10

Interaction of femtosecond laser radiation with chalcogenide glasses of various compositions

© A.E. Rupasov[1], P.A. Danilov[1], A.A. Ionin[1], N.A. Smirnov[1], S.I. Kudryashov[1], R.A. Khmelnitskii[1], S.N. Shelygina[1], A.O. Levchenko[1], V.S. Shiryaev[2]

[1] Lebedev Physical Institute, Russian Academy of Sciences, Moscow, Russia
[2] Devyatykh Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, Nizhny Novgorod, Russia
e-mail: jkljnb16@gmail.com

Received on December 20, 2021
Revised on December 20, 2021
Accepted on December 30, 2021

The interaction of femtosecond laser radiation with a wavelength of 1030 nm with chalcogenide glasses of various compositions has been studied. The dependence of the optical transmission of chalcogenide glasses on the pulse energy and frequency has been experimentally established. The compositions of glasses for their use as an optical medium for laser micromachining in the infrared range have been established. It is shown that Ge7Se93 glass is the most suitable optical medium for spectral studies of diamond in the near and mid-IR range.

Keywords: direct laser recording, femtosecond laser pulses, chalcogenide glasses, IR optical materials.

DOI: 10.21883/EOS.2022.04.53731.53-21

Introduction

In recent decades, chalcogenide glasses (CGs), i.e., materials based on arsenic and germanium sulfides, selenides, or tellurides, have attracted considerable research interest because of their unique optical properties. CGs are characterized by high transmission in the IR region (from 0.6 to 25 μm, depending on the composition), low phonon energy (250−350 cm^{-1}), high chemical resistance, low tendency to crystallization, high linear and non-linear refractive indices [1,2]. The linear refractive index strongly depends on the composition of the glass and varies from 2.04 for glassy germanium disulfide to values of 3.0 and higher for glasses enriched in tellurium. Chalcogenide glasses have the large third-order nonlinearity, the low two-photon absorption coefficient, and the absence of absorption on free carriers in the photosensitive region. This unique combination of properties is almost ideal for photonic devices, opens up the possibility of creating new elements and systems of nonlinear and integrated optics namely, IR optical fiber lasers and amplifiers, high-speed switches, Raman lasers, frequency converters and supercontinuum generators [3–6].

The existence of a wide range of possible glass-forming systems of various chemical compositions and good resistance to crystallization makes it possible to obtain glasses with such optical properties as high nonlinearity, low optical losses in the IR range, good light sensitivity, which can be optimized for photonic applications. In addition, CGs are sensitive to the absorption of electromagnetic radiation, exhibiting various photoinduced effects when illuminated; thus, they are an excellent candidate for fabrication of photonic devices by femtosecond laser writing. Also, CGs can serve as an optical medium for laser processing (by femtosecond pulses) and spectral studies in the IR range of some materials, such as diamond.

However, one of the disadvantages of CGs is their relatively low radiation resistance. In particular, CGs can be catastrophically damaged when exposed to high intensity laser pulses. Under laser exposure, it is necessary to prevent the damage threshold of chalcogenide glasses. Damage threshold depends on the properties of the material (glass composition and its impurity- and phase-pureness, surface condition) and on the laser parameters (pulse repetition frequency, duration and wavelength). For example, a sharp increase in the ablation threshold of As_2Se_3 glass with decreasing micropulse duration was shown in the paper [7]. Femtosecond laser damage thresholds for chalcogenide glasses were studied mainly on commercially available As_2Se_3, as well as on some glass compositions of Ge−As−S and Ge−As−Se systems [7–11]. It was found that when glasses of the Ge−As−S and Ge−As−Se systems are irradiated with femtosecond laser pulses, the damage threshold increases with increase in the Ge concentration, i.e., with increase in glass transition temperature.

