259(1) | 256.5(5) |
| z                       |        | 0.2601(12) | 0.253(22) | 0.248(54) | 0.258(32) | 0.241(36) |
| x                       |        | 0.2567(0) | 0.243(0) | 0.246(0) | 0.241(0) | 0.234(0) |
| $m_{Fe}, μ_B$/f.un.     |        | 0.38(1) | 0.33(16) | 0.75(9) | 0.594(2) | 1.19(1) |
| $R_{wp}$, %             |        | 14.7 | 15.3 | 19.0 | 22.2 | 20.2 |
| $R_B$, %                |        | 5.45 | 5.54 | 5.69 | 10.0 | 8.33 |
| $R_{Mag}$, %            |        | 17.9 | 20.9 | 9.36 | 33.5 | 10.2 |
| $R_F$, %                |        | 4.36 | 4.43 | 4.36 | 7.09 | 15.0 |

The linear parameters of the compressibility of a unit cell of the tetragonal structure were calculated from the formula: $k_i = (1/a_{i0})(da_i/dP)_T$, where the $a_i = (a, c)$ are parameters of the crystal lattice at a pressure of $P = 0$ and 4.7 GPa. They have the values: $k_a = 0.001774 (GPa^{-1})$ and $k_c = 0.001759 (GPa^{-1})$ at $T = 290$ K.
Figure 7. Dependencies of bond-lengths between metal-ligand: a) Fe – O and b) Mo – O versus pressure.

Table 2. Distances between the metal - oxygen ions in the crystal structure of the double perovskite $Ba_2FeMoO_6$ determined at various ambient pressures by the Rietveld method within the framework of sp. gr. I4/mmm (No 139).

| Ions   | Count | P, GPa   |
|--------|-------|----------|
|        |       | 0      | 1     | 2.1   | 2.9    | 4.7    |
|        |       | Bond-length, Å |        |        |        |        |
| Fe1 - O1 | x2 | 2.09(1) | 2.02(16) | 2.0(1) | 2.1(2) | 1.933(4) |
| Fe1 - O2 | x4 | 2.073(5) | 1.96(1) | 1.982(2) | 1.94(1) | 1.875(4) |
| <Fe1 - O> | x6 | 2.079 | 1.98 | 1.988 | 1.993 | 1.894 |
| Mo2 - O1 | x2 | 1.94(1) | 2.02(16) | 2.0(1) | 1.9(2) | 2.068(4) |
| Mo2 - O2 | x4 | 1.965(5) | 2.07(1) | 2.04(2) | 2.08(1) | 2.129(4) |
| <Mo2 - O> | x6 | 1.957 | 2.053 | 2.027 | 2.02 | 2.109 |
The effect of external pressure on the magnitude of metal-oxygen bond-length for $Ba_2FeMoO_6$ in the tetragonal symmetry structure I4/mmm (No 139) is shown in Fig. 7 and in Table 2. This crystal structure consists of two types arranged in staggered order asymmetrically distorted oxygen octahedrons $FeO_6$ and $MoO_6$ where bond-lengths $Fe/Mo - O_{1 \text{apical}}$ and $Fe/Mo - O_{2 \text{equatoria}}$ have different values. Two $O_{1 \text{apical}}$ coaxial anions located at the vertex of oxygen octahedron $FeO_6$ along the tetragonal $c$ axis move off iron ion whereas four coplanar $O_{2 \text{equatoria}}$ ions located in the $ab$-plane of the octahedron shift to iron ion nearer. The situation in the $MoO_6$ octahedron is reversed: the coaxial $O_{1 \text{apical}}$ anions are at a more distance from the $Mo$ ion than four coplanar $O_{2 \text{equatoria}}$ ions. Bond lengths of $Fe - O_{1 \text{apical}}$ and $Fe - O_{2 \text{equatoria}}$ as well as $Mo - O_{1 \text{apical}}$ and $Mo - O_{2 \text{equatoria}}$ have close values therefore it is expedient to investigate the pressure dependences of their averaged values: $\langle Fe - O \rangle$ and $\langle Mo - O \rangle$ (Table 2). An increase of the external pressure leads to a reduction of the interionic distances $\langle Fe - O \rangle$ and, conversely, to a slightly increase of the interionic distances $\langle Mo - O \rangle$ (Fig. 7, a and b).

