Nonlinear optical $ZnGeP_2$ crystals: the history of technology

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Received November 12, 2001

Main problems in development of the technology of functionally new optical materials for modern remote monitoring devices are considered using nonlinear $ZnGeP_2$ crystal as an example. The results of investigation carried out at the Laboratory of Optical Crystals of the IOM SB RAS are presented. Studying the causes of optical losses in $ZnGeP_2$ crystals and their sequential elimination gave us a feasibility to obtain high-quality single crystals to be used under conditions of high-intensity laser radiation. Basic technological and production potentialities of the Laboratory of Optical Crystals are briefly described.

Introduction

Development of high-intensity radiation sources gave rise to theoretical and experimental research into nonlinear optical effects in various media. This became especially urgent with the advent of lasers. By the mid-60s, nonlinear optics found a powerful theoretical foundation,[1–3] which was supported by experimental data on optical harmonic generation, parametric amplification of optical signals, and combinative frequency mixing of optical beams. By the late 60s – early 70s, the requirements on materials for high-efficiency nonlinear parametric conversion of optical radiation from one spectral region to another were formulated[4,5] and theoretical and semiempiric methods of estimating the potential nonlinear-optical efficiency were developed.[6–9]

Analysis of estimates and experimental data on linear and nonlinear susceptibility of various materials has shown that the highest index of nonlinear-optical figure of merit $M = d^2/n^3$ (d is the square nonlinear susceptibility, n is the refractive index) are characteristic of materials with covalent atomic bonds, among them diamond-like semiconductor compounds with the structure of chalcopyrite, whose study only began at that time.[10] In particular, the highest figures of merit were found for the following materials: $CdGeAs_2$ ($n = 3.58$, $d = 236\cdot10^{-12}$ m/V [Ref. 11]), $ZnGeP_2$ ($n = 3.11$, $d = 75\cdot10^{-12}$ m/V [Ref. 12]), $AgGaSe_2$ ($n = 2.62$, $d = 33\cdot10^{-12}$ m/V [Ref. 13]), and $AgGaS_2$ ($n = 2.41$, $d = 12\cdot10^{-12}$ m/V [Ref. 14]).

The unique combination of properties[15,16] in chalcopyrite materials – high nonlinear-optical figure of merit and birefringence sufficient for phase-matching interaction of optical beams – promised their wide application[16,17] as nonlinear-optical media with the potential efficiency exceeding twofold or even threefold that of nonlinear-optical materials used at that time. This turned out to be a significant factor stimulating development of production technologies for single crystals of both known multicomponent diamond-like compounds and new ones. Already by the late 70s, the crystals of compounds most promising for nonlinear optics were produced,[18–22] and that allowed experimental testing of the feasibility of using these materials for high-efficiency conversion of the laser radiation frequency.[22,23]

Progress in nonlinear optics and technology of nonlinear-optical materials favored intense studies of both purely scientific and applied problems. High-efficiency (more than 28% at the pump power density close to the threshold of optical breakdown, and 15–20% under non-critical pumping conditions) frequency doublers based on $CdGeAs_2$ crystals[22] allowed the development of the first systems for remote gas analysis based on differential absorption of the second-harmonic radiation of a CO_2 laser. References 24 and 25 reported the measurements of the atmospheric pollution concentrations with gas analyzers equipped with nonlinear-parametric frequency converters of laser radiation. They gave a powerful incentive to close cooperation between the Joint Institute of Atmospheric Optics (JIAO) SB RAS and the Kuznetsov Siberian Physical Technical Institute (SPhTI), which carried out the intense study of physical properties of $A^{II}B^{IV}C^{V}_2$ compounds and developed the basic technology of growing the single crystals.[21,26–30] First experiments on CO_2 laser second harmonic generation in $ZnGeP_2$ crystals were started at the JIAO in late 1980. Since 1982, the works on frequency conversion of the IR laser radiation in $ZnGeP_2$ crystals have found their reflection in regular publications (see Refs. 31–39). In 1984 the first domestic gas analyzer based on the CO_2 laser with a frequency doubler made of the $ZnGeP_2$ single crystal began to operate at the IAO.[40–44]

Publications on the parametric frequency conversion in $ZnGeP_2$ crystals[31–39] gave impetus to resumption of technological researches into nonlinear-optical materials in the USA,[45] which were suspended there in the mid-80s.