In this work, the interaction of femtosecond laser radiation with the most typical representatives of amorphous chalcogenides, including various stoichiometric ratios, is considered. The dependence of the transmission of glasses on the pulse energy is established. The main objective of our work is to search for optimal compositions that have a high damage threshold when interacting with femtosecond laser pulses. Chalcogenide glasses with refractive index close to that of diamond can be used as immersion media for the visible and near-IR ranges, in which all the absorption and fluorescence bands of point defects in diamond are located. Chalcogenide compositions will make it possible to identify exactly uncut diamonds by their

Thickness of samples

Sample	Se	$Ga_{1.3}Ge_{24.4}As_{13.2}Se_{55.1}$	$Ga_{3.5}Ge_{20.75}Sb_{10.75}Se_{65}$	As_2S_3	$As_{36}Se_{64}$	$As_{41}S_{32}Se_{27}$
Thickness, mm	1.1	3.26	4.08	5.26	3.345	3.01
Sample	Ge_7Se_{93}	$Ge_{19}Se_{81}$	$Ge_{18}As_{22}S_{60}$	$Ge_{25}Sb_{10}S_{65}$	$Ge_{25}As_{15}Se_{60}$	$Ge_{17.7}Sb_{10.1}Se_{65.8}In_{2.5}I_{3.9}$
Thickness, mm	4.35	2.78	3.15	7.47	1.6	5.01
Sample	$Ge_{25}Sb_{10}S_{65}$	$As_{40}S_{50}Se_{10}$	$As_{40}S_{10}Se_{50}$	$As_{40}S_{20}Se_{40}$	$As_{40}S_{30}Se_{30}$	$As_{40}S_{40}Se_{20}$
Thickness, mm	8.18	0.064	0.065	0.05	0.055	0.055

spectral characteristics, including with spatial resolution, by the characteristic distribution of defects, as well as the possibility of laser modification of the internal volume of a diamond, including for the purpose of its signature.

Experimental units

Samples of ultra-pure chalcogenide glasses of various compositions were taken for research. The samples were obtained by melting the initial mixture in evacuated quartz ampoules using special chemical-distillation methods for purification of the initial components and the glass-forming alloy [2,12–14]. The content of impurities in glasses was: hydrogen and oxygen — $< 1 \cdot 10^{-5}$ mas%, carbon — $< 2 \cdot 10^{-6}$ mas%, silicon — $< 4 \cdot 10^{-5}$ mas%, transition metals — $< 1 \cdot 10^{-5}$ mas%.

The samples were studied using Satsuma femtosecond fiber laser [15] based on a fiber doped with ytterbium ions (Yb^{3+}). The main laser radiation wavelength $\lambda = 1030$ nm with pulse duration $\tau \sim 300$ fs. The pulse energy range varies from 10 nJ to 10 μJ. Control can be carried out both through the control panel and using a control program on an external computer. To control the power of the incident laser radiation and measure the nonlinear absorption coefficient, Ophir laser pulse power and energy meters with a JUNO digital interface and StarLab software were used.

The experimental scheme for measuring the nonlinear transmittance is shown in Fig. 1. Pulses of the fundamental harmonic of the femtosecond fiber laser at frequency of 10 kHz were directed to the sample placed at the lens focus (200 mm, spot diameter $\sim 60\,\mu$m). Under these focusing conditions, the surface and volume of the targets were not destroyed, and surface disruption was observed on several samples at laser pulse energies close to the maximum. The transmitted radiation was recorded by a laser pulse energy meter PD-10-C (Ophir) with JUNO digital interface in the StarLab environment. To control the incident energy, the convertible mirror was located directly in front of the sample, which made it possible to direct the laser beam into another Ophir meter.

The samples are a set of plates of various thicknesses, the values of which are given in the table. The plates were mounted on holder with adjustable tilt angle, the holder

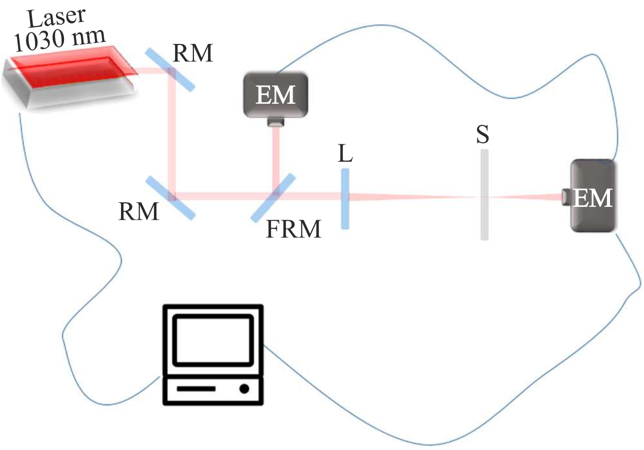

Figure 1. Experimental unit scheme. RM — reflecting mirrors; FRM — convertible mirror for measuring the energy of incident pulses (Faraday rotator mirror); L — lens with focal length 200 mm; S — irradiated sample; EM — energy meters of laser impulses.

was mounted on a three-coordinate translation platform with minimum movement step 150 nm.

