



Article

Application of Infrared Digital Holography for Characterization of Inhomogeneities and Voluminous Defects of Single Crystals on the Example of ZnGeP₂

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Abstract: In this work, the method of IR digital holography intended for detection of volumetric defects in ZnGeP₂ single crystals has been tested. The holographic method is verified by a comparison of the results obtained with the data obtained by other methods. The spatial resolution of the experimental setup is ~15–20 μm. The volumetric defects of the ZnGeP₂ crystal structure (in samples with thickness up to 50 mm) such as growth striations, dislocation chain, and inclusions of the second phase (Zn₃P₂) shaped as needles up to ~100 μm long and ~10 μm wide have been visualized by the method of IR digital holography.

Keywords: digital holography; inhomogeneities; voluminous defects; single crystals; ZnGeP₂

1. Introduction

ZnGeP₂ single crystals are unique nonlinear media for parametric frequency conversion of optical radiation in the middle IR range, possessing high nonlinear optical (NLO) properties [1].

In addition, interest in the application of the ZnGeP₂ crystals is additionally stimulated by high potential for their application as tunable terahertz (THz) radiation sources that has not yet been realized [2–4].

Among the most dangerous defects of nonlinear optical materials that make them unsuitable for their intended purpose, the volumetric inclusions, whose properties differ strongly from the matrix properties, should be mentioned. They destroy the synchronism of the interacting optical waves and hence, decrease the efficiency of optical parametric conversion of pumping radiation into radiation of the signal (or idler) wave practically to zero. At high radiation densities, when the nonlinear effects are becoming significant, even smeared defect boundaries (transition layers) can decrease the conversion efficiency (due to wave phase mismatching) or can become a source of primary electrons forming the electron avalanche that results in optical damage of materials. Given that the technological requirements of semiconductor manufacture are met, the incorporation of inclusions in the form of particles of foreign crystal phases into the crystal volume can be considered unlikely, but the appearance of inclusions in the form of particles of secondary phases formed from the major crystal matrix components seems to be highly likely.

Due to the presence of two easily volatile components (Zn and P) that can form stable binary phases in the ZnGeP_2 compound, the initial stage of compound synthesis involves the formation of intermediate binary phases [5,6] whose subsequent reaction results in the formation of ternary compounds. Since the synthesis proceeds during limited (finite) time of intermediate phase interaction, some intermediate phases have no time to be transformed into the ternary compound, thereby leading to uncontrollable deviations of the composition of the synthesized material from the stoichiometric one.

During subsequent single crystal growth from the melt of the preliminary synthesized compound, variations in the composition of the polycrystalline batch and additional losses of volatile components during non-isothermal growth lead to uncontrolled doping of ZnGeP_2 crystals by the intrinsic non-volatile component—mostly by Ge and/or by some amount of binary compounds of metal components with phosphorus—GeP and/or Zn_3P_2 . Such doping may cause the formation of defects with sizes up to $\sim 10\text{--}50\ \mu\text{m}$ that decrease the optical quality of the material and hence, its potential efficiency.

For the examined materials with high refractive indices, and especially for crystals intended for IR radiation nontransparent in the visible range, the determination of the defect parameters turns into a difficult technical problem. Therefore, the development of technical means of control, that is, detection, visualization, measurement, and classification of the volumetric single crystal defects in one measuring experiment is an urgent technical problem. It is important not only from the viewpoint of investigation of intrinsic material defects and physical mechanisms leading to them, but also from the viewpoint of technological control and quality assurance certification of single crystals.

Knowledge of the volumetric defect distribution in crystals intended for IR range acquires special significance for production of NLO elements when it is required to choose the crystal region with preset orientation, sizes, and minimal optical absorption.

At present, there are different methods of qualitative and quantitative analysis of defects, such as the polarization-optical method, X-ray topography, IR microscopy, shadow method, and so on [7–9]. However, a disadvantage of the most methods of investigation of single crystal defect structure is that the preparation of special samples (thin polished plates with thickness of $\sim 1\ \text{mm}$ or less) is required that cannot further be used for NLO element production.

Moreover, the control and visualization methods used in the process of manufacture should be fast and contactless, which is characteristic exactly for the holographic methods.