Coefficients of the linear compressibility have following values: for the bond $\langle Fe - O \rangle$, $k_{(Fe-O)} = -0.019 \, \text{GPa}^{-1}$ and for the $\langle Mo - O \rangle$, $k_{(Mo-O)} = 0.017 \, \text{GPa}^{-1}$. The different signs of coefficients of linear compressibility for octahedron $FeO_6$ and $MoO_6$ indicate their different behavior under the influence of external pressure.

### 3.4. Magnetic structure

The electroneutrality in double perovskites can be carried out by two possible valence states of iron and molybdenum ions: 1) $Fe^{2+}$ ($3d^6$) and $Mo^{6+}$ ($4d^0$) or 2) $Fe^{3+}$ ($3d^5$, $S = 5/2$) and $Mo^{5+}$ ($4d^1$, $S = 1/2$), respectively. In the first case, the magnetic moment of molybdenum ions is $\mu_{(Mo^{5+})} = 0\mu_B$ therefore the total magnetic moment of this material will be determined by the nominal value of the ordered magnetic moments of ions in iron sublattice $\mu_{(Fe^{2+})} = 4\mu_B$. In the second case, the magnetic structure of the double perovskite should be formed by the ferromagnetic ordering of the magnetic moments of iron ions in $FeO_6$ octahedrons and by the antiferromagnetic ordering of the magnetic moments of molybdenum ions in $MoO_6$ octahedrons with nominal values $\mu_{(Fe^{3+})} = 5\mu_B$ and $\mu_{(Mo^{5+})} = 1\mu_B$, accordingly. Therefore, in the fully magnetically ordered state (in the low-temperature region) the total magnetic moment of $Ba_2FeMoO_6$ should have $4\mu_B$/f.\text{un.}

The observation of the diffraction spectra of the sample over a wide range of pressures (from 0 to 4.7 GPa) allows one to analyze the change of its magnetic structure. The presence of additional superstructural magnetic reflexes on the neutron diffractograms (Fig. 4) is not observed. This indicates that in the case of the ferrimagnetic structure its wave vector is $\mathbf{k} = [0,0,0]$. The dependencies of magnetic moments of sublattices of $Ba_2FeMoO_6$ compound versus ambient pressure are shown in Fig. 8 (a) - for ferromagnetic and (b) for antiferromagnetic models. For ferromagnetic model, the value of magnetic moment of Mo sublattice is equal to 0 whereas for Fe sublattice magnetic moment monotonically increases from 0.15 $\mu_B$/f.\text{un.}$ to 1.17 $\mu_B$/f.\text{un.}$ with increasing of ambient pressure from 0 to 4.7 GPa. Magnetic moments of iron sublattice are ordered along easy magnetization axis, which coincide with tetragonal axis. The scheme of the ferromagnetic structure of $Ba_2FeMoO_6$ is shown in inset of Fig.8, a. In the case of antiferromagnetic structure, magnetic moments of molybdenum sublattice are ordered in opposite direction to iron sublattice. The scheme of the antiferromagnetic structure of $Ba_2FeMoO_6$ is shown in inset of Fig.8, b. The value of magnetic moment of iron sublattice monotonically increases up to 1.23 $\mu_B$/f.\text{un.}$, whereas of molybdenum sublattice up to 0.15 $\mu_B$/f.\text{un.}
Figure 8. Dependencies of the magnetic moments of iron and molybdenum sublatices of $Ba_2FeMoO_6$ versus ambient pressure: (a) - for ferromagnetic and (b) - for antiferromagnetic models. In the inset are shown schemes of the magnetic structure of $Ba_2FeMoO_6$.

