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23

Prospects for the use of liquid immersion based on germanium nanoparticles in IR spectroscopy

© A.A. Nastulyavichus, R.A. Khmelnitskii, S.N. Shelygina, K.S. Pervakov, S.I. Kudryashov

Lebedev Physical Institute, Russian Academy of Sciences, Moscow, Russia

e-mail: ganuary_moon@mail.ru

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Using the methods of nanosecond laser ablation in isopropyl alcohol and dry grinding of germanium, germanium nanoparticles were obtained for their possible application in liquid high-index immersion. Structural, chemical, and optical characterization of colloidal nanoparticles was carried out using scanning electron microscopy, IR spectroscopy, and energy-dispersive X-ray spectroscopy.

Keywords: Germanium nanoparticles, laser ablation, liquid immersion, diamonds, IR spectroscopy.

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Introduction

The study of materials with a high refractive index, such as diamond, is of great interest [1]. Diamond is used in many areas of science and technology, including medicine, construction, nuclear power, jewelry [2–5].

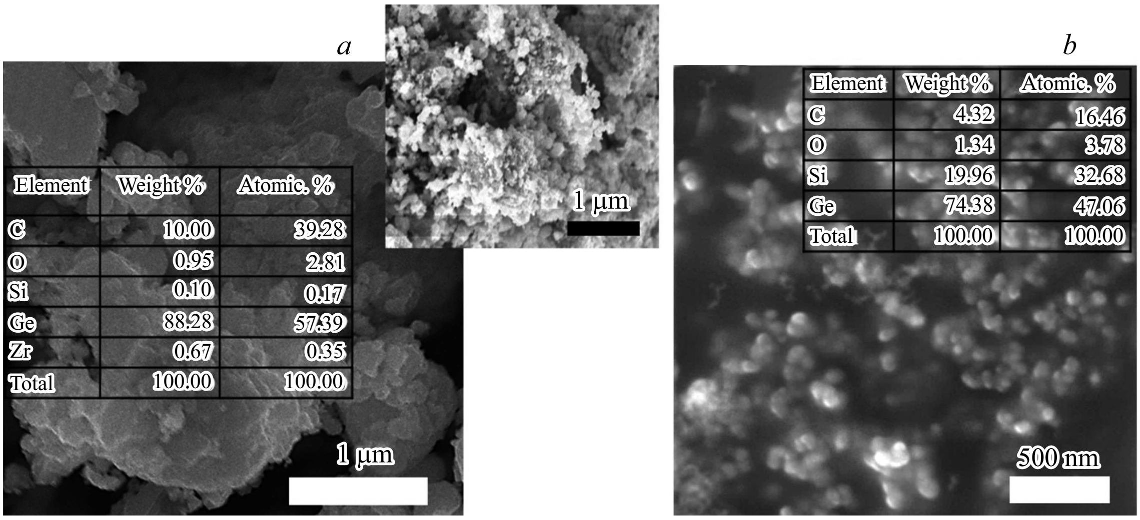
Methods such as photoluminescence, electron paramagnetic resonance spectroscopy, secondary ion mass spectrometry [6–8] are used to study diamonds. The most common method that is used in recognizing the authenticity of diamonds, as well as in determining the type of diamond and other necessary information, is IR Fourier spectroscopy [9,10]. Fourier spectroscopy is non-destructive and relatively inexpensive method. This method allows obtaining information about impurities in the diamond lattice. From the absorption value for different wavelengths, one can obtain information about the interactions between the configurations of nitrogen and boron impurities with the surrounding carbon atoms.

