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| | Experiment title: Structure and Dynamics of Ferrimagnetic M-type Hexaferrites BaFe ₁₂ O ₁₉ and BaFe _{11.35} Se _{0.65} O ₁₉ from 5 K to 300 K | Experiment number: 01-02-1072 |
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Report:

Compounds with chemical formula AFe₁₂O₁₉ (A=Ba, Sr, Pb) comprise a large class of ferromagnetic oxides called M-type hexaferrites that are structurally isomorphic to magnetoplumbite mineral. A member of the family, the natural magnetoplumbite PbFe₁₂O₁₉ has a complex chemical composition due to the presence of various oxides like MnO, Mn₂O₃, Al₂O₃, TiO, and its actual formula is Pb₂Fe₁₅Mn₇(AlTi)₃₈. Although the natural form of the mineral does not contain any Fe²⁺ ions, it exhibits a considerable residual magnetization that makes it particularly attractive for industrial applications. Indeed, one of the various artificial magnetoplumbite phases, Pb²⁺Fe₁₂³⁺O₁₉, exhibits excellent magnetic properties and it is used for manufacturing permanent magnets [1]. Some of the hexaferrite compounds not only possess outstanding magnetic characteristics, they also show signs of multiferroicity. For example, the diluted compound BaFe_{1-x-δ}Sc_xMg_δO₁₉ (δ=0.05) with x = 1.6 and x=1.75 reveals the formation of multiferroic phase with the robust magnetoelectric effect [2]. Recent measurements of the artificial magnetoplumbite PbFe₁₂O₁₉ suggest a large residual polarization of P=104 μC/cm² [3], however, the results should be verified since they could be influenced by a rather high conductivity of the studied samples.

In a recent work [4], we have detected an anomalous optical response of the BaFe₁₂O₁₉ single crystal at terahertz frequencies connected with a specific multi-minimum potential relief that determines the dynamics of the iron ion (Fe²⁺) in the (2b)-position. The anomalous behavior reveals itself in the form of a low-frequency A_{2u} polar soft mode that indicates a possible phase transition to the polar phase with spontaneous polarization along the six-fold c-axis; meaning that the BaFe₁₂O₁₉ compound may show magnetoelectric properties under appropriate atomic substitution or strain engineering. An important structural feature of BaFe₁₂O₁₉ is that the Ba²⁺ ion occupies the position [(2d) - (2/3, 1/3, 1/4)] that is within the same slab as the Fe²⁺-ions. This means that the Ba²⁺ ion should participate in the formation of the lowest-frequency phonon density of states (see, for example, [5]) that is crucial for the soft mode appearance and the formation of electric polarization. It is well-known that, in contrast to the barium analogues, the lead-based

compounds can acquire anomalous properties triggered by the Pb^{2+} cation that has a lone pair of $6s^2$ electrons. The interaction of this lone pair with phonons is expected to significantly diversify the lattice dynamical properties of the crystals [6, 7]. In the present work we aimed at studying changes in the crystal structure and lattice dynamics of $\text{BaFe}_{12}\text{O}_{19}$ induced by the replacement of Ba ion with Pb. More specifically, we wanted to find out whether substitution of Ba by Pb can lead to giant static dielectric properties and spontaneous polarization [3] or to the formation of the low-temperature exotic phases like quantum electric dipole liquid [8, 9]

Using synchrotron radiation diffraction, crystal structure has been determined yielding a $P6_3/mmm$ hexagonal lattice with parameters $a = 5.8971(1)$ Å and $c = 23.3563(4)$ Å. The structural model is developed that comprises two split positions: Fe2 ions at the $(1/2 \times 4e)$ $(0, 0, z)$ position with bipyramidal oxygen environment, and Pb ions at the $(24l)$ (x, y, z) position with generic strongly distorted 12 vertex polyhedron of oxygen. The atomic displacements ellipsoids of the oxygen ions surrounding the lead ion are stretched towards the lead ion within the plane perpendicular to the hexagonal axis. The model is in full agreement with the suggested local symmetry of the Fe2 and Pb ions that is lower than $-6m2$ ($3m$ and 1 , respectively) and with the chemical composition of the sample determined by X-ray fluorescence analysis. Polarized infrared and Raman spectra show good agreement with the results of the factor-group analysis. Two symmetry forbidden A_{1g} and E_{1g} modes are observed in the low-frequency Raman spectra due to selection rules violation caused by a positional disorder of Fe2 and Pb ions. The broad absorption band at 1.2 THz is attributed to the highly damped phonon response involving heavy lead and iron cations that provide main contribution to the low-energy phonon density of states. No signs of (incipient) ferroelectricity was detected.

The results of the experiment formed the basis of the article entitled «Crucial influence of crystal site disorder on dynamical spectral response in artificial magnetoplumbites» by E.S. Zhukova, A.S. Mikheykin, V.I. Torgashev, A.A. Bush, Yu.I. Yuzyuk, A.E.Sashin, A.S. Prokhorov, M. Dressel, and B.P. Gorshunov *Solid State Sci.* (2016) **62**, 13–21 available from: <http://dx.doi.org/10.1016/j.solidstatesciences.2016.10.012>, as well as the part of PhD thesis of A.S. Mikheykin «Features of the phase states of nickel chromites of copper and cobalt» (in Russian)

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