Hertz-to-infrared electrodynamics of single-crystalline barium-lead hexaferrite $Ba_{1-x}Pb_xFe_{12}O_{19}$

L Alyabyeva[1], A Ahmed[1,2], D Vinnik[3], M Savinov[4], P Lunkenheimer[5], B Gorshunov[1]

[1]Laboratory of Terahertz Spectroscopy, Center for Photonics and 2D Materials, Moscow Institute of Physics and Technology, Institutskii lane 9, Dolgoprudny, 141700, Russia
[2]Department of Physics, Faculty of Science, Sohag University, Sohag University St, Sohag, Egypt
[3]South Ural State University, 454080 Chelyabinsk, Russia
[4]Institute of Physics of the Czech Academy of Sciences, Praha 8, 18221, Czech Republic
[5]Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86159 Augsburg, Germany

E-mail: aliabeva.ln@mipt.ru

Abstract. Broadband electrodynamic response of single-crystalline lead-substituted barium hexaferrite $Ba_{1-x}Pb_xFe_{12}O_{19}$ is studied at temperatures from 5 to 300 K in the range from 1 Hz to 240 THz that includes radio, sub-terahertz, terahertz and infrared frequencies and altogether spans over 14 frequency decades. Discovered phenomena include relaxational radio-frequency dynamics of domains and domain walls, temperature-unstable terahertz excitations connected with electric dipoles induced by off-center displacements in the *ab*-plane of the lead ions, narrow terahertz excitations associated with electronic transitions between the fine-structure components of the Fe^{2+}ground state, dielectric gigahertz resonances presumably of magneto-electric origin and polar lattice vibrations.

1. Introduction

Tunable terahertz optoelectronics is at the front-edge of modern communication technologies. These include high-speed broadband telecommunications of next-generation standards, safe bio-scanning, ultra-high-speed information transfer and many others. Rapid development of the field produces ever increasing demand in new functional materials with known characteristics.

Hexaferrites, in view of their outstanding electromagnetic properties, are appeal for various practical applications. Since their discovery in the middle of the last century, these compounds were successfully implemented in most of modern magnetic devices. At the same time, their promising dielectric properties were undeservedly pushed to the background. Recent research showed great prospects of utilization of hexaferrites in 5G devices and other sub-terahertz/terahertz products.

Here, we report on the first detailed study of ultra-broad-band electrodynamic response of single-crystalline lead-substituted barium hexaferrite $Ba_{1-x}Pb_xFe_{12}O_{19}$ in a range from 1 Hz to 240 THz, that includes radio, sub-terahertz, terahertz and infrared frequencies and altogether

spans over 14 decades. The experiments were performed in a configuration when the vector of electric field E is normal to the main crystallographic axis c, i.e. $E \perp c$.

2. Results and discussion

We discover a rich set of excitations (Fig. 1) and explain their origin from the microscopic standpoint. These are magnetic domains and domain walls responses seen as radio-frequency relaxations with temperature activated characteristic times, gigahertz resonance presumably of magneto-electric origin, unusual terahertz ferroelectric-like "soft-mode" (Fig. 2) with non-Cochran and non-Curie-Weiss temperature behaviors, and electronic transitions within the fine-structured Fe^{2+} ground state.

