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Temperature dispersions of refractive indices and absorption coefficients of mercury thiogallate crystals in the terahertz frequency range

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THz absorption and refraction spectra of $HgGa_2S_4$ crystals of various compositions in the temperature range of 300−400 K have been studied, and a change in refractive indices for crystals depending on their stoichiometry has been found. For non-stoichiometric and stoichiometric samples, $\Delta n/\Delta T$ varies more than twice from $1.3 \cdot 10^{-4}$ to $3.1 \cdot 10^{-4}\,K^{-1}$. The absorption coefficient of the studied samples in the range 0.5−1.2 THz was less than $20\,cm^{-1}$. The change in the refractive index of $HgGa_2S_4$ in the range 0.5−1.2 THz was 3.42−3.55 at $T = 300$ K.

Keywords: mercury thiogallate, terahertz spectrum, stoichiometry.

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Introduction

Interest in obtaining THz radiation is associated with the development of various applications, including the development of the smart city concept due to increased urbanization, non-destructive testing in agriculture, non-invasive imaging methods in medicine, and the development of high-speed communications [1]. One of the ways of obtaining THz radiation is to implement the conditions for nonlinear optical transformations in crystals when pumped by laser radiation. $HgGa_2S_4$ as an effective nonlinear optical material of the type $A^{II}-B_2^{III}-C_4^{VI}$ has a chalcopyrite structure and belongs to the $\bar{4}$ group. $HgGa_2S_4$ crystals are transparent in the mid-IR range and have a 1.8 times larger nonlinear coefficient d_{36} than the $AgGaS_2$ [2]. Various nonlinear optical devices based on difference frequency generation, optical parametric amplification, implemented on the basis of $HgGa_2S_4$ crystals, effective generation of high power radiation in the mid-IR range with continuous wavelength tuning in the range 4−12 μm [3,4].

Currently, intensive work is underway to study the generation modes of THz radiation on nonlinear optical crystals belonging to the chalcopyrite group [5]. In addition, an important area of research is feedback on THz properties and improving the technology for their growth. Broadband THz generation is implemented in many important nonlinear optical materials, for example, in $ZnGeP_2$, $AgGeSe_2$, through the processes of difference frequency generation and optical pulse rectification [6,7]. However, $HgGa_2S_4$ as one of the outstanding crystals for pumping 1 μm by laser radiation has not been studied in the THz frequency range. The potential use of this material in the THz frequency range is associated with the characteristics and analysis of the optical properties of the material in this range to assess the temperature adjustment of the matching conditions, assessing the temperature mismatch in the case of interaction of a powerful radiation source.

Previously, the authors [8] showed that the presence of deviations from stoichiometry in the composition of nonlinear optical crystals leads to differences in the temperature dependence of the refraction indices of interacting waves in the THz range. This work presents temperature-dependent studies of the refraction index and absorption in the THz range of $HgGa_2S_4$ crystals of various chemical compositions.

Characteristics of objects and research methods

Mercury thiogalate crystals $HgGa_2S_4$ — nonlinear optical crystals for converting laser radiation in the mid-IR range. Mercury thiohalate crystals grown in the Laboratory of Advanced Technologies of Kuban State University using the Bridgman−Stockbarger method were selected as objects of study. Crystal samples for research are represented by a yellow crystal of stoichiometric composition with bulk and surface luminescence centers at wavelengths of 580 and 550 nm, respectively, and an orange crystal of non-stoichiometric composition with an excess of Ga_2S_3 with an additional absorption band at 475 nm. The thickness of sample № 1 was 2.33 mm, the thickness of sample № 2 — 3.47 mm.

Measurements of crystal spectra in the THz frequency range were carried out using a Menlo Tera K15 Kit spectrograph. Heating of the sample and maintaining the set temperature according to the signal from a chromel-alumel thermocouple was provided by an Omron E5CK controller. The samples were heated in the temperature range 300−400 K to prevent high-temperature oxidation of their surface and distortion of characteristics. To measure refraction and absorption spectra using time-resolved spectroscopy, a fast Fourier transform was used and the

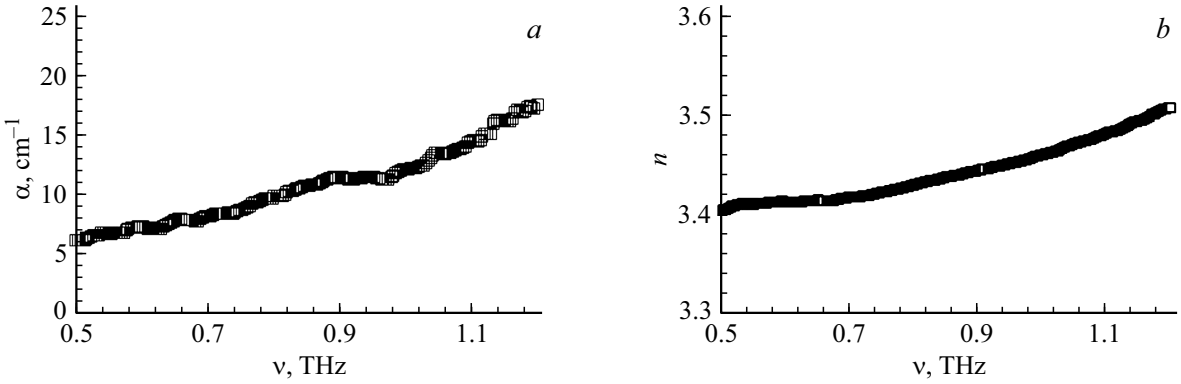

Figure 1. Absorption (a) and refraction (b) spectra of sample № 1 at $T = 300$ K.

reference signal was correlated with the signal recorded after passing through the crystal samples.