0235-6880/02/01 61-08 $02.00

Prerequisites for creation of new technical base for research into technology of nonlinear-optical materials

The study of $ZnGeP_2$ properties that began in the SPhTI in 1974 was based on the technology of growing $ZnGeP_2$ crystals developed in the Ioffe Physical-Technical Institute (Leningrad).[15]

In its productivity, the process of synthesizing this compound developed in the SPhTI 50–70 times surpassed known analogs[28,30] and allowed the use of large polycrystal seeds of up to 150–200 g weight that were less critical to conditions of growing.

In some cases, this allowed[28,30,46–48] production of single $ZnGeP_2$ crystals with record, for that time, dimensions (diameter up to 25 mm and length up to 150 mm) and, what is even more important, with record optical quality – optical loss of some crystals in the window of maximum transparency (3–8 μm) did not exceed 0.02 cm^{-1} (Ref. 38).

The progress of SPhTI in the study of multicomponent compounds could be even more significant provided the thermal equipment used for synthesis and growth of single crystals had stable characteristics. Marked variation of thermal conditions in the working space of furnaces (sometimes during one high-temperature process) led to low repeatability of temperature-time conditions of synthesis and crystallization. Instability of conditions, especially, at synthesis of $ZnGeP_2$ had a negative effect on the quality of the synthesized material, giving rise to uncontrolled deviations of the material composition from stoichiometry. Consequently, the synthesized material had to be purified of excessive components.

Because of competition between the processes of purification and contamination, multiple re-crystallization, most usable in production of high-purity substances, provides the maximal optical quality of a crystal only at some optimal number of re-crystallization processes. Since this optimal number can hardly be realized because of rapid deterioration of the thermal equipment, the output of single crystals with high optical quality was very low. Therefore, the study of their properties formed under weakly controllable and often irreproducible conditions gave only correlations between the properties, conditions of crystal growth, and the crystal composition. This significantly retarded the study of mechanisms of formation and interaction of defects and, consequently, development of efficient technology for control of material properties.

At the same time, development of prototypes and serial models of remote monitoring facilities capable of operating in the routine mode is closely connected with the need of improving the repeatability of all technological stages of material production which provides their reasonable cost and guaranteed, without chances, production of certified optical elements in needed amounts. The problem of equipping new gas analysis systems with elements of nonlinear optical (parametric) frequency conversion of laser radiation could be solved only on a new technical basis. So, the Laboratory of Optical Crystals (LOS) was organized in the IOM (at that time SDO "Optika") in 1986, the initial staff of which was made of specialists from the SPhTI.

The initial formulation of main problems of the new laboratory remains still urgent:

– provision of JIAO researches with optical materials for nontraditional fields of classic optics, namely, nonlinear optics, magnetooptics, and acoustooptics;

– development of technical and technological base for highly repetitive production of materials with controlled physical properties, in particular, high optical quality.

The initial stage of the Laboratory of Optical Crystals fell on the period of 1986–1988, during which the technological infrastructure was created and key prototypes of thermal facilities were developed with following production of a small series.

Figures 1 and 2 show the systems for synthesis of compounds (horizontal-inclined version) and their crystallization by the Bridgman method (vertical version) developed in the JIAO. The main technical characteristics of the developed and produced systems are tabulated below. Thanks to the capability of executing the whole technological cycle (from elementary components to nonlinear-optical elements), the Laboratory began purposeful studies of $ZnGeP_2$ synthesis in order to develop a new process of production of the material with controlled composition, as well as the technology of growing $ZnGeP_2$ crystals with high technological output.

Fig. 1. Horizontal-inclined system for synthesis of multicomponent compounds and growth of single crystals by the Bridgman method and the floating-zone technique.