We have already published some results of works in this direction. Thus, for example, in [10] the method of digital holography was used to investigate the process of optical damage of a single crystal. In [11], it was proposed to use the digital holography method to visualize the internal inhomogeneities of the nonlinear ZnGeP_2 crystal, and the feasibility was demonstrated to evaluate shapes and typical sizes of defects. In [12], examples of visualization of such defects as growth striae, microcrack accumulations, and needle-like defects were presented. This paper presents the results of verification of data on voluminous defects obtained by the digital holography method for a set of optical inhomogeneities that are necessary for manufacturing of optical elements.

The present work is aimed at verification of the holography method by a comparison of the results obtained with the data obtained by other methods. It has been suggested to use the method of digital IR holography in a new field of volumetric defect detection in single crystal materials, and the possibility of its application for studying optical, chemical, and mechanical volumetric inhomogeneities has been demonstrated experimentally. This is illustrated by experiments with ZnGeP_2 semiconductor materials extremely difficult for experimental investigation because of their large refractive indices (exceeding 3) and non-transparency in the visible range of the spectrum. The practical importance of the present work is that, unlike the previous methods of volumetric defect detection in ZnGeP_2 single-crystal materials, the proposed method obviates the necessity of special preparation of thin samples with thickness less than 1 mm and can be used to investigate samples with thickness up to 50 mm.

2. Digital Holography Method as a Technique for Investigating the Volumetric Defects in Single Crystals

Modern CCD (or CMOS) cameras have sufficient resolution for digital hologram recording. Figure 1 shows the in-line scheme of digital Gabor's hologram recording used in the present work. Light from laser source (1) passes through collimator (2) forming a desired cross section of the beam transmitted through investigated sample (3). In our case, the collimating objective has a focal length of 70 mm.

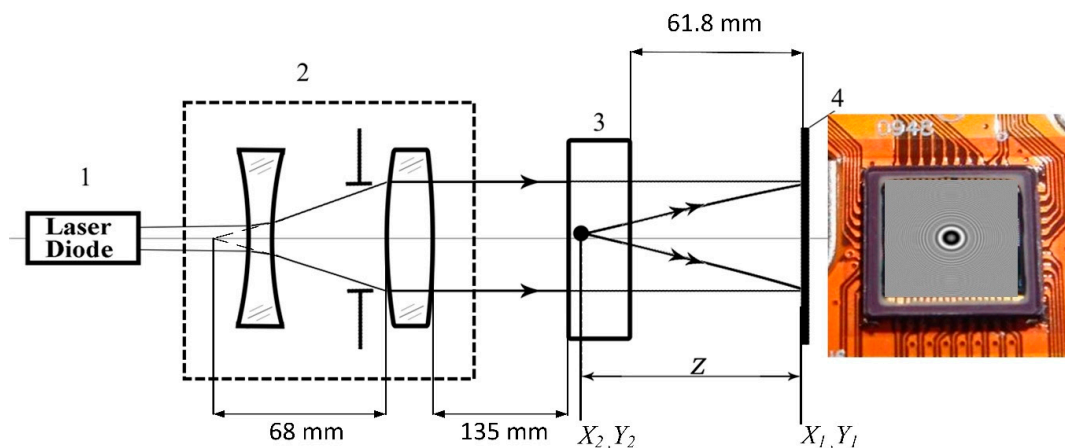


Figure 1. In-line scheme of digital Gabor hologram recording comprising laser—1, expander—2, investigated sample—3, and Videoscans-2020/PC CMOS camera—4.

As a result, an interference pattern is formed by the reference wave (part of radiation passed through the homogeneous sample volume without scattering on inclusions) and the object wave (part of radiation scattered by the inclusions). Camera (4) recorded this interference pattern (the hologram) and stores it in the computer memory.

The digital hologram represents digitized values of the interference field of the reference and object waves [13]. This two-dimensional data file $U(x_1, y_1)$ characterizes the field distribution in the hologram plane under illumination by a plane wave. Then numerical calculation [13] of diffraction integral (1) is used to calculate $U(x_2, y_2)$ —the field distribution in the (x_2, y_2) plane located at distance z from the hologram plane (x_1, y_1) .

$$U(x_2, y_2) = \frac{1}{i\lambda z} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} U(x_1, y_1) e^{i\frac{2\pi}{\lambda}z} e^{-i\frac{\pi}{\lambda}((x_1-x_2)^2 + (y_1-y_2)^2)} dx_1 dy_1, \quad (1)$$

where λ is the wavelength, z is the distance between the hologram plane and the image restoration plane.

