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Isotopic Shift in the IR of Germanium Single Crystals

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A clear correspondence between the position of the peak in the IR absorption spectrum of isotopically pure germanium single crystals and the mass number of the isotope was found. The dependence obtained can be used for express analysis of the mass composition of isotopically pure germanium single crystals.

Keywords: germanium, isotopes, absorption.

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Introduction

Single crystal germanium (Ge) is the first and most studied semiconductor material [1–3]. In addition, it is in high demand as the main optical material for the atmospheric transparency window of $8-14\,\mu$m [4,5], and along with silicon it is a material for the range of $3-5\,\mu$m [6]. Recently widely developed thermal imaging devices use the single-crystal germanium optics extensively [4,5].

It has been shown in [7–12] that the isotopic composition of germanium and a number of other crystals significantly affects many important material properties related to the phonon structure of the material. This is primarily thermal conductivity and a number of optical and electrophysical characteristics.

The crystal lattice perceives another isotope as a kind of structural defect. This defect, of course, has a smaller effect on the physical properties of the crystal than the widely studied structural defects, such as, for example, dislocations. Nevertheless, new, previously unknown properties are found in more perfect monoisotopic single crystals. And the development of an economically acceptable production technology expands the possible fields of their application. This process is clearly observed in the development of technology to produce germanium single crystals.

The development of technology for purification crystals from impurities and structural defects is permanently expanding the scope of these crystals application. To use Ge as detectors of ionizing radiation, highly sensitive low-background infrared radiation (IR) receivers, it is required to ensure the concentration of electrically active impurities in the material at the level of $10^9-10^{10}\,\mathrm{cm}^{-3}$. And this extremely complex technological problem has been solved. The technology of growing dislocation-free crystals has also been implemented [2,3].

The previously underestimated effect of electrically neutral impurities, such as oxygen, on the properties of Ge has been revealed [1]. Further development of research of germanium has shown that a number of new possibilities for the use of this material are opening up, associated with the development of technology for producing isotopically pure single crystals [13–15]. Natural germanium ($^{\mathrm{nat}}$Ge, atomic number is 32, atomic weight is 72.59) is a mixture of stable isotopes with mass numbers 70, 72, 73, 74, 76 (^{70}Ge — 20.57%, ^{72}Ge — 27.45%, ^{73}Ge — 7.75%, ^{74}Ge — 36.50%, ^{76}Ge — 7.73%) [7].

Back in 1942, I.Ya. Pomeranchuk theoretically predicted [8] and subsequently discovered a significant anomaly in the temperature dependences of thermal conductivity for isotopically pure and structurally perfect single crystals of germanium, silicon, and diamond [9,15.18].

The heat capacity and thermal conductivity of germanium crystals with different isotopic compositions were measured in [9,11,19] in the temperature range of $2.8-100\,\mathrm{K}$. It has been found that monoisotopic Ge, in comparison with the natural material, not only has a significantly higher thermal conductivity in this range but also features a thermal emf [20,21]. This information is of practical interest when using germanium components in space research.

A „giant“ contribution to the hypersound damping coefficient from the scattering of sound waves by isotopic disorder in $^{\mathrm{nat}}$Ge single crystals compared to monoisotopic crystals has been predicted in [21]. This is important because experiments using hypersonic waves expand the possibility of gaining new information about the mechanisms of relaxation of phonon modes. The information on the propagation of hypersound in crystals at low temperatures make it possible to use them as a basis for development of storage devices for microwave signals with a large size of dynamic memory.

Monoisotopic Ge is promising for the development of elements of spintronics and quantum computers [22]. Research activities of the possibility to create quantum computers based on solid-state devices are extensively developing. The unit of quantum information (qubit) in them is the nuclear spin state of the atom [23,24]. An ensemble of qubits is created by introducing atoms of elements with non-zero nuclear spin into a matrix of silicon or germanium single crystals. To rule out the uncontrolled interaction of qubits with nuclear spins of matrix atoms, it is required to minimize the content of odd isotopes in the matrix. The odd isotope in germanium is ^{73}Ge [14].

Single crystals of the ^{76}Ge isotope are used as a material of detectors to study double beta decay processes and other fundamental physical processes [11,25,26]. Ge (Ga) detectors are used in neutrino detection experiments and other fields [27].

