

VIBRATIONAL PROPERTIES OF INDIUM DOPED BARIUM HEXAFERRITE AT LOW TEMPERATURE

G.Sh. Ayyubova*

Scientific Research Institute of Aerospace Informatics, Azerbaijan National Aerospace Agency, Baku, Azerbaijan

Abstract. The crystal structure of $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ has been studied using X-ray diffraction method at room temperature. It has been found that, at normal conditions, the samples are characterized by the hexagonal symmetry with space group $P6_3/mmc$. The Raman spectra have been investigated in the range of $\nu = 200\text{--}800\text{ cm}^{-1}$ at low temperature up to $-190\text{ }^{\circ}\text{C}$. It has been found out that, structural changes do not occur and hexagonal symmetry is maintained at the preset temperature range. Temperature dependencies of various vibration modes were obtained.

Keywords: X-ray diffraction, Raman spectrum, crystal structure.

Corresponding Author: G.Sh. Ayyubova, Scientific Research Institute of Aerospace Informatics, Azerbaijan National Aerospace Agency, AZ-1106, Baku, Azerbaijan, e-mail: gulerayyubova90@gmail.com

Received: 11 July 2020;

Accepted: 12 September 2020;

Published: 30 September 2020.

1. Introduction

Barium hexaferrite is a widely studied material due to the ferromagnetic, dielectric and ferroelectric properties which applied in the ceramics technologies industry. Barium hexaferrite and its solid solutions have both ferroelectric and ferromagnetic properties. These types of materials are called multiferroics. Recently, the hexagonal crystal structure of $\text{BaFe}_{12}\text{O}_{19}$ compound become intensively applied due to perfect multiferroic properties. Thus, this compound has a wide range of applications, such as memory elements, various transducer sensors and electromagnetic absorbing materials (Fiebig, 2005).

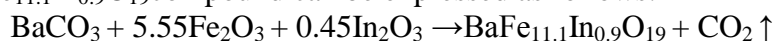
Barium hexaferrite and its solid solutions are multifunctional complex oxides that have a stable crystal structure. This compound has ferromagnetic properties at the high temperature ($T_N = 750\text{ K}$) ranges. $\text{BaFe}_{12-x}\text{Me}_x\text{O}_{19}$ (Me= Al, Ga, Sc etc) solid solutions obtained based on the $\text{BaFe}_{12}\text{O}_{19}$ compound also have a unique physical properties. The ferromagnetic-paramagnetic transition temperature also is sufficiently high ($\sim 740\text{ K}$) in these compounds. X-ray diffraction studies have shown that these solid solutions are crystallized in the hexagonal symmetry with $P6_3/mmc$ space symmetry and hexagonal structure holds in the wide temperature range (Trukhanov *et al.*, 2016).

The Raman investigations on the $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ ($x = 0.1\text{--}1.2$) crystals have shown that 8 maximum are observed at the Raman spectra in the range of $250\text{--}750\text{ cm}^{-1}$. The maximums obtained at frequencies $\nu \sim 289, 337, 413, 469, 525, 617, 684$ and 717 cm^{-1} were explained by vibrations of $\text{Fe}(1)/\text{Al}(1)\text{O}_6$, $\text{Fe}(4)/\text{Al}(4)\text{O}_6$ and $\text{Fe}(5)/\text{Al}(5)\text{O}_6$ octahedra, $\text{Fe}(2)/\text{Al}(2)\text{O}_5$ bipyramids and $\text{Fe}(3)/\text{Al}(3)\text{O}_4$ tetrahedra (Jabarov *et al.*, 2015). The Raman spectroscopy investigations also were conducted for $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$.

compound at room temperature, as well as in the high temperature ranges. It was determined that Raman modes observed at room temperature also existed up to $T=450^{\circ}\text{C}$ of temperature and there was not observed any structural phase transition (Agayev *et al.*, 2020). In this study, $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ compound was synthesized by partial substitutions of magnetic iron ions with diamagnetic indium ions in the $\text{BaFe}_{12}\text{O}_{19}$ hexaferrite compound. The atom dynamics of the powdered research samples have been studied in the low temperature ranges.