Changing z , the image of the investigated sample volume can be formed. In this case, inclusions are visualized in each restored image of the single crystal cross section. Hence, their sizes, shapes, orientations, and localizations in the single crystal are determined.

This procedure can be called a virtual microscope, because the process of restoration of images of volume cross sections is analogous to the process of longitudinal microscope focusing. In this case, the defects are visualized in each restored image of the volume cross section, which makes it possible to determine the defect sizes, shapes, orientations, and positions and hence, to identify the defects. Figure 2 illustrates the image of the ZnGeP_2 plate with thickness of 6 mm containing a volumetric defect at a depth of 2.4 mm recorded with the digital holographic camera. The back face of the plate was at a distance of 61.8 mm from the matrix and at a distance of 67.8 mm from the front face of the plate. The defect (whose shape resembled a butterfly) was at a distance of 64.2 mm from the photodetector matrix, since the best defect focusing was observed exactly at this value of z .

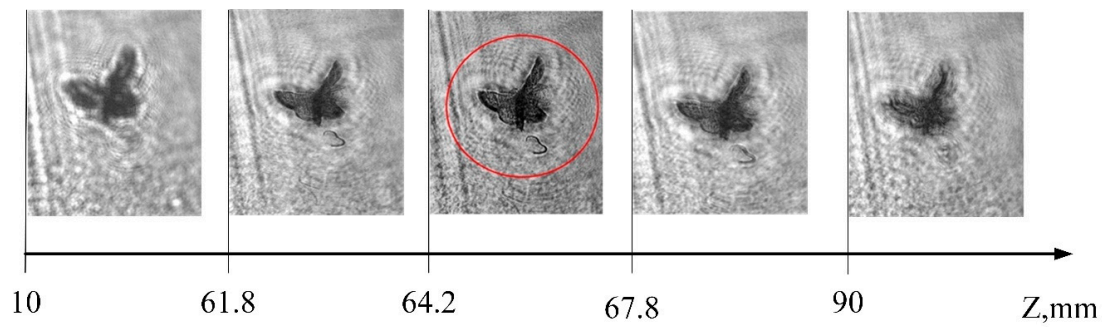


Figure 2. Restored images of planes of the ZnGeP_2 plate located at distances Z from the photodetector matrix.

In digital holography, the above-described process of information recording and restoration has already been used to study plankton and settling particles in a liquid [14,15]; it can also be successfully used for diagnostics of defects in optical materials [11,16]. The unique property of holography is the possibility of recording information about a sufficiently large volume of the medium in a single hologram and at the same time, with high spatial resolution sufficient for obtaining data on each particle, inhomogeneity, or defect in the volume of the medium (including its size, shape, and coordinates). In the examined case of digital holography, a hologram can be transferred via communication lines, and recording of a time sequence of digital holograms makes it possible to create a video of the investigated process based on the holographic data [14].

Thus, digital holography provides unique possibilities for investigation of inhomogeneities of different types in optical materials, especially for diagnostics of optical material of single crystals intended for operation with optical radiation of high intensity (high optical density), including nonlinear optical elements of optical parametric oscillators (OPO). In the present work, results of application of digital holography to investigation of inhomogeneities in ZnGeP_2 single crystals are presented.

Since the Gabor scheme imposes reduced requirements on the spatial and temporal coherence of radiation [12,13], a semiconductor laser diode (denoted by 1 in Figure 1) with wavelength of $1.064 \mu\text{m}$ and output power of 100 mW was used as a radiation source. A CCD camera with 1600×1200 -pixel matrix, pixel sizes no more than $7.4 \mu\text{m} \times 7.4 \mu\text{m}$, and physical matrix size of $2/3''$ was used as a recording camera (denoted by 4 in Figure 1).

