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Temperature dependences of terahertz spectra of rutile grown by various methods

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Abstract. The paper presents measurements of the temperature dependence of the refractive index and the absorption coefficient in the THz range for rutile crystals grown by the cold container method. The obtained parameters are compared with the temperature behaviour of lithium niobate crystals, whose matrix allows significant deviations from stoichiometry. The coefficient of the temperature dependence of the refractive index of rutile crystals in the terahertz range is commensurate with that of heavily doped lithium niobate samples and is $3 \cdot 10^{-3}$ K^{-1}.

Keywords: rutile, THz range, cold container method, stoichiometry._

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Температурные зависимости терагерцовых спектров рутила, выращенного различными методами

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Аннотация. В статье приводятся данные измерений температурной зависимости показателя преломления и коэффициента поглощения в ТГц диапазоне для кристаллов рутила, выращенных методом холодного контейнера. Полученные параметры сравниваются с температурным поведением кристаллов ниобата лития, матрица которого допускает значительные отклонения от стехиометрии. Коэффициент температурной зависимости показателя преломления в терагерцовом диапазоне кристаллов рутила соизмерим с аналогичным значением сильно легированных образцов ниобата лития и составляет $3 \cdot 10^{-3}$ K^{-1}.

Ключевые слова: рутил, ТГц диапазон, метод холодного контейнера, стехиометрия.

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Introduction

The development of technologies for producing nonlinear optic materials wield major influence on the advantages of their practical use, the use of devices and components based on them. A promising area of nonlinear optic materials implementation is terahertz devices and technologies. One of the important methods for generating and detecting the THz radiation, along with the frequency up-conversion from the microwave range, is the down conversion using nonlinear optic conversion [1]. Therefore, the question of the effectiveness of such nonlinear optic conversions and the related question of the attenuation of the generated THz radiation in a nonlinear optic material and the temperature dependence of the attenuation is extremely important.

Technologies for the manufacture of gallium nitride, nitride heterostructures, are developing at a tremendous pace, allowing producing more powerful microwave devices that operate at higher temperatures than gallium arsenide [2]. One of the important directions of development of gallium nitride technology is the production and perfection of substrates. In addition to manufacturing substrates directly from gallium nitride, sapphire, which may be an expensive technology, rutile crystals have been also considered. The use of low-cost methods of growing rutile crystals reduces the cost of substrates.

Both of these areas of use of rutile crystals are important in themselves and in their totality. However, the rutile crystal allows significant deviations from stoichiometry, which entails changes in the defective structure and, as a consequence, other physical parameters.

Lithium niobate can also be considered as a nonlinear material with significant deviations from stoichiometry. The measurement of its optical properties, the temperature dependence of optical properties up to the THz range allowed us to conclude about the contribution of the defective structure to the temperature dependence of refractive indices in the THz range, depending on the type and level of its doping [3].

A number of papers are devoted to the research of THz spectra of nonlinear optical materials [4]. The methods used were far-infrared spectroscopy, which allowed us to establish the regularities of the absorption and refraction coefficients in the THz range, but the lens effect did not allow us to achieve unambiguity in the data obtained. Other methods [4] used TDS (time domain sensitive) methods for generating THz radiation by semiconductor antennas after pumping with femtosecond laser pulses. In these works, the temperature dependence of the refractive and absorption coefficients of lithium niobate crystals grown by the traditional Czochralski method is compared with the coactivation of crystals with different amounts of magnesium ions to reduce photorefraction. However, studies of the temperature change of optical properties in the THz range associated with the activation of carriers in the crystal, depending on the method of preparation, have not been conducted. Therefore, in this paper, the THz absorption and refraction spectra of rutile crystals produced by the cold container method are investigated.

