Influence of the preparation conditions on optical properties of single crystals ZnGeP$_2$ in THz range

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Abstract. The influence of growth conditions and post-growth treatment processing on the quality of the ZnGeP$_2$ single crystals obtained was considered. It was revealed that the properties measurements carried out in the THz region have shown that the refractive index of the ordinary beam is greater than the extraordinary one, in contrast to the IR spectral range. It was found that the refractive indices of crystals ZnGeP$_2$ in THz band under heat treatment are reduced. The absorption coefficient of an ordinary beam in the THz range of crystals ZnGeP$_2$ is smaller than that of an extraordinary one. The absorption coefficients in the 250-1000 μm region increase for the annealed crystals ZnGeP$_2$ (600°C, 300-400 h). For wavelengths >1000 μm, the absorption coefficient of crystals ZnGeP$_2$ doesn’t exceed value 0.1 cm$^{-1}$. The correlation of the optical quality of the ZnGeP$_2$ single crystals in THz region with the growth conditions and post-growth processing was established.

1. Introduction

Nowadays terahertz electromagnetic radiation with wavelengths in 0.1-3.0 mm range attracts the attention of scientists and engineers of many leading laboratories in the world. The terahertz (THz) radiation has the ability to penetrate into various non-conductive materials. It can pass through paper, clothing, cardboard, wood, brick, plastic, ceramics, although it can’t penetrate deep into the environment with high humidity. Metal objects are completely opaque to THz radiation.

The technical potential of THz radiation is huge: from scanners safe for the human’s body for the inspection of air passengers to spectrometers that allow absolutely unmistakable and at a considerable distance from the object to identify any substances and compounds known to science which may be in the earth, in the air, in the air cells or in space. The creation of pulses of coherent terahertz radiation is an urgent scientific and technical task. The solution of this task is necessary for the development of a number of promising applications.

At present time developed and produced powerful sources of THz radiation such as backward-wave tubes and gyrotrons are actively used in practice. However, there is no information about the creation by traditional means of powerful THz radiation sources with a small angular divergence in scientific literature.

The problem of creating THz sources with a narrow radiation pattern can be solved by frequency conversion of the radiation of lasers of visible, near and middle IR (0.5-11 μm) ranges in nonlinear optical crystals by parametric down-conversion. The main assumed advantages of such source are:
- the absence of strong magnetic fields;
- the absence of necessity to use high-voltage power supply for electrovacuum devices.

Besides, the work on the creation of small-size sources of high-power pulses of coherent radiation in the THz range, characterized by a narrow radiation pattern and the absence of side lobes of radiation is topical and in demand, since the possibilities of the practical application of THz radiation in various fields of human activity are already shown today.

The single crystalline zinc-germanium diphosphide ZnGeP\textsubscript{2} was chosen as the research object because of the ZnGeP\textsubscript{2} single crystals have the following properties \cite{1}:

- high threshold of optical breakdown, allowing to work with pumping high-intensity pulsed sources;
- good thermal conductivity, which is necessary for work with passing through the crystal radiation of high power density;
- large values of temperature, angular and spectral widths of synchronism and high mechanical strength, what allow easy adjustment of converters based on ZnGeP\textsubscript{2} single crystals for synchronism and allow stable operation in vibration conditions;
- durability of crystals to conditions of high humidity and even to aggressive environments, allowing to work in the field.

The technology of growing and post-growth treatments of zinc-germanium diphosphide crystals allows to obtain crystals of high optical quality in the middle IR range - absorption coefficient in 2–8.5 μm can be reduced down to values not more than 0.05 cm\textsuperscript{-1}. However, the absorption of radiation in the THz region varies within very wide limits – from several units to hundredths of the inverse centimeters, according to the data presented in the literature. For highly efficient nonlinear-parametric conversion of radiation, it is necessary to achieve minimum absorption levels at all three operating wavelengths. The available data on the effect of technological operations on the optical properties of ZnGeP\textsubscript{2} crystals in the THz region don't allow choosing by anybody purposefully approach to the selection of crystal production conditions for efficient THz radiation generators by now.

The purpose of this work is to obtain missing data on the relationship of technological conditions with the optical properties of crystals in the THz range.

Studies of the properties of ZnGeP\textsubscript{2} crystals were performed on a Millimeter-submillimeter-wave quasi-optical spectrometer STD-21 and Mach-Zahnder interferometer IMZ TD-01. This installation is designed to measure the electrodynamic properties of objects in the range of millimeter and submillimeter wavelengths. It allows to do quick and accurate records of spectra of the absolute values of the real and imaginary parts of the electrodynamic functions of the sample response in real time regime by direct and non-contact method. Two quantities are experimentally measured at the facility: the transmission (Tr) of the plane-parallel sample and the phase shift of the radiation passing through this sample. Then the system of two equations with two unknowns (n and k, where n is the refractive index, and k is the absorption index, according to the terminology introduced by Yu.I. Ukhanov \cite{2}) is solved using software built into the unit processing unit. The obtained spectra of the optical constants values can then be compared with the conditions for obtaining crystals and draw conclusions about the correlation dependence of the optical properties from the previously varied technological conditions at the preparation and post-growth processing of single crystals ZnGeP\textsubscript{2}. The properties of such crystals in the middle IR range are listed in table 1.