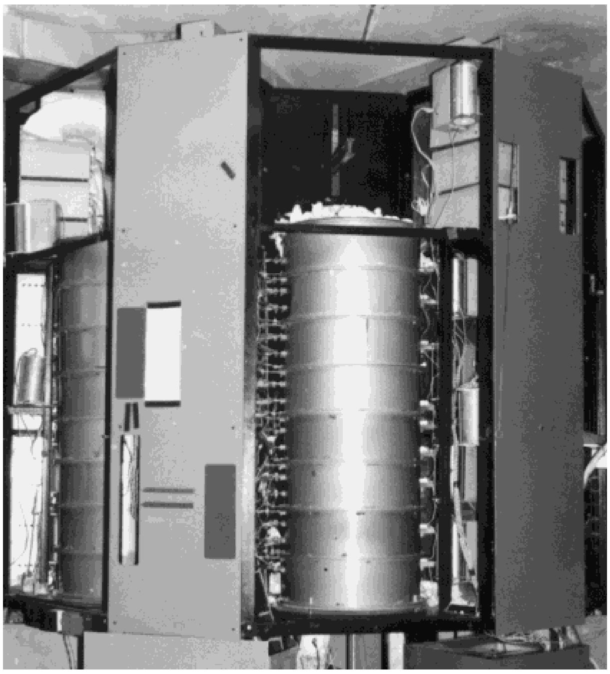

Fig. 2. Vertical system for crystal growth by the Bridgman method.

Specifications of systems for synthesizing compounds and growing crystals

Design	module-disk-shaped
Number of sections	8–9
Dimensions, mm:	
diameter	500
height	1350
Dimensions of the working space, mm:	
diameter	60
height	935
Working temperature, °C	up to 1100
Accuracy of temperature maintenance, °C	0.1
Temperature gradients, °C/cm	0.3 – 30
Speed of container movement, m/h	0.1–4
Accelerated speed of container movement, mm/min	4
Travel, mm	up to 235
Supplied power, kW	3

Development of technology of synthesizing $ZnGeP_2$ with controlled composition

The detailed analysis of the behavior of the ternary mixture Zn–Ge–P in a nonisothermal system with spatially distributed feeding of phosphorous and the equiatomic mixture of zinc and germanium has shown that the main problem in synthesis of $ZnGeP_2$ with minimal deviations of the composition from stoichiometry is connected with the Zn loss from the high-temperature reaction zone due to diffusion and temperature gradient. The problem of synthesizing $ZnGeP_2$ with controlled composition can be reduced to determination of conditions, under which the diffusion of zinc is suppressed. Such conditions can appear when the phosphorous vapor flows in the opposite direction to the diffusing zinc and this flow acts during the period of non-isothermal synthesis. To control the phosphorous flow, we should know *a priori* the starting temperature of the synthesis reaction in the two-temperature scheme, composition of phases formed in the reaction zone under dynamic nonisothermal conditions, and dependence of the phosphorous consumption rate during its reaction with the Zn–Ge mixture melt.

Using the technique of frozen reactions, we have determined that in the two-temperature synthesis of $ZnGeP_2$ with separate loading of phosphorous and the Zn–Ge mixture the marked interaction of phosphorous vapor with the Zn–Ge melt begins at the melt temperature exceeding 900°C. This differs significantly from the results obtained when studying the stages of the single-temperature synthesis.[15,16,51] The X-ray phase analysis of the reaction products has shown that at the initial stage of the two-temperature synthesis the ZnP_2 and Zn_3P_2 compounds are formed (as expected, see Refs. 16 and 51), as well as germanium phosphides Ge_xP_y. This seemed unlikely in advance of our experiments because of the high pressure of phosphorous vapor[52] needed for existence of the compound at the used temperatures of the Zn–Ge melt.

The conducted studies revealed other peculiarities of the two-temperature method. In particular, formation of $ZnGeP_2$ in the single-temperature (quasistatic) version begins already at the temperature ≈ 900°C. It turned out that under dynamic conditions of the two-temperature synthesis in the products of reaction of phosphorous with the Zn–Ge melt the marked fraction of $ZnGeP_2$ was formed at the temperatures exceeding 950°C. The fraction of $ZnGeP_2$ in the melt increases with increasing the melt temperature and the exposure time. It was found that more than 95% of phosphorous feed at the temperature ≈ 1010°C bonds chemically with the melt components. For this temperature, we determined experimentally the rate of consumption of phosphorous, whose temperature was maintained at 515–517°C corresponding to the pressure of 10–12 atm.

The studies carried out for the period 1989–1991 allowed justified selection of the temperature-time conditions, under which 500–600 g of $ZnGeP_2$ with no more than 0.1% deviation of its composition from stoichiometry is synthesized for one process. The results of these studies are published in Ref. 53. One of the synthesized bars of polycrystal $ZnGeP_2$ is shown in Fig. 3.