The long-wavelength boundary of the spectral sensitivity of the employed CCD camera was at $\sim 1.1 \mu\text{m}$. The working spectral range of the ZnGeP_2 transmittance in which the absorption coefficient did not exceed $\sim 1 \text{ cm}^{-1}$ was in the range $0.9\text{--}8.3 \mu\text{m}$. Thus, sources generating radiation in the spectral region near $1.06 \mu\text{m}$ and CCD matrices operating in the visible range can be used to investigate the ZnGeP_2 single crystals by the digital transmission holography method.

These problems were considered in detail in [11,16,17]. According to the estimate presented in [17], the minimum recorded defect sizes are $\sim 15\text{--}20 \mu\text{m}$ for matrix pixel size of $\sim 7 \mu\text{m}$ and wavelength of hologram recording of $\sim 1 \mu\text{m}$. In the present work, the minimum sample thickness ($< 1 \text{ mm}$) was limited only by the possibility of its manufacturing, and the maximum thickness of 50 mm was limited only by the absorption coefficient of the material at a wavelength of $1 \mu\text{m}$, the sensitivity of the CCD camera, and the output power of the laser diode. The maximum thickness of the sample can be increased by increasing the laser diode power or by improving the sensitivity of the camera.

From Figure 1 it can be seen that the investigated volume is bounded by the aperture of the matrix camera (denoted by 4 in Figure 1). Due to small matrix size ($2/3''$), sample scanning by a motorized positioner was used in the setup. In this case, the investigated single crystal was clamped in a holder mounted on the object-table of the positioner.

The software developed for the setup (Figure 1) provided numerical restoration of images of investigated sample cross sections and subsequent interactive measurements of defect images within

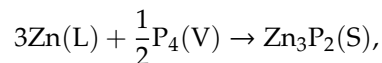
the restored images of sample cross sections displayed on the screen by setting the cursor in the position determined by an operator.

Note a special advantage of the digital holography important for solving the problem under study. The hologram is recorded in the invisible IR range (range of single crystal transparency), and the results of numerical image restoration are visualized for the operator on the computer display in the visible range.

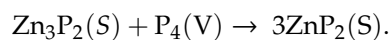
3. Experimental Results and Discussion

In this Section, images of defects of different types observed in the ZnGeP₂ crystal that were recorded by the digital holography method are discussed. Physical interpretation of the results obtained is provided, and they are compared with the results obtained by other methods.

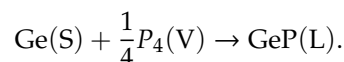
The synthesis of the ZnGeP₂ crystalline compound by horizontal single-temperature or double-temperature Bridgeman technique [5,6,18], albeit supposes different technical arrangement and regimes, but the reactions running during ZnGeP₂ synthesis and their sequence are the same for all realizations. As shown in [5], the synthesis of the ZnGeP₂ compound involved the stage of forming binary phosphides in different temperature ranges. Thus, for temperatures in the range 480–550 °C, molten zinc reacts with phosphorus vapor forming the compound with a low content of phosphorus [6]:



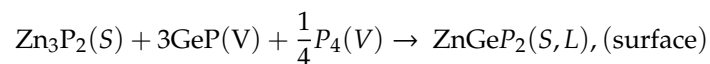
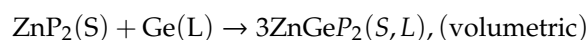
where S, L, and V denote solid, liquid, and vapor phases, respectively. As the phosphorus temperature increases to ~550–850 °C together with its pressure, zinc phosphide with low phosphorus content is transformed into the ZnP₂ compound:



The rate of phosphorus atoms diffusion into the solid phosphide cannot be high; therefore, during period of synthesis-reactor heating to temperatures at which the reaction of triple phosphide formation is possible, zinc phosphide Zn₃P₂ with low phosphorus content is transformed into ZnP₂ only partially. At a temperature of ~750 °C, germanium phosphide can be formed:



At temperatures exceeding ~900 °C, the ternary compound synthesis begins with two reactions [7]:



Unlike the volumetric (two-component) reaction, the surface (ternary-component) reaction requires contact of condensed reagents with the vapor phase limited by the condensate-vapor interface itself, so its rate is significantly less than the rate of the volumetric reaction, and the residual (unreacted) condensed phases—zinc phosphide with low phosphorus and germanium contents—can be presented in the final product of the ZnGeP₂ synthesis. These residual phases are found predominantly in the part of the synthesized ingot that contacts poorly (or does not contact at all) with the vapor phase. These impurities from the intrinsic components of the compound form volumetric needle-shaped inclusions [19] with typical transverse size of ~10 μm and length up to several millimeters.