2. Experiment

The research material of $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ compound has been synthesized using high purity Fe_2O_3 , In_2O_3 and BaCO_3 compounds. The oxides and carbonates were first mixed in appropriate amounts and then heated in the open air at 1200°C for 6 hours. In the last stage, it was heated in the open air at 1300°C for 6 hours. After synthesis, the samples were cooled slowly ($100^{\circ}\text{C}\cdot\text{hour}^{-1}$). The chemical reaction to obtain powder samples of $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ compound can be expressed as follows:



The crystal structure of the obtained samples was investigated X-ray diffraction method at the D8 Advance (Bruker) diffractometer with the parameters 40 kV, 40 mA, $\text{CuK}\alpha$ -radiation ($\lambda = 1.5406 \text{ \AA}$). Obtained spectra were stored in the multichannel analyzer and then analyzed by the Ritveld method using the FullProf program (Rodriguez-Carvajal, 1993).

Raman spectra were studied at the LabRam spectrometer with 632 nm wavelength and obtained results were analyzed by Gaussian function using Origin 9 software.

3. Results and discussion

X-ray diffraction spectrum of the $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ compound obtained at room temperature and normal condition is shown in Figure 1. The crystal structure of the compound has been determined by Ritveld method based on this spectrum. X-ray diffraction spectra reveals the $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ compound has hexagonal symmetry with $\text{P6}_3\text{mmc}$ space group at room temperature. The lattice parameters of the unit cell are corresponds to $a = 5.888(4) \text{ \AA}$, $c = 23.194(6) \text{ \AA}$, which these results consistent with the results of previous structural studies conducted on the ceramical $\text{BaFe}_{12-x}\text{Me}_x\text{O}_{19}$ ($\text{Me} = \text{Al}, \text{Ga}, \text{Sc}$ etc) crystals (Trukhanov *et al.*, 2016). There are observed shifting in the atomic coordinates when Fe atoms partially substituted with In atoms in the $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ compounds. Obtained values for atomic coordinates are shown in Table 1.

Raman spectra of the $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ compound were obtained at room temperature and in the frequency range of $\nu = 150 - 1000 \text{ cm}^{-1}$ (Figure 2).

Each of the obtained maxima in the spectra was interpreted using the Gaussian function. As can be seen from spectrum, there are eight maxima in the frequency range of $\nu = 50\text{-}1000 \text{ cm}^{-1}$. These maxima in the Raman spectrum of the $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ at room temperature are $\nu_1 = 80$, $\nu_2 = 155$, $\nu_3 = 175$, $\nu_4 = 319$, $\nu_5 = 406$, $\nu_6 = 512$, $\nu_7 = 613$ and $\nu_8 = 673 \text{ cm}^{-1}$. These modes of oscillation are interpreted in accordance with oscillation modes of substituted barium hexaferrite as follows:

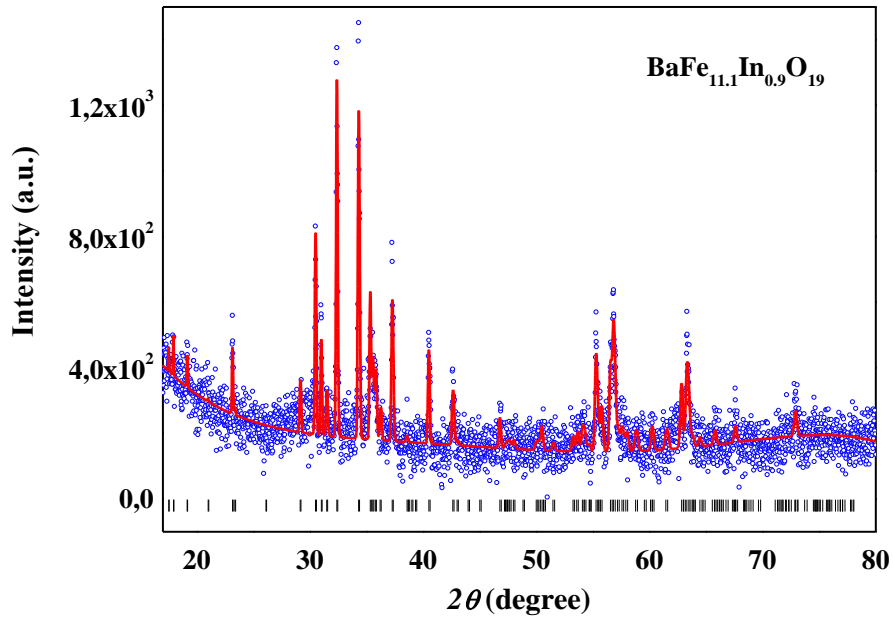


Fig. 1. X-ray diffraction spectrum of the $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ compound