Research method

Titanium dioxide crystals of rutile phase were grown at Kuban State University by the cold container method on a Crystal 400 series installation designed for direct high-frequency melting and crystal growth by directional crystallization with a container load capacity of 12 kg of charge. A metal Mg was used for the initial heating. The resulting crystals were fused druses of dark color. Next, rutile plates were cut out of single crystals, oriented along the direction <001>, and polished to optical quality. The grown rutile crystals allowing significant deviations from stoichiometry were compared with lithium niobate crystals produced by Czochralski method with liquid make-up [5] at Kuban State University.

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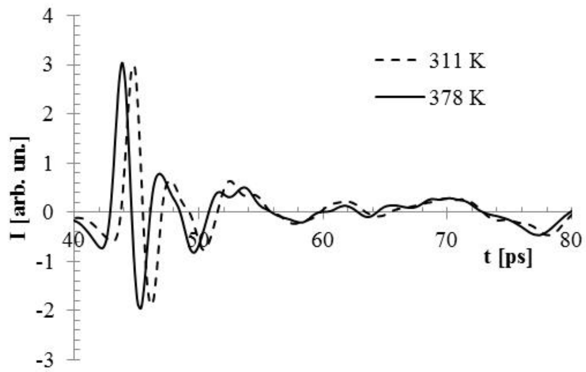

Fig. 1. Laser pulse after passing a rutile crystal at different temperatures

Further, the samples of the grown crystals were placed in a terahertz spectrograph TeraK15Kit with the possibility of changing the temperature of the sample during measurements (Fig. 1).

The spectrograph measurement mode and accumulation time were selected in the range from 10 ms to 100 ms. As a reference signal for measuring the refraction and absorption spectra, a signal recorded through the atmosphere inside the spectrograph was selected. To reduce the influence of water vapor in the atmosphere, the spectrograph space was purged with argon.

Rutile crystal samples obtained by the cold container method and lithium niobate samples obtained by the Czochralski method with liquid make-up were heated using the resistive heating element coupled via the TRM101 controller with a type K thermocouple. The spectra were measured after stabilization of the set sample temperature. Stabilization of the sample temperature was carried out using the built-in PID controller in TRM101 within 1K.

The obtained temperature dependences of the femtosecond laser pulse change after passing the crystal samples are shown in Fig. 1. The figures show that with an increase in temperature, the shape of the pulse is tightened and its amplitude decreases. Further processing of the pulse shape was carried out in the program part of the spectrograph.

Results and Discussion

A typical view of the obtained dependences of the refractive index on frequency and temperature in the THz range is shown in Fig. 2. It can be seen that as the temperature of the crystals under study increases, the refractive index in the THz range increases, and this applies to the entire range of crystals under study in the temperature range of 290–390 K. However, the rate of increase in the refractive index values with increasing temperature turns out to be different compared to lithium niobate crystals, which allows significant deviations from stoichiometry (Figs. 2, 3). The constructed linear trends over the temperature range at arbitrarily selected frequencies, for example, 0.8 THz, 0.9 THz, 1 THz, have different slope coefficients depending on the following:

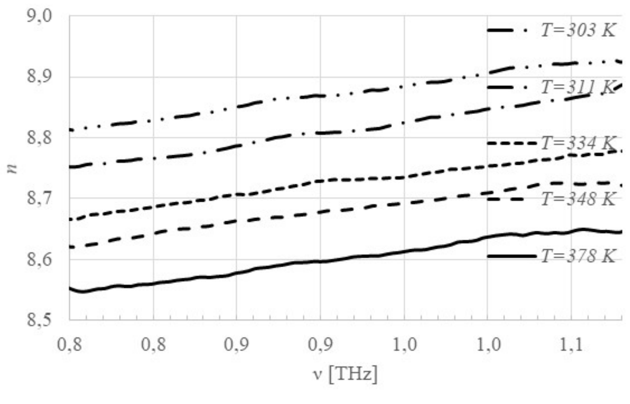

Fig. 2. Spectral dependence of the rutile index grown by the cold container method in the THz range at different temperatures

the type of crystal matrix (rutile or lithium niobate), the type of crystallographic orientation for lithium niobate (X-slice or Z-slice), the type of impurity (more precisely, its crystallographic radius and the degree of distortion of the crystal lattice of lithium niobate with ions Yb^{3+}, Er^{3+}) [6].