Figures 3 and 4 vividly illustrate the presence of the above-discussed inclusions in the material. The second phase inclusions—the needle-shaped phosphide crystals up to ~500 μm long and up to ~15 μm in diameter—were also detected in the experiment (Figure 4). Analogous second-phase inclusions of the intrinsic components were observed in [9] by the method of optical transmission

microscopy of thin ZnGeP_2 plates with thickness no more than 1 mm cut along the growth axis. They were also present on X-ray topograms [9].

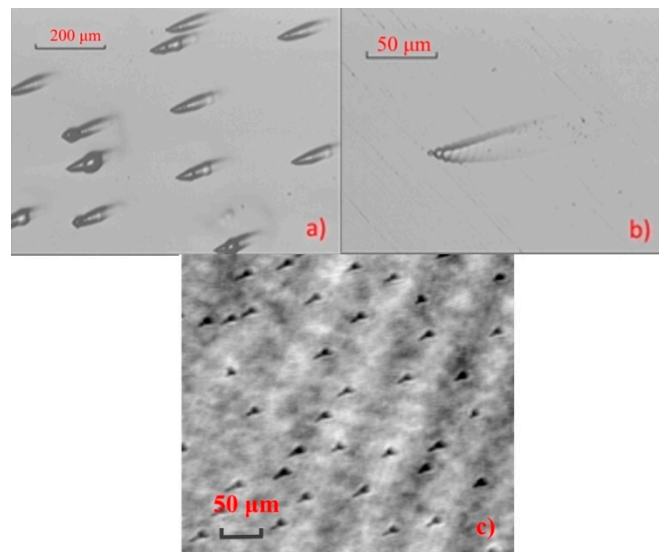


Figure 3. Images of the etched cut tilted to the crystal growth axis at indicated zooming (a,b) and image of the cut tilted to the crystal growth axis reconstructed from the hologram (c).

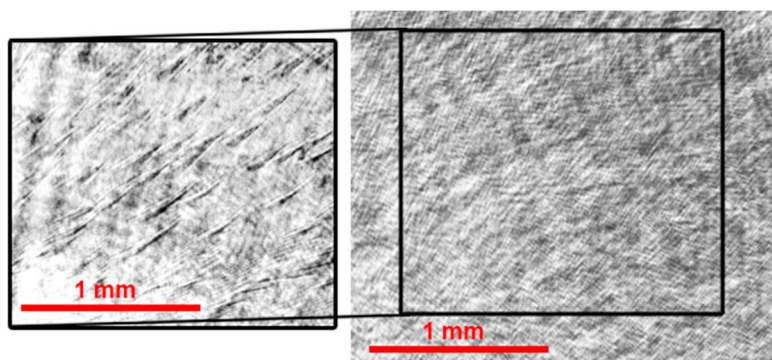


Figure 4. Hologram of the ZnGeP_2 plate with thickness of 6 mm cut parallel to the growth direction (on the right) and restored image of the plate cross section containing a volume defects at a depth of 4.8 mm (on the left).

The total composition of elementary components in the crystal is assumed stoichiometric, excluding pre-designed deviations for scientific research purposes. The appearance of zinc phosphide inclusions automatically raises a question: where and in what form is the part of Ge batch unreacted with zinc phosphides distributed? According to the results of calculations performed in [18], melted ZnGeP_2 crystallizes have relatively high equilibrium concentration of vacancies $[V_p]$ in the phosphor sublattice that decreases significantly with the crystal temperature. At the same time, the concentration of vacancies $[V_{zn}]$ in the zinc sublattice first increases with decreasing temperature and then remains almost independent of the temperature in a certain temperature interval (~ 25 K). This means that the total germanium solvability, proportional to the concentration of vacancies in the corresponding sublattices, should significantly depend on the temperature oscillations at the crystallization front; moreover, the amplitude and time characteristics of the temperature oscillations for crystals grown by the vertical Bridgeman method are determined by the following factors [20]:

- supersaturation of the ZnGeP_2 melt by the doping component (in our case—Ge) and axial temperature gradient influencing on the rate of forming temperature inversion layers at the crystallization front;
- viscosity of the melt and radial temperature gradient influencing on the period of convectational melt flow instability;
- crystallization front speed influencing on the period of concentration instability.