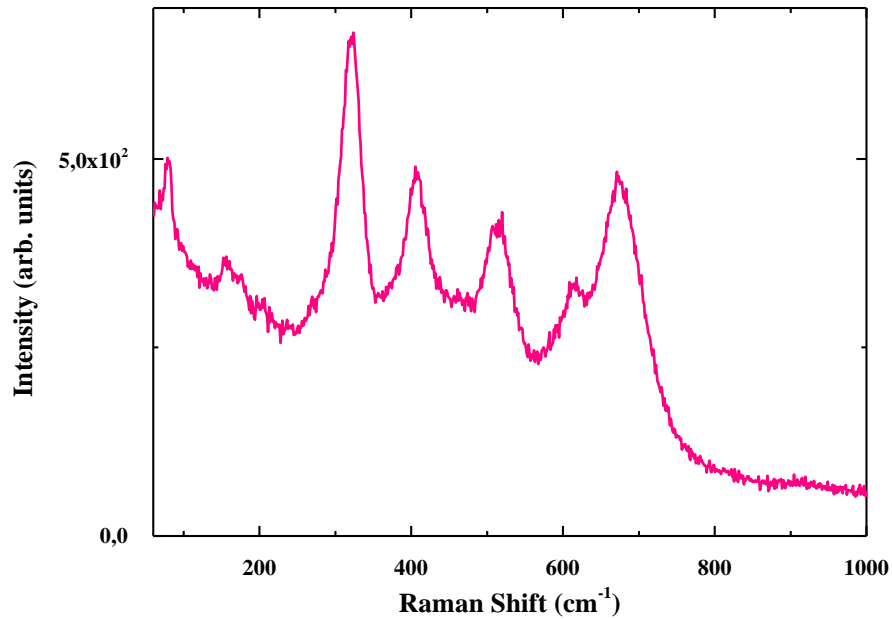


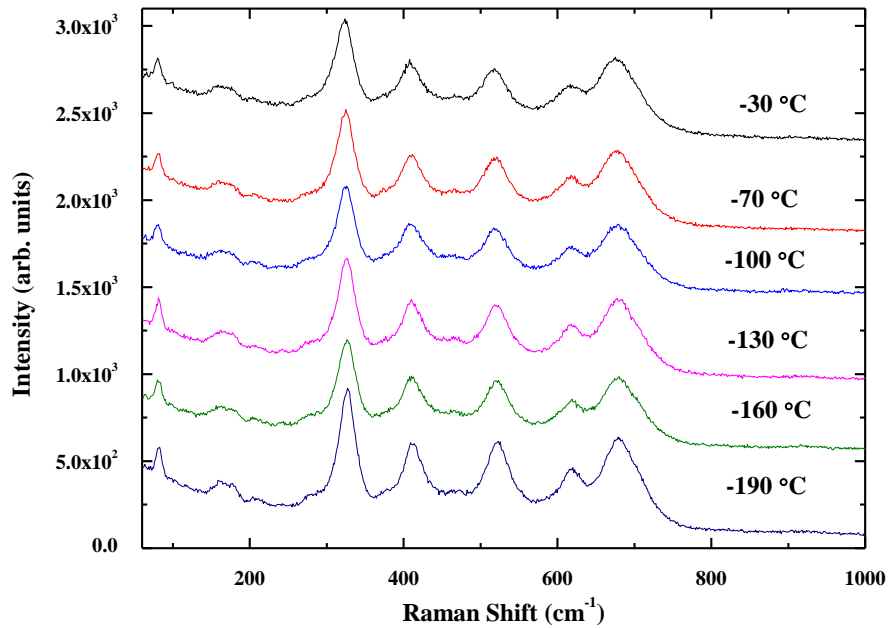
Fig. 2. Raman spectra of the $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ compound at room temperature

- ❖ $\nu_1 = 80 \text{ cm}^{-1}$ mode: corresponds to whole spinel block oscillations,
- ❖ $\nu_2 = 155 \text{ cm}^{-1}$ mode: corresponds to whole spinel block oscillations,
- ❖ $\nu_3 = 175 \text{ cm}^{-1}$ mode: corresponds to whole spinel block oscillations,
- ❖ $\nu_4 = 319 \text{ cm}^{-1}$ mode: corresponds to oscillations of O-Fe/In-O bonds,
- ❖ $\nu_5 = 406 \text{ cm}^{-1}$ mode: corresponds to oscillations of Fe/InO₆ octaeders,
- ❖ $\nu_6 = 512 \text{ cm}^{-1}$ mode: corresponds to oscillations of Fe/InO₆ octaeders,
- ❖ $\nu_7 = 613 \text{ cm}^{-1}$ mode: corresponds to oscillations of Fe/InO₆ octaeders,
- ❖ $\nu_8 = 673 \text{ cm}^{-1}$ mode: corresponds to oscillations of Fe/InO₅ bipyramides.

Table 1. Atomic coordinates of $\text{BaFe}_{11.1}\text{In}_{0.1}\text{O}_{19}$ compound at room temperature

Atom	x	y	z
Ba	2/3	1/3	1/4
Fe1(In1)	0.00000	0.00000	0.00000
Fe2(In2)	0.00000	0.00000	0.2573(1)
Fe2(In2)	0.00000	0.00000	1/4
Fe3(In3)	1/3	2/3	0.027(2)
Fe4(In4)	1/3	2/3	0.189(18)
Fe5(In5)	0.167(6)	0.3374(1)	-0.107(8)
O1	0.00000	0.00000	0.148(3)
O2	1/3	2/3	-0.054(3)
O3	0.182(11)	0.3643(1)	1/4
O4	0.154(10)	0.3129(1)	0.052(19)
O5	0.505(15)	0.0052(1)	0.148(14)

The low temperature (in the range of $T = 20 - -190$ °C) Raman spectroscopy measurements in the frequency range of $\nu = 150 - 1000$ cm^{-1} for $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ compound is presented in Figure 3.

**Fig. 3.** Raman spectra of the $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ compound in the low temperature range

It was determined that each of the modes existed at room temperature are observed in the low temperature ranges (to $T = -190$ °C). However, there are shifts to the low-frequency range in the values of the frequencies of vibration modes which is explained by the compression of the interatomic bonds at low temperatures.

If we compare the obtained modes in the Raman spectra of the $\text{BaFe}_{11.1}\text{Al}_{0.9}\text{O}_{19}$ and $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ compounds, the difference between Al^{3+} and In^{3+} ions ($R_{\text{Al}^{3+}} = 0.525$ Å, $R_{\text{In}^{3+}} = 0.814$ Å) are also observed in the changes of atomic dynamics (Bugayenko *et al.*, 2008).

