Optical properties of lead germanate $Pb_5Ge_3O_{11}$ in terahertz range

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Abstract. We measured ordinary and extraordinary refractive index and absorption of ferroelectric lead germanate in the range of 0.1–1.3 THz by the method of terahertz time-domain spectroscopy. We studied soft mode behaviour with the rise of temperature by fitting imaginary part of the complex dielectric permittivity with three Lorentz oscillators. We found that high birefringence and dichroism of lead germanate or its analogues can be used for manufacturing of effective terahertz polarizing filters.

1. Introduction

Lead germanate $Pb_5Ge_3O_{11}$ (PGO) is a uniaxial ferroelectric which crystalline structure belongs to P3 space group at room temperature. This crystal is one of the few ferroelectrics that exhibit birefringence and optical activity at the same time [1]. It demonstrates structural phase transition to non-polar state which crystalline structure belongs to $P\bar{6}$ space group at the critical temperature of $T_c \approx 446$ K. Linear and nonlinear optical properties of lead germanate and their dependence on the temperature are well studied at the visible wavelengths [2–4].

Behaviour of PGO optical modes above and below the phase transition point was also studied in the terahertz (THz) frequency range by the methods of Raman scattering spectroscopy [5,6] and spectroscopy based on backward wave oscillators [7]. It was determined that lead germanate is a displacement type ferroelectric at the temperatures far from the phase transition point, i.e. its polar axis is characterized by the presence of phonon soft mode. Its frequency f_0 is defined by the formula $f_0^2 \sim \frac{|T - T_c|}{T_c}$, which equals ~38 cm^{-1} at the room temperature. Complex dielectric permittivity $\tilde{\varepsilon}(\omega)$ can be well approximated by the model of one Lorentz oscillator $\tilde{\varepsilon}(f) = \frac{S}{f_0^2 - f^2 + if\gamma}$, where S – oscillator strength, f – frequency, γ – damping constant [7].

It is obvious that application of nonlinear optical medium for generation, detection and control of terahertz radiation requires knowledge of its optical properties at laser radiation wavelength as well as at terahertz frequencies. This work studies optical properties of lead germanate single crystals in the terahertz range.

2. Experimental setup

The samples under study were cut as plane-parallel plates with the thickness of ~250 μm from single crystals of lead germanate grown from solution-melt by the Czochralski process. The plates were cut to contain optical axis in the plane of the sample. The measurements were made by terahertz time-domain spectrometer. It measured signal proportional to the amplitude of terahertz electric field. Time-domain scan allowed measurement of terahertz pulses; Fourier transform allowed obtaining its spectrum. Lead germanate crystal has significant anisotropy – dichroism and birefringence – in the terahertz range. Due to this peculiarity it was important to control if two orthogonal components of electric field of terahertz pulses were detected after passing through the studied crystal. Owing to the fact that the terahertz pulses were observed in the time-domain it was possible to discern and reduce parasitic polarization component by carefully adjusting polarization optics of the spectroscopy system.

Typical measurement included scanning of two terahertz pulses – signal with the sample under study and reference without the sample. To allow for continuous series of measurements of signal and reference pulses at different temperatures we manufactured a symmetrical sample holder with two identical holes. One of the holes stayed free as the other one held the sample. The holes interchangeably were subjected to the terahertz radiation by a motorized translation stage. We then calculated the sample properties: refractive index, absorption, complex dielectric permittivity and thickness.

3. Results and discussion

The results of calculations of optical properties – refractive index and absorption – of lead germanate are shown on the **Figure 1** and **Figure 2**. Subscripts indicate material properties when polarization of terahertz field is perpendicular (*o*, ordinary) and parallel (*e*, extraordinary) to the *z* optical axis of the crystal. Several phonon modes for absorption α_o can be seen on the **Figure 1**. Positions of their maximum are in accordance with the frequencies of E modes previously measured by Raman scattering spectroscopy (see Table 4 in [6]): 0.933 THz (31.1 cm^{-1}), 1.11 THz (37 cm^{-1}). Phonon modes of higher frequencies (1.332 THz, 1.419 THz, 1.554 THz etc.) were not observed in our experiment directly. However their left wing increased average absorption in the frequency range under study. As we approached the phase transition temperature two phonon lines merged together, made up a shoulder and completely disappeared in paraelectric state. However, several phonon modes with higher frequencies didn't move and defined the level of absorption in the studied range. Refractive index n_o didn't change a lot in the range of 4.4–4.7 at the frequencies up to 0.8 THz as the temperature increased.