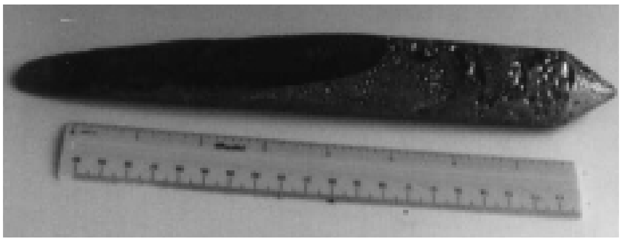

Fig. 3. Polycrystal bar of $ZnGeP_2$ synthesized at the IOM, feed mass of 415 g.

Output parameters of the developed process suggest that the new technology of $ZnGeP_2$ *synthesis meeting the demands of serial production was developed at the Laboratory of Optical Crystals of the IOM in 1991.*

Solution of problems of stable growth of crystals

In parallel with solution of problems of $ZnGeP_2$ synthesis, the Laboratory carried out systematic studies of the stability of crystal growth and optimization of growing conditions in order to increase the output of crystals and, finally, to develop a highly reproducible technology.

High reproducibility of the growth process cannot be oriented at spontaneous nucleation; consequently, it was necessary to develop the method of growing with the use of seed crystals. This method assumes pre-selection of some suitable container material, seed orientation, and temperature fields in the working volume of the system.

The tests of various covers of quartz containers (titanium nitride, silicon nitride, silicon carbide, and boron nitride) have shown that fastening seed crystals in rigid quartz containers is a difficult problem. It was solved by using crucibles of pyrolytic boron nitride − soft and plastic material unwettable by $ZnGeP_2$ melt, in particular, at its noticeable dissociation.

To choose the optimal orientation of seed crystals, we have analyzed the results of X-ray difractometric study of the orientation of single crystals (and/or large blocks) formed in the process with spontaneous nucleation. Statistics revealed marked advantages in the growth of blocks with crystallographic orientations [116] or [132] convenient for production of the second harmonic CO_2 laser generators, and with orientation [102], which is convenient for production of parametric oscillators, but significantly increases the risk of cracks due to anisotropy of the thermal expansion factor.[15,16,19,20]

To minimize experimental works, numerical simulation of optimal temperature fields was used. Heat transfer processes in axisymmetric systems for crystal growing by Bridgman and Stober methods were simulated for different versions of packing of containers with different geometry and heat-transfer properties.[54]

The works on transformation of the unstable laboratory technology into the stable one with crystal output ~ 50% were completed in 1994−1995.

The main results of these works were presented at the international seminar in Germany and published in Refs. 53 and 54. Figure 4 depicts some $ZnGeP_2$ crystals grown at that period with the use of seed crystals with different orientations.

In parallel with technology search, the Laboratory continuously took part in preparation of experiments on frequency conversion of laser radiation in cooperation with leading laser institutes and firms.[55–60] In the absence of corresponding metrological facilities, these experiments allowed rather reliable characterization of optical quality of the grown crystals, what was needed for correction of technological conditions.

The technologies of $ZnGeP_2$ synthesis and seed growing of crystals by the Bridgman method were developed in the IOM by 1995. These technologies allowed production of crystals, more than half of which had the optical quality sufficient for production of second-harmonic generators of CO_2 lasers, i.e., the level of warranted production was achieved. However, in the region of 2 μm the optical quality of produced $ZnGeP_2$ crystals (absorption coefficient ≈ 0.5 cm^{-1} for pumping radiation) *met only the minimal requirements* of parametric generation and was *insufficient for production of high-efficiency* parametric light oscillators pumped by 2-μm lasers.

Fig. 4. $ZnGeP_2$ crystals grown by the vertical Bridgman method on seeds with different orientation: [116], [132], [102], and [100].

To eliminate this restriction on the application of $ZnGeP_2$ as a highly efficient medium for parametric light oscillators, further search for optimal conditions at different stages of the technology of $ZnGeP_2$ production was needed. Further development of the technology was also necessary in order to reach the required level of reproducibility of the material with high optical quality in the region of 2 μm, i.e., with the absorption coefficient no higher than 0.15 cm^{-1} for a ray with ordinary polarization.

A new step in development of the $ZnGeP_2$ technology turned out to be closely related to solution of two problems:

– further optimization of thermal conditions for single crystal growth, including analysis and elimination of instability factors in the interface between the liquid and solid phases;

– solution of the problem of optical quality based on the studying the nature of optically active defects and processes of their formation.