The study of the internal structure, defects inside the diamond is an important task. In addition, the position of defects and inclusions affects the color of the stone and therefore its price. Due to the fact that the beam undergoes a large number of reflections in a cut diamond, its studies, including IR spectroscopy, are difficult due to a weak signal output. Therefore, one solution to this problem is to create a medium surrounding the diamond, the refractive index of which is comparable to the refractive index of diamond, in order to obtain surface transparency due to immersion. The immersion medium allows direct transmission of rays. Currently, due to the lack of other decisions, liquid immersions with an insufficient refractive index and high toxicity are used [11,12]. It is also known that the condition of equality of the refractive index simultaneously with the liquid aggregate state of immersion can be achieved at temperatures of the order of hundreds of degrees Celsius, which are inconvenient for work. In this regard, installations based on liquid immersion are technically complex and expensive, and the production process is quite dangerous [13,14]. It is also widely known to use low-melting chalcogenide glasses for immersion, for example, AsGeSI, As_xS_{100-x}, which are used to seal diamonds as a result of heating [12].

In this work, the preparation of germanium nanoparticles for their possible application in liquid immersion for IR spectroscopy is considered. Immersion based on nanoparticles would simplify the process of studying the internal structure of diamonds, since in this case the sample does not need to be heated and does not require long-term cleaning after research.

Materials and methods

Germanium nanoparticles were obtained in isopropyl alcohol by ablation of germanium wafer (single-crystal, purity 99.99%) using the radiation of a fiber laser marker HTF MARK 20 (Bulat) on Yb^{3+} ions with wavelength of 1064 nm, pulse duration at half-height 120 ns, maximum energy per pulse 1 mJ and pulse repetition frequency up to 80 kHz. For laser generation of germanium nanoparticles, laser radiation with a pulse energy of 0.7 mJ, frequency of 20 kHz, and scanning rate of 300 mm/s (≈ 4 pulses per point) was used directly. Surface area 5×5 mm was selected on the sample, on which scanning was performed for 15 min. Germanium was placed in the glass cell and filled with isopropyl alcohol, the height of which above the wafer surface was ≈ 2 mm. The radiation was focused by Galvano scanner with a lens focal length of 160 mm. Laser ablation was associated with the formation of an erosive subcritical laser plasma of an ablation plume and the appearance of bubbles. Germanium nanoparticles were also obtained using the planetary ball mill in argon atmosphere. The centrifuge was used to separate the fraction of smaller nanoparticles. Germanium powder was centrifuged in isopropyl alcohol at 3000 rpm for 10 min.



Element	Weight %	Atomic %
C	10.00	39.28
O	0.95	2.81
Si	0.10	0.17
Ge	88.28	57.39
Zr	0.67	0.35
Total	100.00	100.00

Element	Weight %	Atomic %
C	4.32	16.46
O	1.34	3.78
Si	19.96	32.68
Ge	74.38	47.06
Total	100.00	100.00

Figure 1. (*a*) SEM visualization of germanium nanoparticles obtained by milling, inset: nanoparticles after centrifugation, (*b*) by laser ablation, inset: EDRS results.