4. Conclusions
The behavior of the crystalline and magnetic structures of the double perovskite $Ba_2FeMoO_6$ has been investigated by the neutron diffraction method in a wide range of ambient pressures (0 - 4.7 GPa). An increase of ambient pressure does not lead to a change the type of crystalline and magnetic structures. It has been determined that a ceramic sample of $Ba_2FeMoO_6$ prepared by the solid state method under $H_2/Ar$ stream has an ordered tetragonal structure with sp. gr. $I4/mmm$ (No 139) and contains less 10% of anti-site defects. It was shown the influence of ambient pressure to the average interionic metal-ligand distances in the oxygen octahedrons of $FeO_6$ and $MoO_6$. The average bond length $\langle Fe - O \rangle$ decreases as the ambient pressure is increased whereas $\langle Mo - O \rangle$ increases. Coefficients of the linear and all-round compressibility were determined for the tetragonal structure of $Ba_2FeMoO_6$. The average value of the magnetic moment of the iron sublattice increases up to $1.17 \mu_B/f.un.$ monotonically with increasing of ambient pressure in the case of ferromagnetic model and up to $1.23 \mu_B/f.un.$ for antiferromagnetic structure, whereas magnetic moment of molybdenum sublattice increases up to $0.15 \mu_B/f.un.$
Acknowledgments
The financial supports by the 04-4-1121-2015/2017 project are acknowledged.

References
[1] Patterson F K, Moeller W C and Ward R 1963 Inorg. Chem. 2 196
[2] Colis S, Stoeffler D, Meny C, Fix T, Leuvrey C, Pourroy G, Dinia A and Panissod P 2005 J. Appl. Phys. 98 033905
[3] Park B J, Han H, Kim J, Kim Y J, Kim C S, Lee B W 2004 J. Magn. and Magn. Mater. 272-276 1851
[4] Venimadhav A, Vickers M E and Blamire M G 2004 Solid State Communications 130 631
[5] Huang Y H, Karppinen M, Yamauchi H and Goodenough J B 2006 Phys. Rev. B 73 104408
[6] Ogale A S, Ogale S B, Ramesh R and Venkatesan T 1999 Appl. Phys. Lett. 75 537
[7] Singh V N and Majumdar P 2011 Europhys. Lett. 94 47004
[8] Stoeffler D and Colis S J. Phys. Cond. Mat. 17 6415
[9] Panguluri R P, Xu Sh, Moritomo Y, Solovyev I V and Nadgorny B 2009 Appl. Phys. Lett. 94 012501
[10] Patterson F K, Moeller W C and Ward R 1963 Inorg. Chem. 2 196
[11] Galasso F S 1966 J. Chem. Phys. 44 1672
[12] Kobayashi K-I, Kimura T, Sawada H, Terakura K and Tokura Y 1998 Nature (London) 395 677
[13] Sleight A W and Weiher J F 1972 J. Phys. Chem. Solid. 33 679
[14] Prinz G 1998 Science 282 1660
[15] Kozlenko D P, Savenko B N, Glazkov V P and Somenkow V A 2005 Neutron News 16 13
[16] Piermarini G J, Block S, Barnett J D and Forman R A 1975 J. Appl. Phys. 46 2774
[17] Rodriguez-Carvajal J 1993 Physica B 192 55
[18] Balcells L, Navarro J, Bibes M, Roig A, Martinez B and Fontcuberta J 2001 Appl. Phys. Lett. 78 781
[19] Hemery E 2007 Magnetic and Transport Studies of Strongly Correlated Perovskite Ceramics (Victoria University of Wellington, thesis) p 112
[20] Birch F J, 1986 J. Geophys. Res. 91 4949
[21] Yu R C, Zhao P, Li F Y, Liu Z X, Liu J and Jin C Q 2004 Phys. Rev. B 69 214405