Optimization of thermal conditions for crystal growing

One of restrictions in the increase of output of $ZnGeP_2$ crystals at their growing by the vertical Bridgman method was connected with crystal twinning by the plane (112). The use of seeds with orientation [116] or [132] led to twinning roughly in every second case with formation of relatively quickly degrading twin blocks. The use of seeds with orientation [102] led to twinning in all cases with the twinning plane crossing the whole bar. This problem was solved through selection of temperature-time conditions providing for stable growth of crystals from seeds with orientations, for which the overgrowth of nuclei under the conditions of spontaneous nucleation is observed extremely rarely.[54]

Measurements of temperature profiles in the systems for crystal growing have shown that application of highly efficient thermal insulation materials in order to minimize power consumption of thermal facilities, developed and made in the IOM, results in marked influence of the growing container and its surroundings on the temperature field of the furnace working area, what, in its turn, can give rise to macroscopic longitudinal inhomogeneity in the properties of the crystals under growing. To estimate (and then suppress) this undesirable effect, we have calculated thermal fluxes and temperature fields at the actual geometry of the furnace working area and its loads at different stages of the growing process. Numerical simulation of the heat transfer processes has shown that the actual velocity of the interface between the liquid and solid phases is a wavy function of the longitudinal coordinate (time) that modulates the linear velocity of the mechanical movement of the growth container with respect to the furnace. Correction of the temperature-time conditions of the growing allowed us to produce crystals being homogeneous along almost the whole length.

In the longitudinally inhomogeneous medium, in particular, near the liquid/solid interface, the temperature gradients should be established for reaching a steady state of the thermal flux. Ratio of the gradients depends on the ratio of the heat transfer coefficients of the phases being in the thermal contact. Since the thermal conductivity of $ZnGeP_2$ near the melting point was unknown, we estimated it experimentally in order to justify the selection of the temperature profile in the working volume. It was found that for stability of the crystallization front, the temperature gradient in the $ZnGeP_2$ seed should be approximately three times higher than in the melt.[61] The determined ratio of temperature gradients is especially important near the seed/melt interface and in the area, where the conic part of the crystal turns into the cylindrical one.

The main results of this research were represented at the 12th International Conference on Crystal Growth held in Jerusalem, Israel in 1998. Doctor G.A. Verozubova for the report presented at this conference was awarded by the International Union of Crystallography for outstanding achievements in crystal growth.

Control for the $ZnGeP_2$ properties

Controlling for properties of some material, in addition to knowledge of relations between the properties and certain defects of a structure, requires a solution of a very wide spectrum of problems on revealing the mechanisms of formation of the structural defects (point, linear, and volume) and determination of the role of interaction of point defects with each other and with impurities at all stages of the technology. The influence of the technological process of the material production on its properties becomes especially strong as its composition complicates. Therefore, only a stable technological chain allows one to direct its attention on solution of problems connected with formation of defects and, finally, to solve the problem of controlling the material properties.

We began to study the possibilities of controlling $ZnGeP_2$ properties, based on research into optical absorption characteristics in this material in 1995, when about 50% annual technological output of crystals was achieved.

Taking into account the known data on the decisive role of natural defects in formation of $ZnGeP_2$ properties, the program of studying the nature of optical loss in this compound included all kinds of doping by its own components (from the melt and vapor phase at crystal growing), post-growth thermal processing under rigidly controlled conditions, and radiative doping by fast electrons making thermodynamically nonequilibrium elementary point defects – vacations and internodes capable of interacting with defects of the initial ensemble at a relatively low temperature.

Some of LOC programs on the study of the nature of optical loss in the region of impurity absorption by $ZnGeP_2$ were supported by DERA Malvern (UK). Our joint researches have been conducted since 1997. Several programs were completed within the framework of the cooperation between IOM and DERA Malvern, namely:

Study of the influence of controlled deviations of the melt composition from stoichiometry due to doping by its own components on the properties of $ZnGeP_2$ crystals.

Study of influence of the conditions of post-growth thermal processing on the spectra of impurity optical absorption by $ZnGeP_2$ crystals grown from melts doped by their own components.

The results of joint studies were reported at Materials Research Society (MRS-99) and published in Ref. 62. The studies have shown that $ZnGeP_2$ crystals in the post-growth state (without additional technological operations) are characterized by different values of optical loss at the level of 0.4–1.2 cm^{-1} in the region of 2 μm depending on doping. Post-growth thermal processing under optimal thermal conditions decreases the coefficient of optical absorption near 2 μm to the level close to the needed one 0.1–0.15 cm^{-1}. However, the output of $ZnGeP_2$ crystals suitable for production of parametric light oscillators pumped by 2-μm lasers proves to be rather low (at high cost) and the achieved level of optical loss significantly limits the power characteristics of optical elements made of this material.