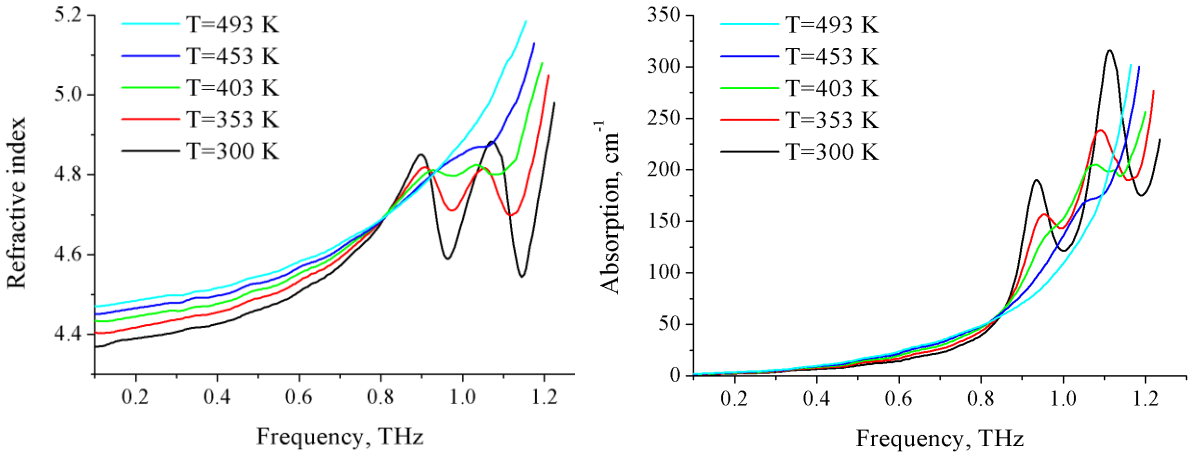

Figure 1. Refractive index n_o (left) and absorption α_o (right) of lead germanate at different temperatures

Figure 2 shows spectral dependence of extraordinary refractive index n_e and absorption α_e. It can be seen that the properties greatly depend on the temperature which can be explained by the softening of a particular phonon mode. PGO as a displacement type ferroelectric is characterized by a phonon mode which frequency decreases when approaching critical temperature T_c.

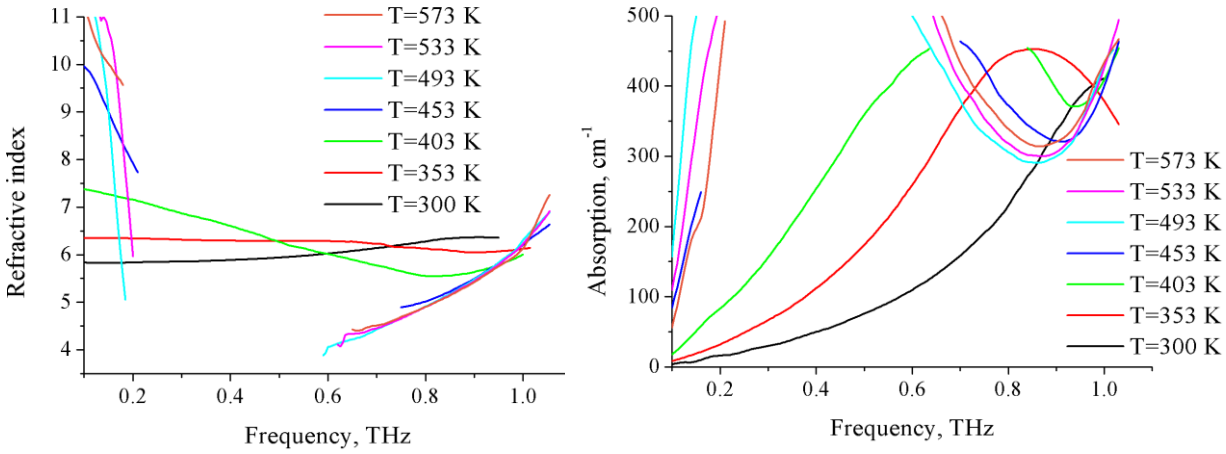

Figure 2. Refractive index n_e (left) and absorption α_e (right) of lead germanate at different temperatures.

In order to study characteristics of the soft mode with the change of the temperature we calculated complex dielectric permittivity $\tilde{\varepsilon}_e = \varepsilon_e' + i\varepsilon_e''$ from the complex refractive index $\tilde{n}_e = n_e + i\frac{\alpha_e c}{4\pi f}$, where c is the speed of light. Its imaginary component ε_e'' was fit by a sum of three Lorentz oscillators. The frequency of the first one was zero, the second oscillator represented the soft mode, and the frequency of the third oscillator was fixed at 1.14 THz. The frequency of the third peak was taken from the results of Raman scattering spectroscopy (see Table 3 in [6]). **Figure 3** demonstrates good agreement between the experimental and modelling results at the temperature of 423 K.