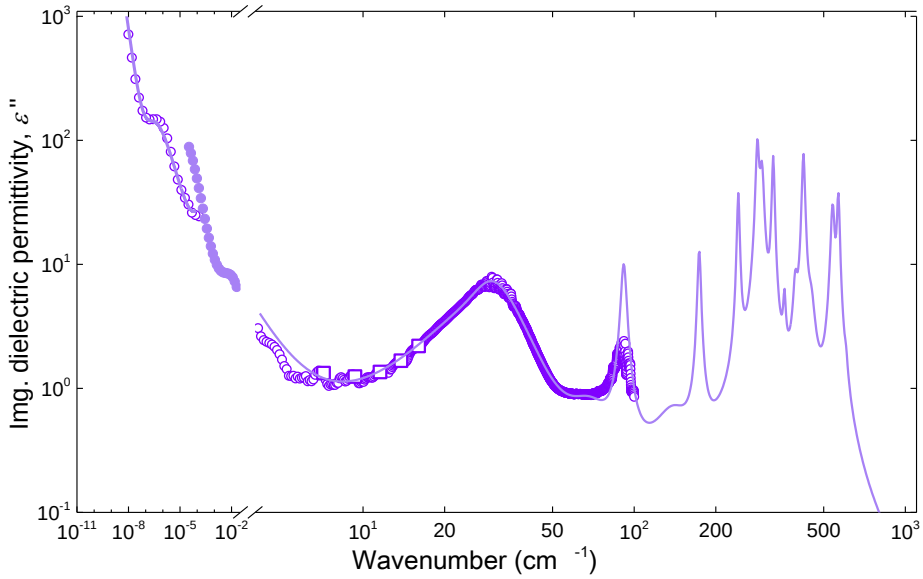

Fig. 1 Imaginary part of dielectric permittivity in $E \perp c$ polarization in single-crystalline $Ba_{1-x}Pb_xFe_{12}O_{19}$, x=0.2. T=300 K. dots are experimental data. Solid circles correspond to reflectometric setup. Open squares are manual calculation by interferometric maxima in spectra of complex transmissivity. IR spectrum obtained by modeling spectra of reflectivity.

Low-frequency experiments were performed using impedance spectroscopy (for frequencies from 1 Hz up to 4 MHz) and coaxial reflectometric setup (frequencies from 4 MHz to 300 MHz). Here, four relaxation processes were detected. Variation of setups, contact materials, thicknesses of the samples allowed us to assign two of the observed relaxations to extrinsic (contact) effects. The other two are, indeed, a manifestation of the intrinsic physics of the lead-substituted hexaferrites. The activation energies of these two intrinsic effects are of 18 and 43 meV, the values typical for dynamic response of domains and domain walls.

Terahertz response, measured in the range 300 GHz - 3 THz with the time-domain terahertz spectroscopy and BWO-spectroscopy techniques, is dominated by a strong excitation that red-shifts with cooling (the "soft mode'). The presence of the soft mode in the spectra was an unexpected finding for the $E \perp c$ polarization. In hexaferrites, soft polar A_{2u} phonon active in the $E||c$ polarization was reported in [1] and in [2,3]. At the same time, to the best of our knowledge, no traces of the soft modes in the $E \perp c$ configuration in M-hexaferrites were reported so far. We attribute the origin of the soft mode to the dynamics of the dipole moments induced by the off-center displacements of the lead ion within the *ab*-plane. Corresponding liberator-rotetor model was introduced in [4]. The detected changes of the soft-mode behavior

caused by variation of lead content might indicate vicinity of the compounds to the quantum critical point. The quantum critical behavior in pure hexaferrite $BaFe_{12}O_{19}$ was shown to be suppressed by quantum fluctuations [5], but can be stabilized by inducing the negative chemical pressure [6] generated, e.g., by substitution of barium with lead. Indeed, according to the literature data [7] and our results, increase of lead content in the studied compounds leads to enlargement of the *a* lattice-parameter thus producing negative chemical pressure within the *ab*-plane.

On the right shoulder of the soft-mode, the weak absorption lines manifest themselves at low temperatures (Fig. 2). The lines were attributed to the electronic transitions within the fine-structured ground state ^5E of tetrahedrally coordinated Fe^{2+} (d^6) [2,8].

Infrared resonances observed at frequencies 3 - 240 THz with FTIR spectroscopy were attributed to the E_{1u} polar phonons.