The natural continuation of works within the programs of cooperation with DERA Malvern and under its financial support is the study of the effect of natural point defects introduced by fast electrons on the optical spectra of $ZnGeP_2$. Within this study, the flow dependence of optical loss in $ZnGeP_2$ crystals with different defects, edge effects, and the dynamics of accumulation of radiative defects were estimated. Main stages of low-temperature annealing of radiative defects and zones of thermal stability of optical properties in $ZnGeP_2$ crystals modified by fast electrons were found. The optimal e-beam fluxes providing for minimal optical loss in crystals with different defects were determined.

The study of the effects of radiative doping of $ZnGeP_2$ crystals (in the post-growth state and after thermal processing under controlled conditions) confirmed the earlier data[26,63] and showed the possibility of further decrease of optical loss in the spectral region of 1.5–2.5 μm through combined thermal and radiative processing. In the region of 2 μm, the optical loss in $ZnGeP_2$ was decreased down to the level of 0.02–0.04 cm^{-1}.

Thus, under the optimal conditions, application of the through technological process, including synthesis of the material with the controlled composition, seed growth of single crystals with high output, post-growth annealing, and irradiation by fast electrons, allows the absorption coefficient of $ZnGeP_2$ crystals to be decreased down to the level no higher than 0.05 cm^{-1} at the wavelength of 2 μm. Transformation of absorption spectra of $ZnGeP_2$ crystals at different stages of their technological processing is illustrated in Fig. 5.

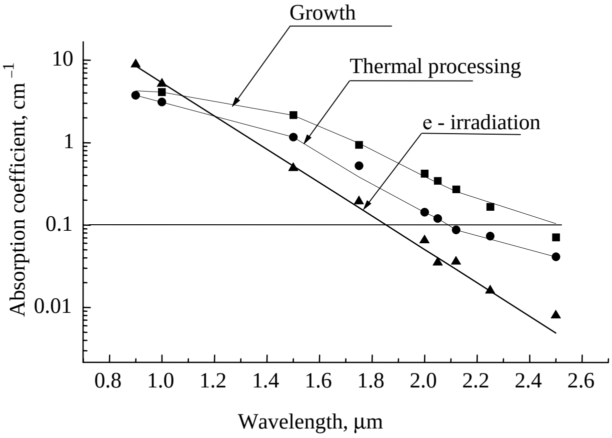

Fig. 5. Optical absorption spectra of $ZnGeP_2$ crystals.

The results of this study were partly reported at the V International Conference on Material Modification by Particle Beams and Plasma Flows (Tomsk, 2000) and published in Proceedings of this conference.[64] The main results of this work were presented in our final report to DERA Malvern (UK) for 2000 and at the 13th International Conference on Crystal Growth held in Kyoto, Japan in 2001.

Conclusion

The Laboratory of Optical Crystals organized in the IOM possesses the basic technological infrastructure and equipment needed for research connected with development and small-series production of optical materials for high-efficiency frequency converters of IR radiation tunable within a wide spectral region; such converters are needed for remote real-time monitoring of the atmosphere.

For the period of LOC existence, the Laboratory gained qualified specialists having a significant experience in development of technologies for production of optical materials with complex composition.

The most important achievements of the Laboratory are the following:

The process of synthesis of $ZnGeP_2$ with the composition close to stoichiometric one is developed.

The technology of growing the $ZnGeP_2$ single crystals with high output (> 50%) is worked out.

Optimal parameters are determined for a series of technological operations, including synthesis of $ZnGeP_2$, growing of crystals, their post-growth annealing, and irradiation by dosed beams of fast electrons, which provide for production of $ZnGeP_2$ crystals with high optical quality, i.e., with optical loss no more than 0.02–0.04 cm^{-1} at the wavelength ≈ 2 μm.

One of the main objectives of the Laboratory now is an extension of the list of optical materials based on the experience gained at development of the technology for production of $ZnGeP_2$.

The priority objects of study in material science are, in our opinion, highly efficient and functionally new optical materials – nonlinear-optical, supplementing or extending the spectral region of $ZnGeP_2$, and magneto-optical, which can be used in non-traditional measuring systems capable of solving multiparameter problems of modern optical monitoring.

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