The main reason for the formation of ferroelectric properties (spontaneous polarization) in complex oxide ferroelectrics is the different rotations of the polyhedra formed around the metal atoms by oxygen atoms around certain axes of symmetry. The polarization occurs when atoms move from ideal centers in displacement-type ferroelectrics. The long-range magnetic order cannot occur if the metal ions located in the centers of the polyhedra move. The magnetism in the barium hexaferrite and its solid solutions are sufficiently high and magnetic properties are observed at room temperature. Because, the spontaneous polarization in these compounds is not due to the displacement of the metal atoms from their ideal positions, but to the rotation of the polyhedral (Trukhanov *et al.*, 2017). Raman studies show that the changes in atomic dynamics occur when the concentration of In ions increases in the compounds. It is known that unlike the Fe atoms, the magnetism become decrease, long-range magnetic order weakens when increase the concentration of the In diamagnetic atoms, accordingly, atoms can slip from their positions, which has an effect on the atomic dynamics.

4. Conclusion

It has been determined that the crystal structure of this compound has $P6_3/mmc$ space group. The lattice parameters at the hexagonal symmetry are determined as: $a = 5.888(4) \text{ \AA}$, $c = 23.194(6) \text{ \AA}$. The coordinates of the atoms located on the different crystallographic positions in the crystal lattice were determined. Raman spectroscopy investigations were carried out in the range of $20^\circ\text{C} \leq T \leq -190^\circ\text{C}$ temperature and the various oscillations of barium hexaferrite have been investigated using Raman spectroscopy.

References

- Agayev, F.G., Jabarov, S.H., Ayyubova, G.Sh., Mirzayev, M.N., Trukhanov, S.V., Trukhanova, E.L., Darwish, M.A., Podgornaya, S.V., Vinnik, D.A., Hoang, T.P., Dang, N.T., Trukhanov, A.V. (2020). Structure and thermal properties of $\text{BaFe}_{11.1}\text{In}_{0.9}\text{O}_{19}$ hexaferrite. *Physica B: Condensed Matter*, 580, 411772.
- Bugaenko, L.T., Ryabykh, S.M., Bugaenko, A.L. (2008). A nearly complete system of average crystallographic ionic radii and its use for determining ionization potentials. *Moscow University Chemistry Bulletin*, 63, 303-317.
- Fiebig, M. (2005). Revival of the magnetoelectric effect. *J. Phys. D: Appl. Phys.*, 38, R123.
- Jabarov, S.H., Trukhanov, A.V., Trukhanov, S.V., Mammadov, A.I., Turchenko, V.A., Mehdiyeva, R.Z., Huseynov, R.E. (2015). XRD, DTA and TGA investigations of the $\text{BaFe}_{12-x}\text{Al}_x\text{O}_{19}$ ($x = 0.3, 0.9$ and 1.2) solid solutions. *Optoelectronics and Advanced Materials-Rapid Communications*, 9(3-4), 468-470.
- Trukhanov, A.V., Dang, N.T., Trukhanov, S.V., Jabarov, S.H., Kazakevich, I.S., Mammadov, A.I., Mekhdiyeva, R.Z., Turchenko, V.A., Huseynov, R.E. (2016). Crystal structure, magnetic properties, and raman spectra of solid solutions $\text{BaFe}_{12-x}\text{Al}_x$. *Physics of the Solid State*, 58(5), 992-996.
- Trukhanov, A.V., Kostishyn, V.G., Panina, L.V., Jabarov, S.H., Korovushkin, V.V., Trukhanov, S.V., Trukhanova, E.L. (2017). Magnetic properties and Mössbauer study of gallium doped M-type barium hexaferrites. *Ceramics International*, 43(15), 12822-12827.
- Rodriguez-Carvajal, J. (1993). Recent advances in magnetic structure determination by neutron powder diffraction. *Physica B: Condensed Matter*, 192, 55-69.