Fig. 3 shows the temperature dependences of the refractive index for rutile plates. The birefringence for lithium niobate in the THz range [6] is 1.4, 1.5, which is 21–23% compared to the value of the refractive index for an ordinary wave in this range of 6.44. This value of birefringence in the THz range is almost five times greater in percentage terms of birefringence in the visible range.

Another interesting feature of the refractive indices of a rutile single crystal grown by the cold container method presented in Fig. 3 is a higher sensitivity to temperature changes of $3\cdot10^{-3}$ K^{-1} than for lithium niobate X-section in the THz range, where the temperature coefficient is $0.7\cdot10^{-3}$ K^{-1}. In addition, the temperature dependences of the refractive index of rutile grown by the cold container method shown in Fig. 3 have the same slope at frequencies of 0.8, 0.9, 1 THz, which indicates a monotonic temperature spectral dependence of crystals. Compared with the measured coefficients of the temperature dependence of the refractive spectra of lithium niobate crystals ($3.5\cdot10^{-3}$ K^{-1}) activated by Yb^{3+} and Er^{3+} ions, the ionic radius of which exceeds the radius of the main components of the crystal lattice, the temperature dependence of rutile crystals has a comparable temperature dependence. This dependence may be due to strong stresses in the crystal lattice of rutile, taking into account the inherent deviation of the composition from stoichiometry and the formation of various kinds of defects.

The obtained temperature dependences of refractive indices in the THz range for the studied rutile and lithium niobate crystals grown by the cold container and Czochralski methods with

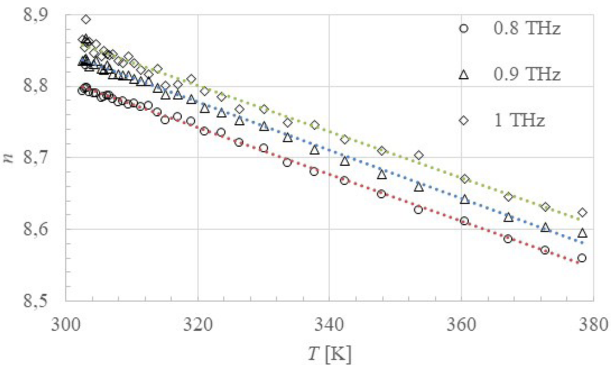

Fig. 3. Temperature dependence of the refractive index of rutile in the THz range grown by the cold container method

liquid make-up are summarized in Table 1. Attention is drawn to the values obtained from the temperature dependence of the refractive index for heavily doped lithium niobate, which are comparable with those for grown rutile.

A similar analysis of the temperature dependence was carried out for the absorption coefficient of the studied samples in the THz range. Fig. 4 shows the temperature dependence of the absorption index in the THz range for the grown rutile crystal.

Table 1

Refractive index values at T = 300 K

Crystal	n	ν, THz	$\Delta n/\Delta T$, $\cdot10^{-3}$ K^{-1}
$LiNbO_3$	4.8	0.9	0.7
Yb,Er:$LiNbO_3$	4.4	0.7	3.5
TiO_2 (rutile)	8.8	0.9	3.0

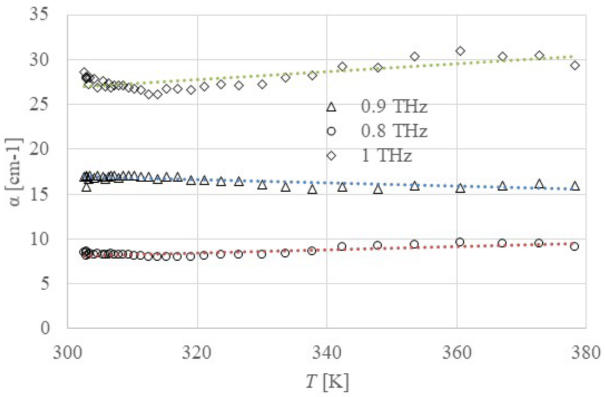

Fig. 4. Temperature dependence of the rutile absorption index in the THz range grown by the cold container method