The above-indicated reasons for the nonstationary motion of the crystallization front lead to the formation of the single crystal material with different concentrations of point and volumetric defects and, as a consequence, to the formation of growth striations and modulation of the absorption along the crystal length [9,19]. The growth striations are clearly seen in Figure 5 recorded by the digital holography method. The striations correspond to the crystallization isotherms and hence, are concave toward the ingot center. This testifies to the presence of the temperature dip in the ingot center in the process of its growth. These results are in good agreement with the data obtained in [9] by optical transmission microscopy of thin plates as well as with the results obtained in [21] using the X-ray transmission topography.

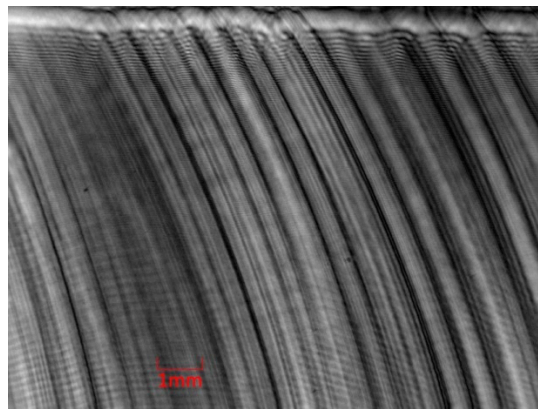


Figure 5. Growth striaes detected by the method of digital holography (restored image of the ZnGeP_2 plate cut parallel to the growth direction of the crystal plane located at a depth of 3 mm from the plate surface).

One of the defect types in a single crystal is a dislocation. Sources of dislocation nucleation in crystals are regions of enhanced dislocation density formed on the lateral surface of the seed crystal below the seed crystal—crystal interface due to the melt inflow between a crucible and a seed crystal. The melt inflow polycrystallizes due to fast induration below the phase interface and causes the high dislocation density $N_d > 10^5 \text{ cm}^{-2}$ [21]. Intense dislocation chain propagates from a highly deformed area on the lateral surface of the seed deep into the growing crystal.

In [20], it was shown that the deformation field around a dislocation results in the appearance of inhomogeneous density variations determined by the sum of main strains. These density variations scatter radiation transmitted through the sample under control. High strain gradients and hence, refractive index gradients in the direction normal to the dislocation lead to significant curvatures of trajectories of beams incident on the crystal in the direction parallel to the dislocation row. Figure 6b,c shows strain distributions in the material recorded by the digital holography method. They lead to refractive index variations and radiation scattering indicating the presence of dislocations. The dislocation rows consist of ~10–50 dislocations. Figure 6d shows the image of dislocation rows recorded by the method of X-ray topography [21].