Measurements of the linear transmittance in the visible and near-IR ranges were carried out using an SF-2000 spectrophotometer (by Experimental design bureau Spektr, Russia). In the IR range, the transmission spectra were measured using a Bruker Vertex IR Fourier spectrometer (Germany).

Experimental results and discussion

Spectroscopy

For processing of diamonds, it is supposed to use laser radiation in the near-IR range (1030 nm), which means that glasses must have a sufficiently high transmittance at the applied laser wavelength. Transmission spectra of glasses in the visible and near IR ranges of 200–1100 nm are shown in Fig. 2.

The linear transmittance T of most samples for a wavelength of 1030 nm lies in the range of 40–70%. The best transmission in the region of interest to us have samples $Ga_{1.3}Ge_{24.4}As_{13.2}Se_{55.1}$, $Ga_{3.5}Ge_{20.75}Sb_{10.75}Se_{65}$, Ge–Sb–S,

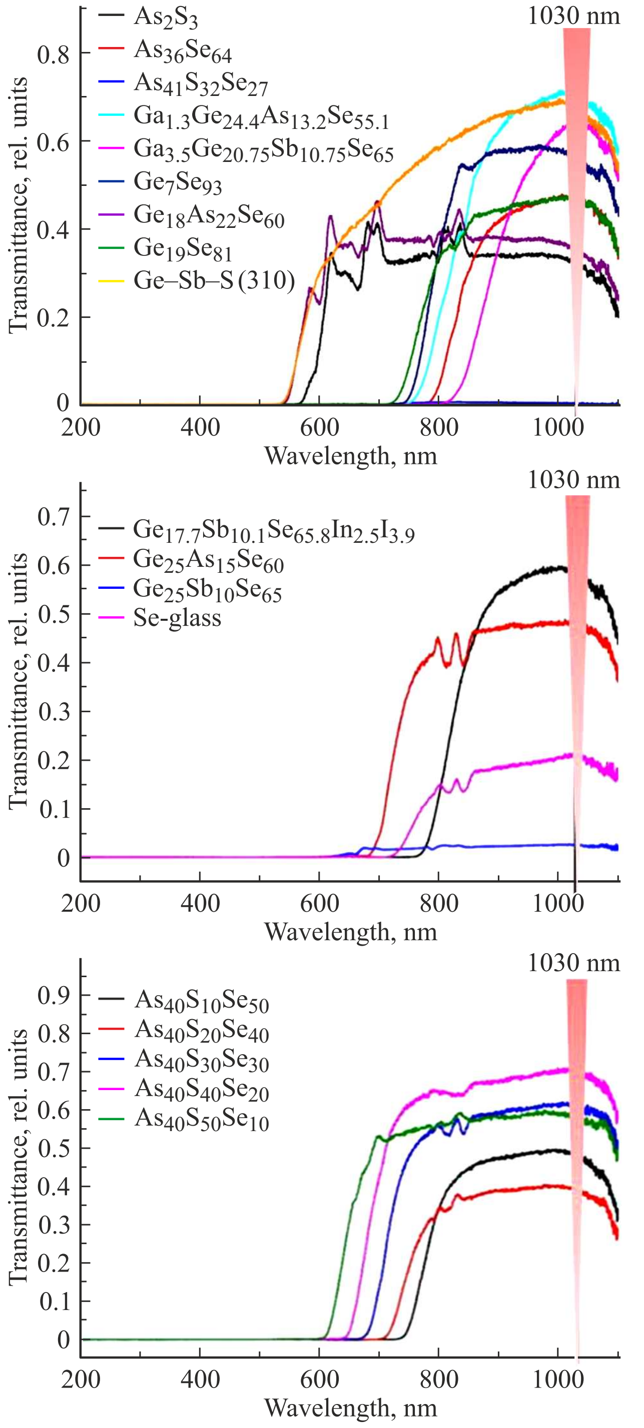

Figure 2. Transmission spectra of chalcogenide glasses with different chemical and stoichiometric ratios.