Experimental results and discussion

The experimental data obtained in the form of absorption and refraction spectra of the sample № 1 are presented in Fig. 1. The signal recording range was 0.5–1.2 THz. It can be seen (Fig. 1, *a*) that at a frequency of 1.2 THz the value of the absorption coefficient for the $HgGa_2S_4$ sample of nonstoichiometric composition is 18 cm^{-1}. This value of the absorption coefficient is less than for lithium niobate crystals of congruous and stoichiometric composition; for comparison, the value of the absorption coefficient at a frequency of 1.2 THz for a lithium niobate crystal is 36 cm^{-1} at $T = 300$ K [9], is comparable to the value of 9.9 cm^{-1} of the absorption coefficient of ZnTe crystals in the range 1–2 THz [10], but exceeds the value of 3.25 cm^{-1} of the absorption coefficient of GaSe crystals at a frequency of 1.04 THz [11]. The refraction spectrum of the crystal (Fig. 1, *b*), measured at $T = 300$ K, shows a change in the refractive index in the range 0.5–1.2 THz from the value 3.41 to a value of 3.52. A further change in the temperature of the samples leads to a transformation of the absorption and refraction spectra (Fig. 2, *a*). In the case of absorption spectra, a change in temperature from 300 to 380 K does not change the value of the absorption coefficient for frequencies 0.5–0.7 THz, but in the region of high-frequency oscillations with a change in temperature there is an increase in the absorption coefficient from 13 to 14 cm^{-1} (1.1 THz). For refraction index values, a temperature change is observed throughout the entire frequency range under study (Fig. 2, *a*). In Fig. 2, *a* the experimental values of the refraction indices are approximated by lines. From the approximating expression, the temperature values of the change in the refractive index for the $HgGa_2S_4$ crystal of nonstoichiometric composition were found, which amounted to $0.13 \cdot 10^{-3}$ K^{-1} in the entire frequency range.

Figure 2, *b* shows, respectively, the temperature dependences of the refraction indices of the $HgGa_2S_4$ crystal of stoichiometric composition (sample № 2). The absorption coefficient at low frequencies is practically independent of temperature. The refraction index measured at different frequencies in the 0.5–1.2 THz range shows the same temperature dependence; the temperature dependence of the refraction index of the sample № 2, determined by linear approximation of the values, was $3.1 \cdot 10^{-4}$ K^{-1}. Equation of the approximating line for refraction index values at different temperatures at frequency ν:

$$n(\nu) = \Delta n/\Delta T T + a, \tag{1}$$

where ν — frequency in THz, T — temperature in K, $\Delta n/\Delta T$ — temperature coefficient of the refraction index of the sample, a — refraction index value at 0 K.

Equation of the fitting line for absorption coefficient values:

$$\alpha(\nu) = \Delta\alpha/\Delta T T + b, \tag{2}$$

where $\Delta\alpha/\Delta T$ — temperature absorption coefficient of the sample, b — absorption coefficient value at 0 K.

Figure 3, *a, b* shows the spectra of temperature changes in the absorption and refractive coefficients for samples 1 and 2, measured at frequencies 0.7 THz (solid line) and 1.1 THz (dashed line). The difference in behavior between the absorption spectra for the studied samples of stoichiometric and nonstoichiometric composition in the temperature range 300–400 K is characterized by the same slope with temperature changes. As the temperature increases, the difference between the absorption coefficients of two crystal samples tends to zero at the same rate, i.e., for the entire THz spectrum (Fig. 3, *a*). When analyzing the temperature behavior of the difference in refraction indices, a different rate of decrease in differences between samples of stoichiometric and nonstoichiometric composition is found (Fig. 3, *b*): for the high-frequency part of the spectrum (1.1 THz), the difference between the coefficients decreases and at a temperature of 360 K is zero. With a further increase in temperature, the difference changes sign and a sample of stoichiometric composition (sample № 2) now has a higher refraction index at a frequency of 1.1 THz. For the temperature dependence in the low-frequency part of the refractive spectrum (0.7 THz), changes in refraction