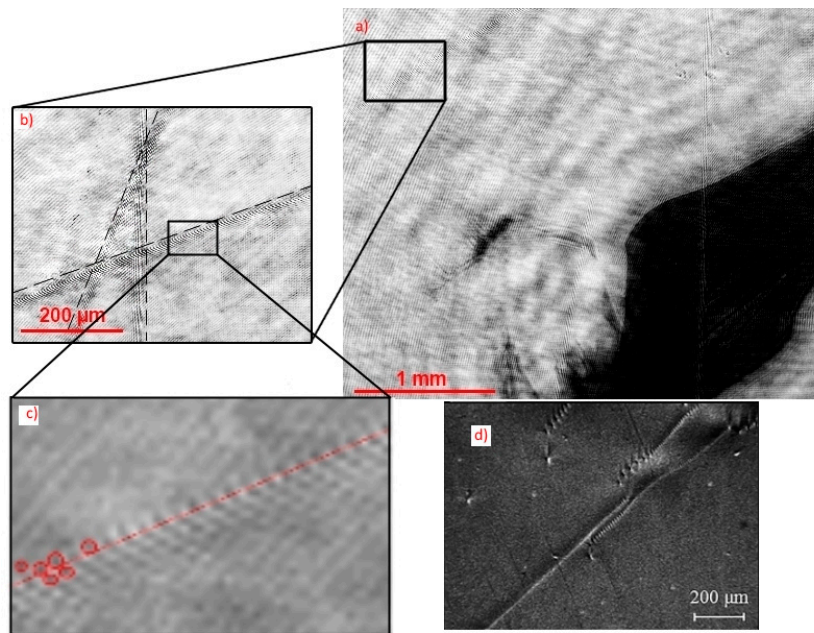


Figure 6. Hologram of the plate of unannealed material with thickness of 50 mm cut perpendicularly to the growth direction (a), holographic image restored from the chosen fragment of the hologram of the crystal plane located at a depth of 9 mm from the plate surface (b), zoomed image of a number of dislocations reconstructed from the restored image (c), and X-ray topogram of the cross section cut of the initial fragment of the single crystal ingot (result of investigations performed in [21] using X-ray transmission topography) (d).

4. Conclusions

The digital holography method used to investigate the volumetric defects of the ZnGeP_2 single crystal structure has allowed us to detect defects and defect pileups of actual ingots with thickness of about 10–50 mm. This makes it possible to cut crystals into nonlinear optical fragments with minimal concentrations of volumetric defects.

The experimental stand described in this work, including the CCD camera with pixel size of $7.4 \mu\text{m}$ and the laser diode emitting radiation at a wavelength of $1.064 \mu\text{m}$ together with the developed software have allowed us to detect and to identify the volumetric defects with minimal linear size of $\sim 15\text{--}20 \mu\text{m}$.

Our experimental investigations of the ZnGeP_2 single crystal samples have demonstrated that the digital holography is promising for application to technological control and quality assurance certification of optical crystals. It has been shown that results of holographic tests allow:

- Diagnostics of inclusions and optical inhomogeneities to ascertain the compliance of the single crystal with the optical quality characteristics, including sizing;
- Diagnostics of materials intended for operation in the optical IR range;
- Optical focusing by the virtual method (numerically, in the post-experiment regime) for wide range of variations of optical thicknesses without limitations peculiar to actual zooming systems connected with finite depth of focusing of zooming systems;
- Construction of the 3-D defect distribution in the investigated volume.