Further development of studies of monoisotopic Ge crystals undoubtedly implies a number of new applications of this material in microelectronics, IR optics, nanophotonics, and other fields of solid state physics. Therefore, the possibility of a relatively fast and simple analysis of the isotopic purity of monoisotopic Ge crystals becomes an essential problem. Since the physicochemical properties of different isotopes of the same material are extremely similar, it is necessary to develop a method for objective identification (express analysis) of the corresponding Ge isotopes.

Usually, in the case of germanium, the method of determining the mass difference of isotopes using the „extended" X-ray absorption fine structure (EXAFS) spectroscopy is used for this purpose. The measurements are carried out with femtometer accuracy by the amplitude of relative atomic vibrations, by the temperature dependence of the difference in the Debye-Waller factors, and by the difference in the average interatomic distances between the nearest neighbors of the first coordination sphere of atoms in isotope samples [28,29]. It is possible to determine isotopic purity by the inductively coupled plasma mass spectrometry (ICP-MS) [14,30]. However, these methods are very time consuming and require the use of relatively rare and sophisticated equipment.

Earlier, in [31,32], when studying the IR absorption spectra of isotopically pure ^{70}Ge and ^{74}Ge single crystals, a shift of the phonon absorption bands was found with a change in the mass composition.

In general, this shift was approximated by the following relationship:

$$\nu = 1.6\nu_0 e^{-kM}, \tag{1}$$

where ν_0 is frequency at the maximum of the corresponding phonon absorption band of natural germanium, M is isotope mass number, k is an exponential coefficient in the range of 0.0062−0.0072.

This study continued the above-mentioned investigation using samples of all five stable isotopes of germanium, and the technology for isotope production differed significantly from that previously used [3,31].

Experiment procedure

The experiments were carried out on samples of isotopically pure germanium single crystals ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, ^{76}Ge. High-purity isotopically enriched germanium was produced by the hydride method at the Devyatykh Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences with subsequent purification of isotopically enriched polycrystalline germanium by zone melting [7,14,33].

Single crystals of germanium isotopes were grown in the laboratory of the Institut für Kristallzachtung (IKZ, Berlin) by the Czochralski method from a quartz crucible in the atmosphere of high-purity argon. Single crystals were grown in the $\langle 100 \rangle$ crystallographic direction; the crystal diameter was 13−17 mm [14,34].

The isotopic purity of the produced germanium ingots at each stage was determined by inductively coupled plasma mass spectrometry (ICP-MS) [14,30].

Samples for the investigations were cut from the grown single crystals and then polished according to a specially developed technology of chemical-mechanical optical processing. The working surfaces of the plates were polished according to class IV (GOST 11141-76), roughness of the polished surfaces corresponded to Rz $0.05\,\mu$m (on a base length of 0.08 mm according to GOST 2789-73).

Transmission spectra were measured (according to the requirements of GOST [35]) on a Bruker Vertex 70 Fourier spectrometer in a spectral range of $1.3-330\,\mu$m. The measurement error for the wave number was $\sim 1\,\mathrm{cm}^{-1}$, and for the transmission coefficient it was 0.5%.

The reference samples were optically processed plates of Ge single crystals of natural isotopic composition ($^{\mathrm{nat}}$Ge) grown at the Tver State University and at the Zaporozhye Titanium and Magnesium Plant from knowingly different batches of initial raw materials and produced by different techniques: Czochralski and Stepanov methods [36]. Zone-refined polycrystalline germanium (GPZ grade) with a material resistivity of more than $47\,\Omega\cdot$cm (at a temperature of 23°C) was used as a raw material.

Experimental results and discussion

It is well known that the absorption of IR radiation in germanium depends on its resistivity [4,37]. In this study, pure, undoped samples with high electrical resistivity were used.

Fig. 1 shows the transmission spectrum of natural germanium (Ge nat) and five monoisotopic germanium samples in a range of $10-40\,\mu$m. The behavior of each spectrum is approximately the same, there is a slight difference in transmission. The main difference consists in the correspondence of the absorption bands to the corresponding wavelength; it is clearly seen that the isotopic composition of crystals affects the position of characteristic Ge absorption bands in the considered spectral range. In the spectral range of $11-40\,\mu$m we have identified 16 absorption bands; this situation corresponds to the data of [38,39]; for the ^{70}Ge isotope, the position of characteristic bands was identified for the first time.