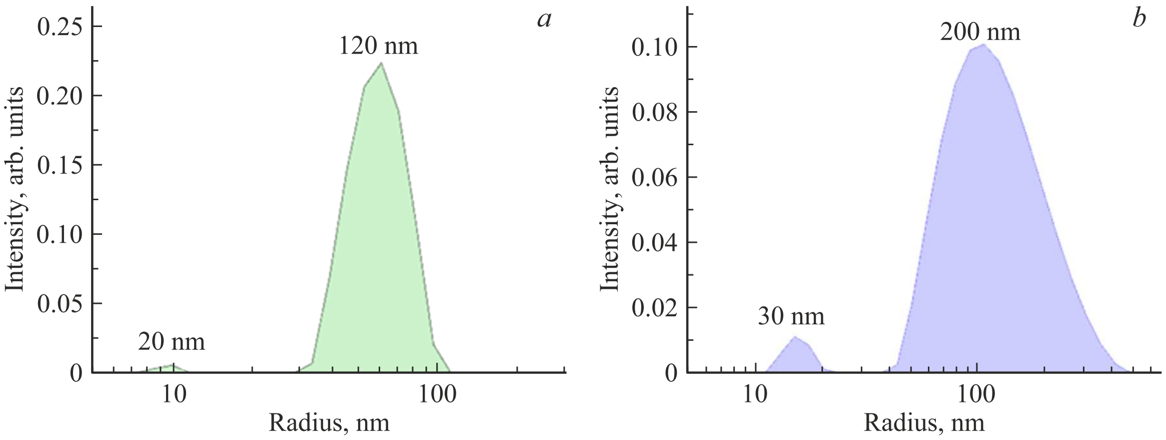


Figure 2. Particle size distribution for nanoparticles obtained by milling after centrifugation (*a*) as a result of laser ablation (*b*).

The germanium nanoparticles were visualized using a scanning electron microscope (SEM, TESCAN VEGA, Czech Republic). For this, colloidal nanoparticles were deposited and dried on a silicon wafer. The chemical composition was studied by the means of energy dispersive X-ray spectroscopy (EDRS) using AZTEC module (Oxford Instruments) of electron microscope. The nanoparticle sizes were measured using the dynamic light scattering method with ?Photocor compact? particle size analyzer (Photocor, Russia). For spectral studies, an IR spectrometer (V-70 (Bruker)) was used; for taking IR spectra, the cell made of zinc selenide plates polished on both sides was used.

Results and discussion

For SEM analysis, germanium nanoparticles were deposited on the surface of a polished silicon wafer. It has been found that the particles obtained by the laser method are predominantly spherical in shape and have a smaller particle size spread (30–300 nm) (Fig. 1, *b*). For particles obtained by grinding in a planetary ball mill, the particle size before centrifugation is from 50 nm to 3 μm (Fig. 1, *a*), after centrifugation is from 10 to 300 nm (Fig. 1, *a*, inset), and the shape of which is diverse (Fig. 1, *a*). The greatest difficulty lies in the fact that a small amount of nanoparticles remains after centrifugation.

The elemental composition of nanoparticles was determined by energy-dispersive X-ray spectroscopy (inset, Fig. 1). Both types of nanoparticles are characterized by the presence of oxygen on the surface. For particles obtained by the laser method, the oxidation is greater and in some cases reaches 15 at.%.

Figure 2 shows particle size distributions obtained using the dynamic light scattering method. Both cases are characterized by bimodal distribution containing the finer fraction of 20–30 nm and nanoparticles with sizes on the

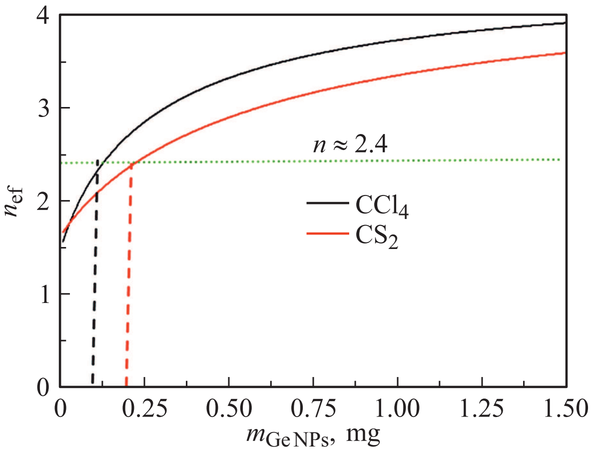


Figure 3. Dependence of the effective refractive index of the immersion medium on the mass of germanium nanoparticles.

order of 100–300 nm. For nanoparticles obtained as a result of milling, data are presented after centrifugation, since for the initial powder there is a large scatter of nanoparticles in size (up to several microns).

To obtain liquid immersion, nanoparticles must be mixed with a liquid that transmits in the IR range. Liquid carbon disulphide (CS_2) and carbon tetrachloride (CCl_4) were used in this work. The refractive index for the immersion medium must then coincide with the refractive index of diamond (≈ 2.412). To identify the correct proportions of the ratio of germanium nanoparticles and liquid the efficient medium method [15] was used.