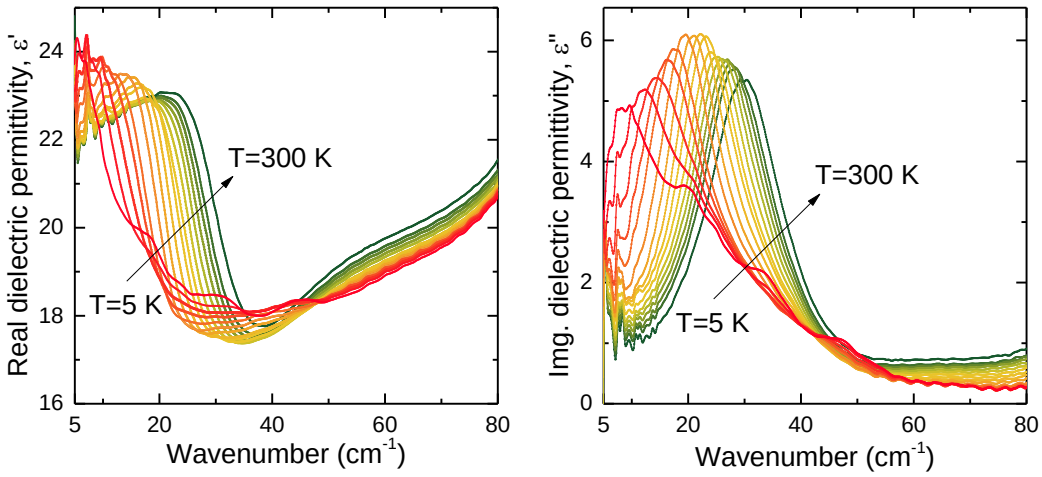

Fig. 2. Terahertz spectra of real and imaginary parts of dielectric permittivity (polarization $E \perp c$) of single-crystalline lead-substituted barium hexaferrite $Ba_{0.9}Pb_{0.1}Fe_{12}O_{19}$. The terahertz soft mode is clearly seen.

Detailed information on physical phenomena that govern the broad-band electrodynamics of the $Ba_{1-x}Pb_xFe_{12}O_{19}$ hexaferrite provides researchers with information that is vital for device-engineering. The discovered tunability of the terahertz spectral response of the compounds paves the way for designing tunable sub-terahertz/terahertz band-filters, phase-shifters, shielding coatings, etc.

Acknowledgements
This study was financially supported by Russian Science Foundation, grant 19-72-00055. LNA acknowledges support of system of President's scholarships for young researchers (SP-777.2021.5).

References

[1] Mikheykin A S *et al* 2014 Lattice anharmonicity and polar soft mode in ferrimagnetic M-type hexaferrite BaFe12O19 single crystal *Eur. Phys. J. B* **87** 232. https://doi.org/10.1140/epjb/e2014-50329-4
[2] Alyabyeva L N *et al* 2019 Influence of chemical substitution on broadband dielectric response of barium-lead M-type hexaferrite *New J. Phys.* **21** 063016. https://doi.org/10.1088/1367-2630/ab2476
[3] Alyabyeva L *et al* 2018 Terahertz-infrared electrodynamics of lead-doped single crystalline BaI-xPbxFel2019 M-type hexagonal ferrite *Proceedings of the 43rd International Conference on*

Infrared, Millimeter, and Terahertz Waves, IRMMW-THz vol 2018-Septe (Nagoya: IEEE catalog o. CFP 181MM-ART) pp 1–2. https://doi.org/10.1109/IRMMW-THz.2018.8510258

[4] Nakajima Y and Naya S 1994 Orientational phase transition and dynamic susceptibility of hindered-rotating dipolar system—a librator-rotator model. *J. Phys. Soc. Jpn* **63**, 904. https://doi.org/10.1143/JPSJ.63.904

[5] Rowley S E *et al* 2016 Uniaxial ferroelectric quantum criticality in multiferroic hexaferrites BaFe12O19 and SrFe12O19 *Sci. Rep.* **6** 25724. https://doi.org/10.1038/srep25724

[6] Kumar K and Pandey D 2017 Quantum phase transitions in Ba(1−x)CaxFe12O19 (0≤x≤0.10) *Phys. Rev. B* **96** 024102. https://doi.org/10.1103/PhysRevB.96.024102

[7] Pollert E, Hejtmaneck J, Doumerc J P, Claverie J, and Hagenmuller P 1983 A photoelectrochemical study of the hexagonal ferrite PbFe12O19 *J. Phys. Chem. Solids* **44(4)**, 273. https://doi.org/10.1016/0022-3697(83)90095-1

[8] Ahmed A *et al* 2020 Terahertz-infrared electrodynamics of single-crystalline Ba0.2Pb0.8Al1.2Fe10.8O19 M-type hexaferrite *J. Alloy Compd* **836** 155462. https://doi.org/10.1016/j.jallcom.2020.155462