Fig. 2 shows in more detail the part of the frequency range of $407-438\,\mathrm{cm}^{-1}$ of the spectrum for the eighth absorption band ($\nu_8 = 423.2\,\mathrm{cm}^{-1}$; the range corresponds to wavelengths of $23-24\,\mu$m), not previously considered in [31,32] due to the large thickness of the samples used. In these studies, the main attention was paid to the investigation of peaks ($\nu_1 = 840.3\,\mathrm{cm}^{-1}$, $\nu_2 = 849.0\,\mathrm{cm}^{-1}$, $\nu_3 = 641.9\,\mathrm{cm}^{-1}$), precise studying of which requires thickness of samples of the order of 1 cm. At the same time, the high absorption coefficient did not allow for reliable recording of the effect observed in the spectral range of $407-438\,\mathrm{cm}^{-1}$. With the thin samples used in this study, the difference can be clearly seen in the shifts of the spectral absorption bands of the samples of natural ($^{\mathrm{nat}}$Ge) and monoisotopic germanium crystals (^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, ^{76}Ge) in the spectral frequency range of $407-438\,\mathrm{cm}^{-1}$. The isotopic shift of this absorption band was clearly determined . Fig. 3 shows the dependences of the frequencies ν of the phonon absorption peaks of these crystals on M, the mass number of the isotope.

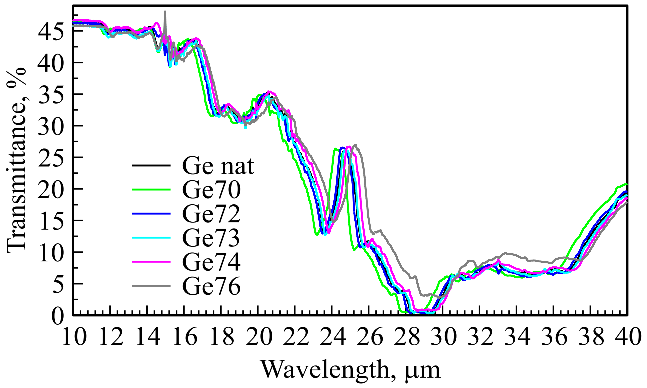

Figure 1. Transmission spectrum of germanium monoisotopic samples in a range of $10-40\,\mu$m.

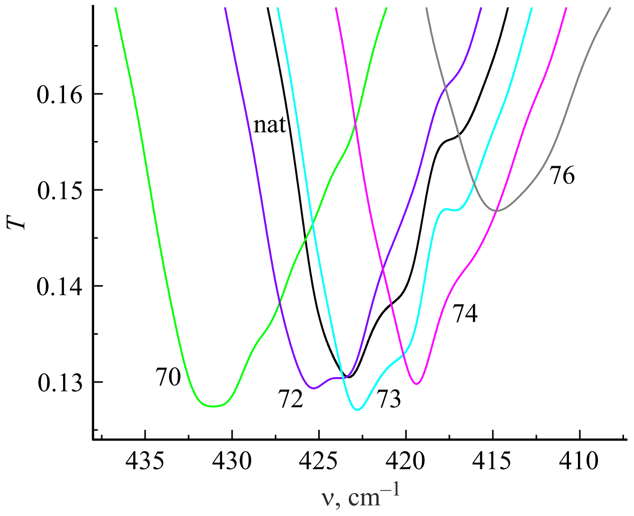

Figure 2. The dependence of the spectral transmission (T) demonstrating positions of the absorption peaks in the spectra of samples of natural (nat) and monoisotopic germanium crystals (mass numbers of isotopes are indicated: ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, ^{76}Ge) in the frequency range of $407-438\,\mathrm{cm}^{-1}$ of the spectrum (corresponding to wavelengths of $23-24\,\mu$m).

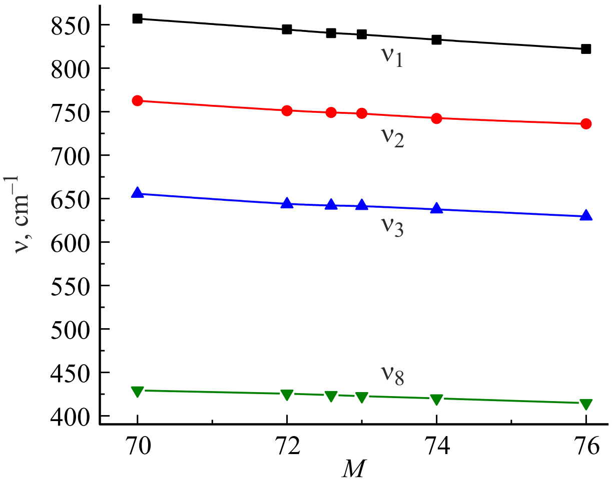

Figure 3. Frequency dependences ν of phonon absorption peaks of isotopically pure germanium single crystals on M, the isotope mass number for the peaks in the table.