$Ge_{17.7}Sb_{10.1}Se_{65.8}In_{2.5}I_{3.9}$, $As_{40}S_{30}Se_{30}$, $As_{40}S_{40}Se_{20}$, $As_{40}S_{50}Se_{10}$ with transmission above 50%

The main absorption, defect, and luminescence bands of diamond lie in the range from 2 to 7 μm. Glass of composition Ge_7Se_{93} looks especially attractive for work in the IR range, the transmission spectrum of which is shown in Fig. 3 in comparison with the transmission spectrum of

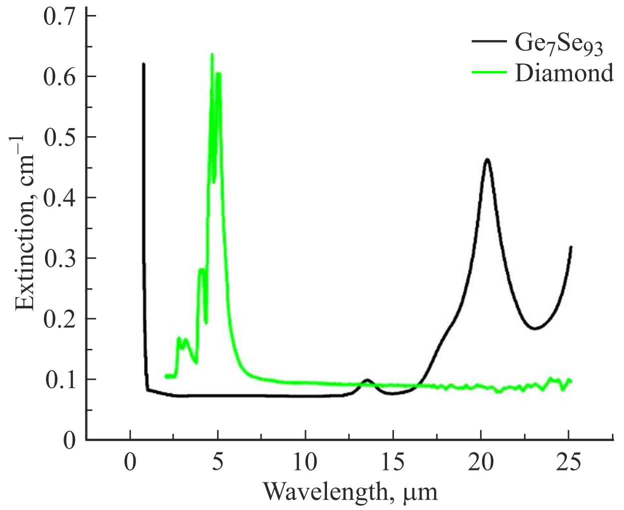

Figure 3. Transmission spectra in the IR range obtained with Bruker Vertex FT-IR spectrometer.

diamond. This glass has a high optical transmission in the wide spectral range ($800-4000\,cm^{-1}$ or $2.5-12.5\,\mu$m) and near-diamond refractive index ~ 2.4 [16].

Measurements of the non-linear transmission coefficient of IR glasses

Nonlinear properties of materials can manifest themselves in the form of absorption saturation or multiphoton processes of interaction of laser radiation with the target material. During the passage of laser pulses at wavelength of 1030 nm, $Ge_{18}As_{22}S_{60}$ and As_2S_3 samples strongly distort the form and direction of propagation of the transmitted radiation, so they are not considered further.

At intensities $> 100\,GW/cm^2$, the sharp drop in transmission $Ge_{25}As_{15}Se_{60}$ (Fig. 4, a) takes place. Transmission dependence Ge_7Se_{93} on intensity has the break at $> 600\,GW/cm^2$, however, at $\sim 700\,GW/cm^2$, surface disruption is observed for it. Immersion compositions Ge−Sb−S, $Ge_{17.7}Sb_{10.1}Se_{65.8}In_{2.5}I_{3.9}$ by nonlinear transmission and absorption have pronounced nonlinearity at the intensity above $300\,GW/cm^2$.

The properties of glasses $Ga_{1.3}Ge_{24.4}As_{13.2}Se_{55.1}$ and $Ga_{3.5}Ge_{20.75}Sb_{10.75}Se_{65}$ (Fig. 4, b) are similar to those described above; the transmittance changes insignificantly at intensities over $10\,GW/cm^2$.

Further, let us consider IR glasses containing As, S, and Se in different proportions. Nonlinear transmission for samples $As_{36}Se_{64}$, $As_{41}S_{32}Se_{27}$, $As_{40}S_{10}Se_{50}$, $As_{40}S_{20}Se_{40}$, $As_{40}S_{30}Se_{30}$, $As_{40}S_{40}Se_{20}$, $As_{40}S_{50}Se_{10}$ and Se-glass (Fig. 4, c). The extinction coefficient of S-containing-glasses is noticeably higher than that of the previously considered ones, which indicates the stronger ($> 20-30\,cm^{-1}$) absorption laser radiation and, as a result, stronger heating of the target surface. Disruption is achieved at intensities $> 400\,GW/cm^2$ at an incident pulse frequency of 10 kHz.