During our research, we have verified the data on voluminous defects obtained by the method of digital holography by their comparison with the results of chemical etching of the single crystal surface and X-ray topography. The minimal size of inclusions detected by the method of digital holography was experimentally determined. For the first time, the dislocation rows have been detected in the nonlinear crystal volume.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Nikogosyan, D. *Handbook Nonlinear Optical Crystals: A Complete Survey*, 1st ed.; Springer: Berlin, Germany, 2005; 427p.
2. Kitaeva, G.K. Terahertz generation by means of optical lasers. *Laser Phys. Lett.* **2008**, *5*, 559–576. [[CrossRef](#)]
3. Gribenyukov, A.I.; Dyomin, V.V.; Polovcev, I.G.; Yudin, N.N. Physical approaches to designing a two-cascade terahertz laser generating difference-frequency radiation in a nonlinear optical ZnGeP₂ crystal. *Rus. Phys. J.* **2018**, *60*, 1980–1986. [[CrossRef](#)]
4. Gribenyukov, A.I.; Dyomin, V.V.; Polovtsev, I.G.; Yudin, N.N. Principles of creation of a tunable terahertz laser with lasing at a difference frequency in a nonlinear ZnGeP₂ optical crystal. *J. Opt. Technol.* **2018**, *85*, 322–325. [[CrossRef](#)]
5. Verozubova, G.A.; Gribenyukov, A.I.; Korotkova, V.V.; Ruzaiкин, M.P. ZnGeP₂ synthesis and growth from melt. *Mater. Sci. Eng. B* **1997**, *48*, 191–197. [[CrossRef](#)]
6. Verozubova, G.A.; Gribenyukov, A.I.; Mironov, Y.P. Two-temperature synthesis of ZnGeP₂. *Inorg. Mater.* **2007**, *43*, 1040–1045. [[CrossRef](#)]
7. Sangwal, K. *Etching of Crystals: Theory, Experiment, Application*; North-Holland: New York, NY, USA, 1987.
8. Gribenyukov, A.I.; Podshivalov, S.N.; Soldatov, A.N.; Shumeyko, A.S.; Yudin, N.A.; Yudin, N.N.; Yurin, V.Y. Defectoscopy of ZnGeP₂ single crystals using a strontium vapor laser. *Quant. Elect.* **2018**, *48*, 491–494. [[CrossRef](#)]
9. Verozubova, G.A.; Okunev, A.O.; Gribenyukov, A.I.; Trofimov, A.Y.u.; Trukhanov, E.M.; Kolesnikov, A.V. Growth and defect structure of ZnGeP₂ crystals. *J. Cryst. Growth* **2010**, *312*, 1122–1126. [[CrossRef](#)]
10. Gribenyukov, A.I.; Dyomin, V.V.; Olshukov, A.S.; Podzyvalov, S.N.; Polovtsev, I.G.; Yudin, N.N. Investigation of the process of optical damage of zngep2 crystals using digital holography. *Russ. Phys. J.* **2019**, *61*, 2042–2052. [[CrossRef](#)]
11. Dyomin, V.V.; Polovcev, I.G.; Kamenev, D.V. The internal defects detection in crystals by digital holographic methods. *J. Phys. Conf. Ser.* **2016**, *737*, 012072. [[CrossRef](#)]
12. Dyomin, V.V.; Gribenyukov, A.I.; Davydova, A.; Zinoviev, M.M.; Olshukov, A.S.; Podzyvalov, S.N.; Polovtsev, I.G.; Yudin, N.N. Holography of particles for diagnostics tasks [Invited]. *Appl. Opt.* **2019**, *58*. [[CrossRef](#)] [[PubMed](#)]
13. Schnars, U.; Juptner, W. *Digital Hologram Recording, Numerical Reconstruction, and Related Techniques*; Springer: Berlin, Germany, 2005.
14. Dyomin, V.V.; Olshukov, A.S. Digital holographic video for studying biological particles. *J. Opt. Technol.* **2012**, *79*, 344–347. [[CrossRef](#)]
15. Dyomin, V.V.; Olshukov, A.S.; Naumova, E.Y.; Melnik, N.G. Digital holography of plankton. *Atmos. Ocean. Opt.* **2008**, *21*, 951–956.
16. Dyomin, V.V.; Polovtsev, I.G.; Kamenev, D.V. Quality control of ZnGeP₂ single crystals using optical methods. *Rus. Phys. J.* **2016**, *58*, 1479–1481. [[CrossRef](#)]
17. Dyomin, V.V.; Kamenev, D.V. Influence of characteristics of the camera used to record digital in-line holograms of particles, on the quality of the reconstructed images. *Rus. Phys. J.* **2013**, *55*, 1307–1313. [[CrossRef](#)]
18. Buehler, E.; Wernick, J.H. Concerning growth of single crystals of the II-IV-V diamond-like compounds ZnSiP₂, CdSiP₂, ZnGeP₂, and CdSnP₂ and standard enthalpies of formation for ZnSiP₂ and CdSiP₂. *J. Cryst. Growth* **1971**, *8*, 324–332. [[CrossRef](#)]
19. Verozubova, G.A.; Gribenyukov, A.I.; Korotkova, V.V.; Vere, A.W.; Flinn, C.J. ZnGeP₂ growth: Melt non-stoichiometry and defect substructure. *J. Cryst. Growth* **2002**, *237–239*, 2000–2004. [[CrossRef](#)]

20. Carruthers, J.H. Origins of convective temperature oscillations in crystal growth melts. *J. Cryst. Growth* **1976**, *32*, 13–26. [[CrossRef](#)]
21. Okunev, A.O.; Verozubova, G.A.; Stasenko, V.A.; Gribenyukov, A.I.; Kolesnikov, A.V. Dislocations, lines of growth and inclusion in $ZnGeP_2$. *Phys. B Phys. Condens. Matter* **2003**, *340–342*, 978–981.



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