The required mass of germanium nanoparticles was calculated by the formula

$$n_{\mathrm{ef}} = \sqrt{\frac{n^2_{\mathrm{Ge\,NPs}} \frac{m_{\mathrm{Ge\,NPs}}}{M_{\mathrm{Ge\,NPs}}} + n^2_{\mathrm{liquid}} \frac{m_{\mathrm{liquid}}}{M_{\mathrm{liquid}}}}{\frac{m_{\mathrm{Ge\,NPs}}}{M_{\mathrm{Ge\,NPs}}} + \frac{m_{\mathrm{liquid}}}{M_{\mathrm{liquid}}}}},$$

where $n_{\mathrm{Ge\,NPs}} = 4.4259$, $n_{CCl_4} = 1.45$, $n_{CS_2} = 1.62$, $M_{\mathrm{Ge\,NPs}} = 72.63$ g/mol, $M_{CCl_4} = 153.81$ g/mol, $M_{CS_2} = 76.14$ g/mol.

Fig. 3 shows the dependence of the effective refractive index of the immersion medium on the mass of germanium nanoparticles for both liquids. As a result, it was found that with 1 ml of carbon tetrachloride, 0.13 mg of germanium nanoparticles are required, with the same amount of liquid carbon disulfide, 0.22 mg of nanoparticles are needed (Fig. 3).

For IR studies, in work the zinc selenide cell was used (Fig. 4), since this material transmits well in the range 2.5–15 μm [16]. The refractive index for this material is 2.4028 at 10.6 μm.

Fig. 5 shows the transmission spectrum of the empty ZnSe cell, as well as the IR spectra of liquids (carbon tetrachloride, liquid carbon disulfide) in the range 400–5000 cm^{-1}. The transmission of zinc selenide is about 70%, which approximately coincides with the transmission range of diamonds. Liquid carbon disulfide transmits about 5% more than empty container. These liquids complement each other. For example, for studies of diamonds in the region of 1200 and 3700 cm^{-1}, CCl_4 has dips in the spectrum, while CS_2 doesn't have them. And in the region 1400 and 2200 cm^{-1} the opposite is true.

As an example for comparison of IR spectra in this work, natural diamond was considered without the use of immersion media, whose spectrum is shown in Fig. 5. The most important characteristics of diamonds are in the mid-IR range ($\sim$ 4000–400 cm^{-1}). The resulting IR spectrum of a diamond crystal contains the peak at 1282 cm^{-1}, which corresponds to *A* defect. It is known that nitrogen centers *A* contain a pair of nitrogen atoms in neighboring lattice sites and cause in the single-phonon region of the IR absorption spectra a system of bands 480, 1100, 1215 and 1282 cm^{-1} [17]. Based on the obtained data, one can say that this is an *IaA* type diamond (with two nitrogen groups). Carbon is responsible for the wide absorption in the range 1800–2700 cm^{-1}. The absorption peak at $\approx$ 3107 cm^{-1} corresponds to hydrogen, and the spectral range 100–1500 cm^{-1} includes absorption from nitrogen. Strong absorption bands between 1600 and 2700 cm^{-1} are also called two-phonon absorption bands, which are characteristic of all natural diamonds. As can be seen from the spectra, the main characteristic bands for diamond fall within the transmission bands for these liquids.

Fig. 5, *b* shows the transmission spectra for germanium nanoparticles obtained by the laser method and dissolved in liquid carbon disulfide and carbon tetrachloride in the zinc selenide cell. With the addition of particles, the transmission decreases in the case of CCl_4. Transmission is observed in the regions 1950–2250 and 3200–3800 cm^{-1}. Unfortunately, with the addition of nanoparticles, the transmission decreases, which is probably due to the content of impurities in the nanoparticles.