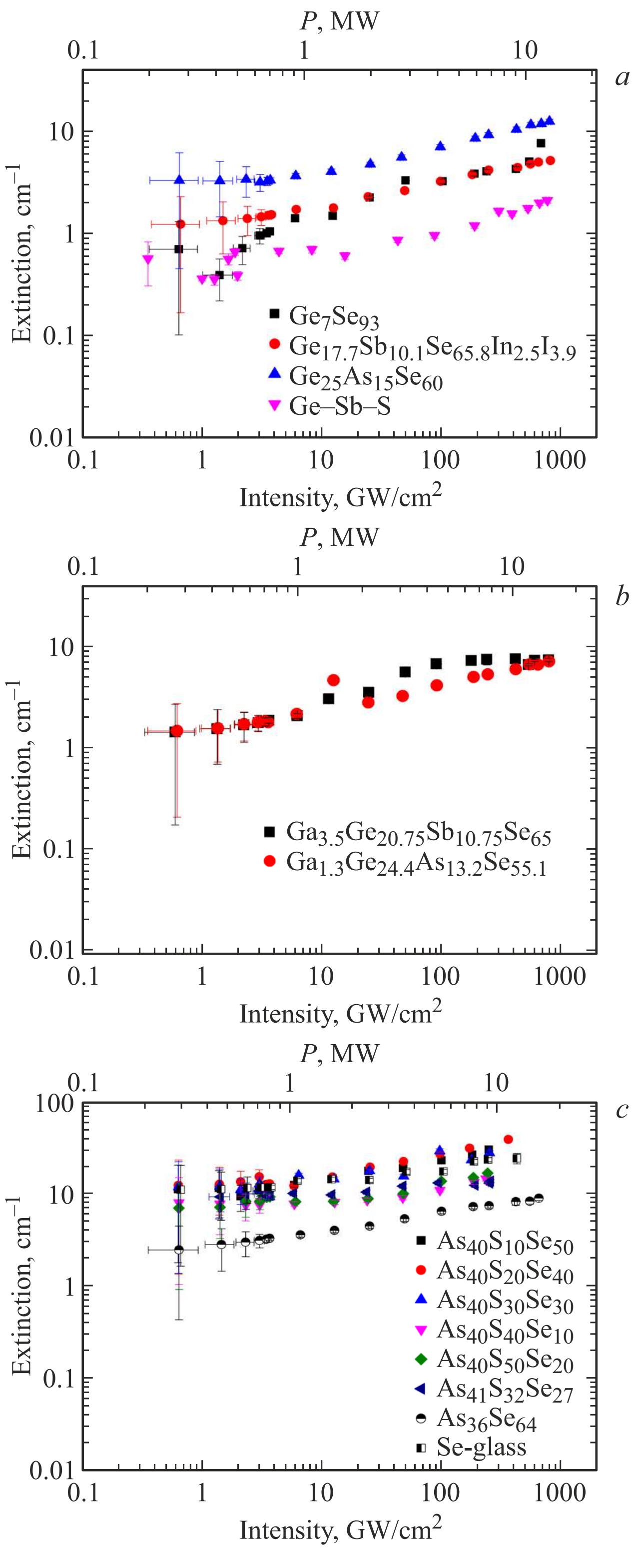

Figure 4. Extinction coefficients of IR glasses depending on the intensity of laser pulses with a wavelength of 1030 nm.

IR glass without sulfur $As_{36}Se_{64}$ in terms of radiation absorption is comparable to the Ge- and Ga-containing glasses considered above. The extinction coefficient of the selenic glass sample (Se-glass) is $> 20\,cm^{-1}$ at intensities $\sim 200\,GW/cm^2$, which is similar to the group of glasses with As, S and Se in the composition.

Conclusion

Summarizing all the results obtained, it can be concluded that the Ge_7Se_{93} material is attractive for use as an optical medium for diamond research in the near and mid-IR ranges. The material has good transmission and near-diamond refractive index: ~ 2.4 and 2.39 at wavelength of 1030 nm, respectively, which makes it an optimal candidate as an immersion composition for spectral measurements of diamond. However, it should be noted that chalcogenide compositions have relatively low linear transmittances in combination with strong absorption when the laser radiation intensity reaches about $100\,GW/cm^2$ at operating wavelength of 1030 nm, which imposes restrictions on both energy parameters laser radiation, and for the time of point laser exposure.