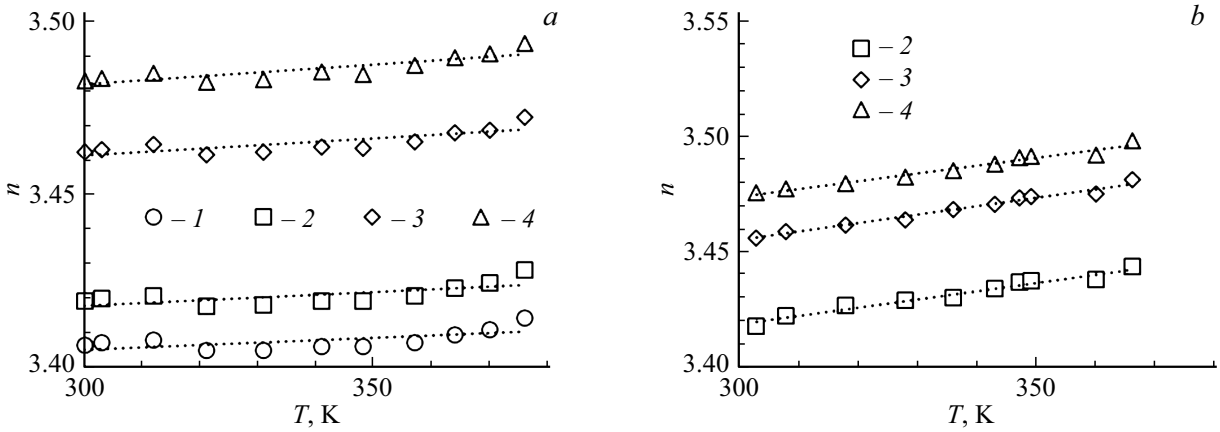

Figure 2. Dependences of changes in the refraction index of samples № 1 (*a*) and № 2 (*b*) at frequencies $\nu = 0.5$ (*1*), 0.7 (*2*), 1.0 (*3*), 1.1 THz (*4*) on temperature.

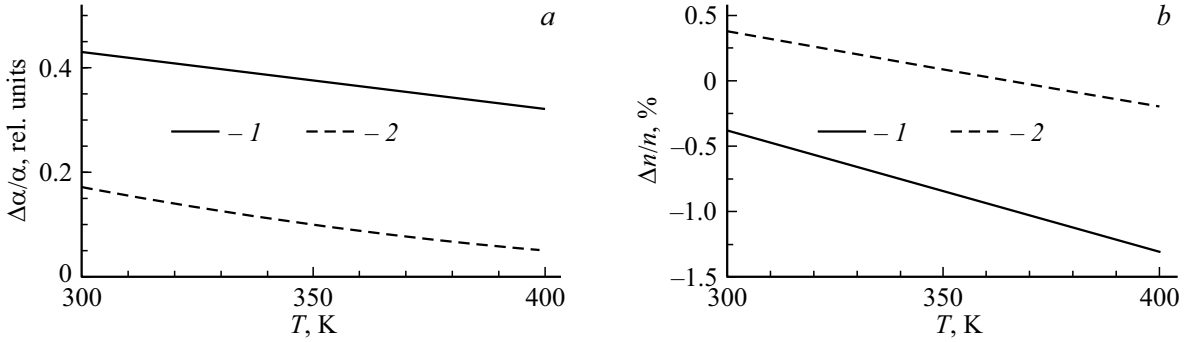

Figure 3. Dependences of changes in absorption coefficient (*a*) and refraction index (*b*) of sample 1 relative to sample 2 at frequencies 0.7 (*1* /) and 1.1 THz (*2*) on temperature.

indices show an increase in the difference with increasing temperature (Fig. 3, *b*).

The obtained values of refraction indices in the frequency range 0.5–1.2 THz show a strong temperature dependence for samples of stoichiometric composition (more than 2 times higher temperature coefficient) than for samples grown with an excess of Ga_2S_3 of nonstoichiometric composition. This difference in the temperature behavior of the refraction index can be explained by a more stable nonstoichiometric phase (closer to the congruous melting point). Besides, this difference in the temperature dependence of the refraction index contributes, on the one hand, to a wider range of temperature adjustment for interacting waves; on the other hand, it requires taking into account thermo-optical distortions in the case of conversion of high-power laser pumping sources.

Conclusion

Studies have been carried out on the THz absorption and refractive spectra of mercury thiogalate crystals of various compositions in the temperature range 300–400 K, and a change in the refraction indices of the crystals depending on their stoichiometry has been discovered. For orange (nonstoichiometric) and stoichiometric samples, $\Delta n/\Delta T$ changes more than twice — from $3.1 \cdot 10^{-4}$ to $1.3 \cdot 10^{-4}\,\mathrm{K}^{-1}$. The absorption coefficient of the studied mercury thiogalate samples in the 0.5–1.2 THz range was less than $20\,\mathrm{cm}^{-1}$. The change in the refraction index of the studied mercury thiogalate samples in the range 0.5–1.2 THz was 3.42–3.55 at $T = 300$ K.

The obtained result contributes to a wide range of temperature adjustment for interacting waves for samples of stoichiometric composition; on the other hand, it requires taking into account thermo-optical distortions in the case of conversion of high-power laser pumping sources.

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Conflict of interest

The authors declare that they have no conflict of interest.

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