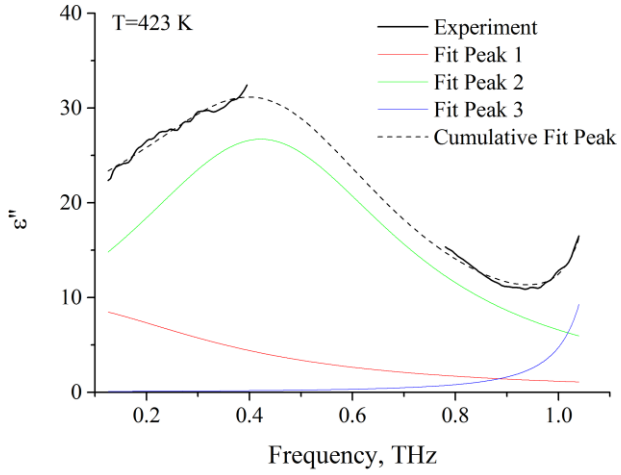

Figure 3. Imaginary part of complex dielectric permittivity ε_e'' at the temperature of 423 K. Experimental results – solid line, approximation by three Lorentz oscillators – dashed line.

Experimental and modelled spectra of imaginary part of complex dielectric permittivity ε_e'' of lead germanate at different temperatures are depicted on **Figure 4**. Behaviour of the squared frequency of the softening phonon mode with the rise of the temperature is shown on the right **Figure 4**. As it was noted in the introduction squared frequency should be proportional to the difference $T–T_c$ for displacement type ferroelectrics. Dashed line on the right **Figure 4** demonstrates this dependence. It can be seen that in the vicinity of the phase transition the frequency of the soft phonon mode does not turn to zero, therefore the model of displacement type semiconductor doesn't describe its behaviour well enough.

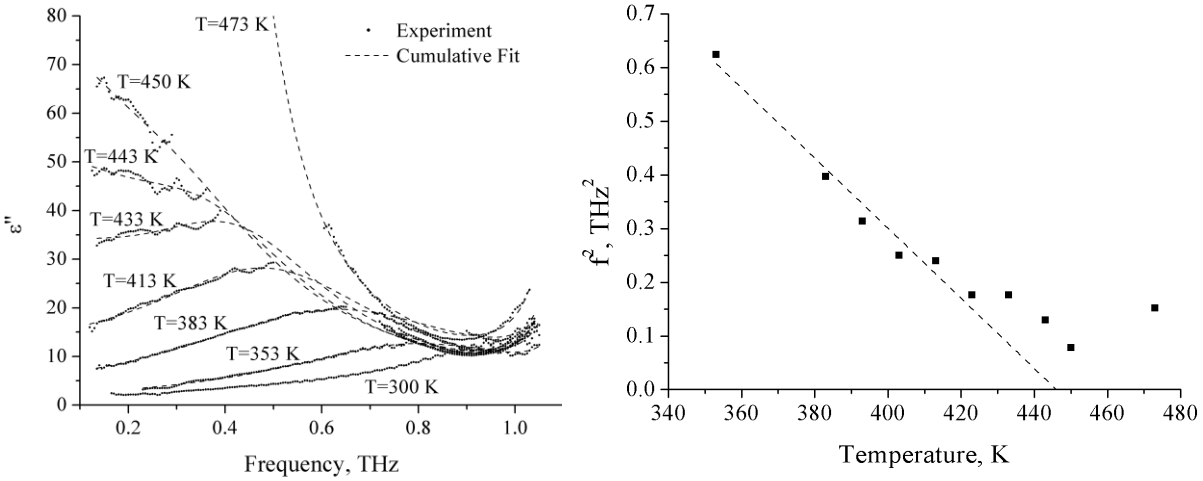

Figure 4. Experimental (solid line) and modelled (dashed line) spectra of imaginary part of complex dielectric permittivity ε_e'' of lead germanate at different temperatures (left). Behaviour of the squared frequency of the soft mode with the rise of the temperature (right). Experimental results – square marks, soft phonon mode model – dashed line.

The results depicted on the **Figure 1** and **Figure 2** show that the lead germanate crystal is highly birefringent and dichroic in the lower terahertz frequency range. For example, at the room temperature at the frequency of 0.5 THz the difference between refractive indices $n_e - n_o$ equals ~1.48 and absorption equals α_e=75 cm^{-1} and α_o=10 cm^{-1}. If the temperature rises to ~400 K absorption α_e gets higher than 400 cm^{-1} in the spectral range of 0.5–0.9 THz, absorption α_o changes by no more than 10 cm^{-1} at the same time. Lead germanate demonstrates that absorption for polarization where the polar mode is active is much higher than the absorption for polarization where the polar mode is not active. Thus lead germanate or its analogues can be used as effective polarizing filters of terahertz radiation. To make sure that the filter doesn't have sharp spectral peculiarities one should choose ferroelectric with a wide central polar mode, or order-disorder type ferroelectric, or ferroelectric with overdamped soft mode.

4. Conclusion

We investigated optical properties of lead germanate crystal in the terahertz range of 0.1–1.2 THz. Both ordinary and extraordinary refractive indices and absorption were measured. It was determined that PGO has significant birefringence and dichroism. High dichroism and its temperature behaviour may become the basis of creation of terahertz polarizes with record specifications.

Acknowledgments

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