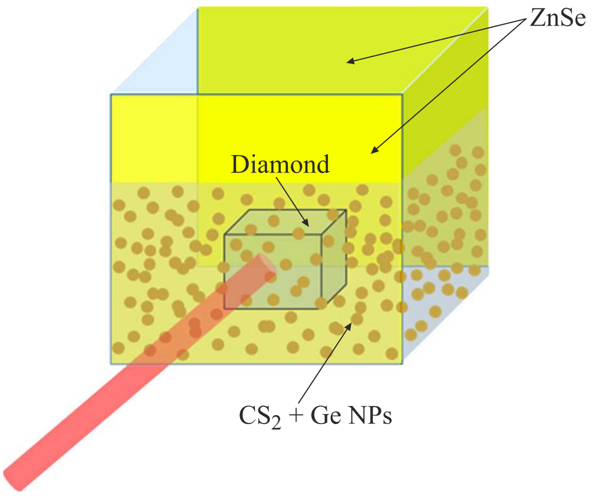


Figure 4. Scheme of IR studies of diamond in an immersion medium.

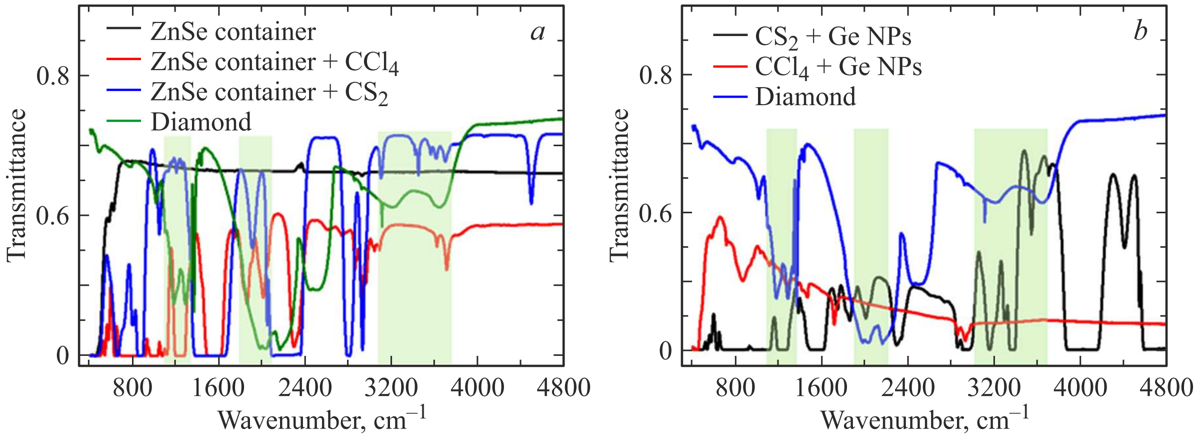


Figure 5. IR spectra of a cell made of ZnSe and with the addition of liquid carbon disulfide and carbon tetrachloride (*a*), germanium nanoparticles dissolved in carbon disulfide and carbon tetrachloride (*b*), in comparison with the spectrum of diamond.

In the course of the work, it became difficult to obtain the required amount of nanoparticles. Also, upon dissolution in CS_2 and CCl_4, the process of coagulation of nanoparticles is observed.

Conclusion

The work shows the prospects for the use of liquid immersion based on germanium nanoparticles for IR-spectroscopy of high-index materials (diamonds). For germanium nanoparticles obtained as a result of nanosecond laser-ablation process mediated by plasma and the formation of bubbles, a spherical shape and sizes in the range from 5 to 300 nm are characteristic. Nanoparticles obtained as a result of milling in the planetary ball mill have a large spread in size from 50 nm to 3 μm. Liquids were selected that transmit in the required range, and the required concentration of nanoparticles was determined. The transmission spectra measured in the IR range of carbon tetrachloride and liquid carbon disulfide, as well as colloidal solutions of germanium nanoparticles, showed that the characteristic bands for diamond fall within the transmission bands for these liquids and nanoparticles, but it is necessary to develop a method for obtaining pure nanoparticles.

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Conflict of interest

The authors declare that they have no conflict of interest.

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