For grown rutile crystals, there are practically no temperature changes in the absorption spectra in the THz range, the temperature has the strongest effect on the values of the absorption coefficient at a frequency of 1 THz compared to the signal recorded at a frequency of 0.8 THz. A similar dependence of the absorption coefficient is observed for lithium niobate crystals grown by the Czochralski method with liquid make-up. The values of the absorption coefficient in the range of 0.8–1 THz are significant and amount to 7–28 cm^{-1} (Fig. 5).

The measurements of the refractive index spectra made it possible to construct and estimate the temperature conditions for matching interacting waves when working with nonlinear rutile and lithium niobate crystals that allow significant deviations from stoichiometry in the THz range. When pumped by powerful laser sources in the materials used for frequency conversion, the samples are heated. In the case of optical fibers with birefringence [7] to obtain a radiation spectrum in the THz range when interacting waves are matched, temperature relaxation along the direction of propagation of powerful pumping radiation occurs due to the large ratio of the surface area of the waveguide to its volume. The realized frequency shift in this case is 3–4 THz [7]. In the case of crystals, when using high-power pumping radiation to obtain a significant gain in the THz range, it is also necessary to take into account the effect of misalignment due to the heating of the crystal. For the rutile crystal under study, the temperature dependence of the refractive index is $3\cdot10^{-3}$ K^{-1} (greater than, for example, for lithium niobate), which reduces the temperature stability of the radiation received. On the other hand, a large value of the temperature dependence of the refractive index will allow four-wave processes to be carried out for a wider range of THz radiation with temperature adjustment for one pump wavelength. It follows from the results obtained that the maximum observed temperature dependence of the refractive index of $3.5\cdot10^{-3}$ K^{-1} is comparable to the value of temperature stability for phase matching condition in the IR range for lithium niobate and $3\cdot10^{-3}$ K^{-1} for rutile crystals grown by the cold container method.

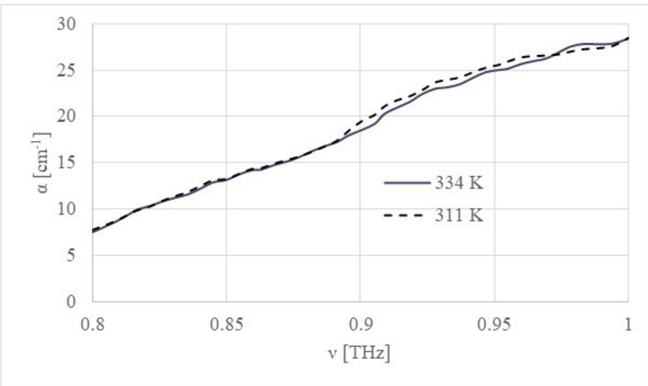

Fig. 5. Spectral dependence of the absorption coefficient of rutile grown by the cold container method in the THz range at different temperatures

Conclusion

Thus, the use of rutile grown by the technological method of a cold container as a substrate and a nonlinear optical medium for the conversion of radiation in the THz range is characterized by a temperature sensitivity coefficient comparable to the temperature sensitivity coefficient of lithium niobate with a high defect population. The high defect population in lithium niobate is due to the activation of the crystal lattice by large erbium and ytterbium ions. In rutile crystals grown by the cold container method, a strong temperature dependence may be due to significant deviations from stoichiometry during crystal growth. However, the measured values of the absorption coefficient of rutile single crystals (7–28 cm^{-1} in the range of 0.8–1.0 THz) is comparable with similar values for lithium niobate, which allows the use of THz radiation generation mode only in the surface layer.

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