Terahertz spectroscopy of lead-substituted barium hexaferrites Ba$_{1-x}$Pb$_x$Fe$_{12}$O$_{19}$

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Abstract. Using methods of terahertz time-domain spectroscopy dielectric response of ceramic barium hexaferrites substituted with lead (Ba$_{1-x}$Pb$_x$Fe$_{12}$O$_{19}$, $x = 0.00 - 0.30$) was studied in the frequency range of 3 - 110 cm$^{-1}$ and at temperatures from 5 to 300 K. Obtained spectra are presented by a rich set of lines of different nature, i.e. excitations associated with electronic transitions within the fine-structure components of Fe$^{2+}$ ions, $A_{2u}$ soft optical phonon, and ferroelectric-like soft mode. The frequency of the soft mode reveals power-law temperature variation $\nu_{SM} \sim (T - T_c)^{0.25}$, which indicates a potential phase transition at $T_c$. Analysis shows that $T_c$ approaches zero for the concentrations $x = 0.20 - 0.25$.

1. Introduction

Hexaferrites are actively used in modern electronic device engineering and occupy the bulk of the world magnetic materials market. They are widely used in both civil and military engineering as permanent magnets, memory devices, components in devices operating at microwave/GHz frequencies, absorbing coatings and highly sensitive magnetic field sensors. Having electromagnetic properties that are highly sensitive to chemical substitutions, hexaferrites provide vast opportunities for development of tunable devices functioning in terahertz range. However, lack of information on corresponding electrodynamic characteristics significantly hinders the potential of such development. Barium hexaferrites are non-transparent materials in the visible part of the spectrum. They have a layered structure with the following lattice constants: $a = 5.88$ Å, $c = 23.18$ Å (space group symmetry P6$_3$/mmc). Fe$^{3+}$ cations occupy five different positions in the crystal lattice: three in the octahedra (2a, 4f$_3$, 12k), one in the tetrahedra (4f$_1$), and one in the trigonal bipyramids (2b). Ba$^{2+}$ cations are located in the oxygen anticoctahedrons (2d) [1]. Here, we report on the dynamics and lead concentration dependence of the soft mode that was discovered in single crystalline compounds of lead-substituted barium hexaferrite in [2]. We believe that our findings will be useful for designing tunable devices of terahertz electronics such as antennas, circulators, phase-shifters, etc. Also, a potential vicinity of the system to the quantum phase transition is expected to be important for a wide range of advanced material applications including, for example, electro-caloric refrigerators, quantum memory devices, and cryogenic electronic switches.
2. Methods
Ceramic samples of lead-substituted barium hexaferrite \( \text{Ba}_{1-x}\text{Pb}_x\text{Fe}_{12}\text{O}_{19} \) (\( x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 \)) were prepared in form of plane-parallel tablets and polished using MultiPrep Precision Polishing System to the thickness of 200 \( \mu \)m. Obtained samples were studied using terahertz time-domain and continuous-wave spectroscopy techniques. Measurements in the frequency range of 6 - 110 \( \text{cm}^{-1} \) at temperatures of 5 - 300 K were conducted with the use of two time-domain spectrometer “Menlo Systems Tera K15” and “Teraview TPS Spectra 3000”. Lower-frequency spectra at 3 - 8.5 \( \text{cm}^{-1} \) were acquired with the use of continuous-wave spectrometer based on backward-wave oscillators as sources of tunable coherent radiation. Spectra of complex dielectric permittivity were calculated from complex transmission spectra using standard Fresnel equations. To describe the absorption lines detected in the spectra, the model of independent Lorentzians was applied.

3. Results
In the obtained spectra of complex dielectric permittivity, numerous absorption lines of different nature were observed, among those are: excitations associated with electronic transitions within fine-structure components of Fe\(^{2+}\) ions [3] and soft optical phonon [1]. Moreover, we discovered a temperature-unstable excitation which is absent in non-substituted compounds [2] (Figures 1 and 2).

![Figure 1. 2D presentation of spectra of imaginary part of the dielectric permittivity of ceramic barium hexaferrite substituted with lead \( \text{Ba}_{0.70}\text{Pb}_{0.30}\text{Fe}_{12}\text{O}_{19} \), measured in the range 5-300 K.](image)

![Figure 2. Terahertz spectra of imaginary part of the dielectric permittivity of lead-substituted ceramic barium hexaferrite \( \text{Ba}_{0.70}\text{Pb}_{0.30}\text{Fe}_{12}\text{O}_{19} \).](image)

Due to strong overlap of the discovered absorption bands, accurate determination of their dielectric strengths and dampings was hampered. Nevertheless, temperature dependences of the resonance frequencies were obtained with a good accuracy. The frequency of the ferroelectric-like “soft mode” varies from \( \sim 30 \text{ cm}^{-1} \) at \( T = 300 \text{ K} \) to \( \sim 8 \text{ cm}^{-1} \) at \( T = 5 \text{ K} \). Temperature dependence of the mode frequency cannot be described by Cochran expression used to model temperature behavior of soft mode frequency in “classical” displacive ferroelectrics, \( \nu_{\text{SM}} \sim (T - T_c)^{0.5} \), or by the expression \( \nu_{\text{SM}} \sim (T - T_c) \) used to model the temperature variation of soft relaxations in order-disorder ferroelectrics, but follows a power-law dependence \( \nu_{\text{SM}} \sim (T - T_c)^{0.25} \) (Figure 3). Such temperature dependence of the resonance frequency indicates a potential vicinity of the system to the phase transition when the temperature reaches values close to \( T_c \). Based on the best fit parameters we
find that $T_c$ depends on the concentration of lead and approaches $T_c = 0$ K for the concentrations $x(\text{Pb}) = 0.20 - 0.25$ indicating possible quantum phase transition.

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