Funding

The study was supported by a grant from the Russian Science Foundation 21-79-30063.

Samples of chalcogenide glasses were obtained under the state assignment 0095-2019-0007.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] J.S. Sanghera, I.D. Aggarwal. J. Non-Cryst. Sol., **256–257**, 6–16 (1999).
[2] V. Shiryaev, M. Churbanov. *Chalcogenide glasses: preparation, properties and applications.* Ed. by J.-L. Adam and X. Zhang, (Woodhead Publishing Series in Electronic and Optical Materials: Nr 44. Oxford, Cambridge, Philadelphia, New Delhi, 2014), Ch. 1, p. 3–35
[3] A. Zakery, S.R. Elliot. *Optical Nonlinearities in Chalcogenide Glasses and their Application.* (Springer, 2007).
[4] V.S. Shiryaev, M.V. Sukhanov, A.P. Velmuzhov, E.V. Karaksina, T.V. Kotereva, G.E. Snopatin, B.I. Denker, B.I. Galagan, S.E. Sverchkov, V.V. Koltashev, V.G. Plotnichenko. J. Non-Cryst. Sol., **567**, 120939 (2021).
[5] S.O. Leonov, Y. Wang, V. S. Shiryaev, G.E. Snopatin, B.S. Stepanov, V.G. Plotnichenko, E. Vicentini, A. Gambetta, N. Coluccelli, C. Svelto, P. Laporta, G. Galzerano. Opt. Lett., **45**, 1346–1349 (2020).
[6] A. Lemiere, R. Bizot, F. Desevedavy, G. Gadret, J.-C. Jules, P. Mathey, C. Aquilina, P. Bejot, F. Billard, O. Faucher, B. Kibler, F. Smektala. Res. in Phys., **26**, 104397 (2021).
[7] P. Hari, J. Adair, N. Tolk, J. Sanghera, I. Aggarwal. J. Non-Cryst. Sol., **352**, 2430–2433 (2006).
[8] A. Zoubir, M.Richardson, C. Rivero, A. Schulte, C. Lopez, K. Richardson, N. Ho, Real Vallee. Opt Lett., **29** (7), 748–750 (2004).

[9] Q. Zhang, H. Lin, B. Jia, L. Xu, M. Gu. Opt. Express, **18** (7), 6885–6890 (2010).
[10] M. Zhang, T. Li, Y. Yang, H. Tao, X. Zhang, X. Yuan, Y. Zhiyong. Opt. Mater. Express, **9** (2), 555–561 (2019).
[11] Z. Liang, Y. Dandan, W. Leilei, Z. Jianghui, Z. Qian, X. Min, Z. Peiqing, D. Shixun. Opt. Mater., **85**, 220–225 (2018).
[12] V.S. Shiryaev, M.F. Churbanov, G.E. Snopatin, F. Chenard. Opt. Mater., **48**, 222–225 (2015).
[13] V.S. Shiryaev, E.V. Karaksina, T.V. Kotereva, M.F. Churbanov, A.P. Velmuzhov, M.V. Sukhanov, L.A. Ketkova, N.S. Zernova, V.G. Plotnichenko, V.V. Koltashev. J. Lumin., **183**, 129–134 (2017).
[14] M.F. Churbanov, V.S. Shiryaev, A.I. Suchkov, A.A. Pushkin, V.V. Gerasimenko, R.M. Shaposhnikov, E.M. Dianov, V.G. Plotnichenko, V.V. Koltashev, Yu.N. Pyrkov, J. Lucas, J.-L. Adam. Inorg. Mater., **43** (4), 506–512 (2007).
[15] A.E. Rupasov, P.A. Danilov, M.P. Smaev, M.S. Kovalev, A.S. Zolot'ko, A.A. Ionin, S.I. Kudryashov. Opt. Spectrosc., **128** (7), 928–931 (2020).
[16] E.D. Palik. *Handbook of Optical Constants of Solids* (Academic Press, Orlando, 1998).