### 2. Results and discussion

The optical characteristics of samples with different orientations were experimentally studied. The crystals were obtained from the nominally stoichiometric melts of the pre-synthesized compound by the Bridgman method in a vertical version on seed crystals and subsequently cut into test samples. Two samples were taken for studies in “as-grown state” and were marked “AG”. Some of AG samples were undergo thermal treatment. Post-growth treatment of the crystals was carried out by annealing in
the presence of a powder-like compound at $T=600^\circ$C for 300 hours. Annealed samples were marked as “AN”. One of AN samples had orientation (001) which differs from others (100).

Table 1. Optical properties of ZnGeP$_2$ crystals in the middle IR range.

| Sample number | Aperture orientation | Method of processing | The absorption coefficient, $\alpha$ ($\lambda=2$ $\mu$m) (m$^{-1}$) | Damage threshold $D_t$ (J/cm$^2$) |
|---------------|----------------------|----------------------|-------------------------------------------------|----------------------------------|
| 1             | 001                  | Annealed             | 0.21                                            | 0.86                             |
| 2             | 100                  | Annealed             | 0.22                                            | 0.7                              |
| 3             | 100                  | Annealed             | 0.23                                            | 0.71                             |
| 4             | 100                  | Annealed             | 0.21                                            | 0.86                             |
| 5             | 100                  | As-grown             | 0.69                                            | 0.79                             |
| 6             | 100                  | As-grown             | 0.742                                           | 0.77                             |

The results of studies of optical characteristics – the main refractive index $n$ and the absorption coefficient $\alpha=4\pi kn/\lambda$, where $\lambda$ is wavelength in vacuum [2] in the THz range (250-2500 $\mu$m) are presented in figure 1 and figure 2, respectively. In contrast to the IR range, the refractive indices of the o-beams in the THz range turned out to be larger than the values of the refractive index of the e-beams, both in the AG crystals ZnGeP$_2$ (see 5 and 6 in figure 1b) and in the heat-treated samples (see 2, 3 and 4 in figure 1a), according to our data.

Figure 1. Dispersions of the refractive indices $n$ of single crystals ZnGeP$_2$ in the THz range with polarization of the ordinary (o-) and extraordinary and (e-) beams, respectively: a) AN samples with different orientation of apertures: 1 – (001); and 2, 3, 4 – (100); b) samples with (100) – orientation of apertures differs by treatment: sample 4 is in AN state, samples 5 and 6 are in AG state.

A preliminary estimate of the values of the refractive index of crystals ZnGeP$_2$ was carried out in accordance with the Sellmeyer equality [3]:

$$n_{FGC} = \frac{A^{1/2} \cdot (B^4 - C \cdot \lambda)^{1/2}}{D \cdot \lambda^2 + (B^4 - C \cdot \lambda)^{2/2}}$$  \hspace{1cm} (1)

The values of constants $A=11.4$, $B=10$, $C=150$, and $D=1.9$ were calculated by using the least squares method and experimental data [4] obtained for the ordinary beam. In the wavelength interval used in our experiments, according to (1), the value $n_0=3.376$ was obtained, which corresponds only to the minimum values calculated from the results of our measurements.

In order to estimate the possible variation in refractive index values, Sample 1 was specially fabricated with (001) optical aperture orientation. For this orientation, any beam incident normally to
the optical surface of the sample will propagate as ordinary one. Measurements carried out for two mutually orthogonal polarizations of the incident THz radiation showed that the refractive indices of these rays (see figure 1a, curves 1/1 and 1/2) differ each from another not more than value of 0.001, which is an order of magnitude smaller than the difference between the values of the refractive indices of o- and e-beams found in other samples. The values of the refractive indices for o-beam of AN crystals (figure 1b, sample 4-o) turn out smaller as compared with refractive indices of AG samples (figure 1b, samples 5-o and 6-o). The same is indicated in case of e-beam. This relation between refractive indices shows an opposite behavior to changes determined for elementary cell volume ZnGeP$_2$ and constant crystalline lattice [5].

![Figure 2](image_url)

**Figure 2.** Spectra of the absorption coefficient $\alpha$ of samples ZnGeP$_2$ in the THz band with polarization of the ordinary (o-) and extraordinary (e-) beams, respectively: a) AN samples: 1 has orientation (001); 2, 3, 4 have orientation (100); b) samples with (100) orientation: 5 and 6 are in AG state and sample 4 is in AN state.

The results of processing the obtained experimental data show that absorption coefficients in the interval 250-1000 $\mu$m (see figure 2) for heat-treated crystals (figure 2a) exceed the values calculated for the samples in the AG state. This result does not agree with the data of [4]. Our measurements had shown that the absorption coefficients of the o-rays are smaller than the absorption coefficients of the e-rays. Thus, the discrepancy between our results and those presented in [4] can be related to orientation effects. The values of the absorption coefficient from 0.5 to 1.5 cm$^{-1}$ at a wavelength of 250 $\mu$m decrease and in the long-wavelength region (>1000 $\mu$m) do not exceed 0.1 cm$^{-1}$.

3. Conclusion

Investigation performed in the THz range have showed the following:

1. The refractive index of the ordinary beam is greater than the extraordinary one, in contrast to the IR range.
2. The refractive indices of crystals ZnGeP$_2$ are reduced under heat treatment.
3. The absorption coefficient of an ordinary beam of crystals ZnGeP$_2$ is smaller than that of an extraordinary one.
4. The thermal annealing of ZnGeP$_2$ crystals (600°C, 300–400 h) result in increase of the absorption coefficients in the 250–1000 $\mu$m region.

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