The experimental results have shown (see the table) that the lattice absorption peaks observed in germanium single crystals of natural isotopic composition in samples of germanium monoisotope crystals (^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, ^{76}Ge) are shifted according to dependence (1). The result is clearly illustrated in Fig. 3 at frequencies for the first three bands ($\nu_1 = 840.3\,\mathrm{cm}^{-1}$, $\nu_2 = 849.0\,\mathrm{cm}^{-1}$, $\nu_3 = 641.9\,\mathrm{cm}^{-1}$) and the eighth band ($\nu_8 = 423.2\,\mathrm{cm}^{-1}$).

Thus, shifts of the peaks of phonon absorption bands were recorded as the germanium isotope mass composition (1) changes from mass number 76 to 70 (within $\sim 18\,\mathrm{cm}^{-1}$ for the first peak, within $\sim 13\,\mathrm{cm}^{-1}$ for the second and third peaks, within $\sim 9\,\mathrm{cm}^{-1}$ for the eighth peak). They are small, however, they are precisely determined and noticeably exceed the error of the instrument.

Moreover, in ^{70}Ge and ^{72}Ge single crystals an increase in the frequency of the absorption band (ν) is observed, and in ^{73}Ge, ^{74}Ge and ^{76}Ge single crystals frequency decreases compared to single crystals of natural isotopic composition (^{72,59}Ge).

Previously, in [31,32] the IR absorption spectra of isotopically pure ^{70}Ge and ^{74}Ge single crystals were studied using a „Hitachi-225“ double-beam IR spectrophotometer. Isotopes were produced by centrifugal separation at the Institute of Molecular Physics of the „Kurchatov Institute“ Russian Research Center with an enrichment of 99.99%.

Position of peaks of phonon absorption bands in Ge crystals of various isotopic compositions

Composition of germanium	Peaks of phonon absorption bands in germanium							
	ν_1, cm^{-1}		ν_2, cm^{-1}		ν_3, cm^{-1}		ν_8, cm^{-1}	
	Experimental data	Calculated by formula (1), $k = 0.00645$	Experimental data	Calculated by formula (1), $k = 0.00645$	Experimental data	Calculated by formula (1), $k = 0.00645$	Experimental data	Calculated by formula (1), $k = 0.00645$
^{70}Ge	856.9	856.0	762.5	762.9	655.6	653.9	429.2	431.1
^{72}Ge	844.6	845.0	751.0	753.2	643.5	645.5	424.4	425.6
^{72,59}Ge (natural)	840.3	841.8	749.0	750.3	643.1	423.2	423.9	
^{73}Ge	838.9	839.6	748.0	748.4	641.5	641.4	421.0	422.8
^{74}Ge	832.6	834.2	742.0	743.5	637.6	637.2	418.4	420.1
^{76}Ge	822.0	823.5	736.0	734.0	629.5	629.1	414.1	414.7

Their fine chemical purification was carried out at the Lawrence Berkeley Laboratory by the method of multiple zone melting (33 runs). Polycrystalline ^{70}Ge and ^{74}Ge ingots thus purified were used as raw materials for growing *n*-type Ge single crystals by the Czochralski method. The technology for producing these isotopes, as well as for growing crystals, described in [9,11,40] differed significantly from the methods for producing samples studied in this work.

However, the values of the isotopic shifts of the IR absorption bands obtained in this case completely correlated with each other and corresponded to dependence (1) experimentally obtained from measurements carried out on samples of isotopically enriched germanium produced by various methods.

Conclusion

The effect of the isotopic composition on the properties of germanium crystals is due to the fact that isotopic disorder breaks the translational invariance of the lattice. This leads to the scattering of phonons, hence the shift of the peaks of phonon absorption bands with a change in the mass composition of the germanium isotope.

The isotopic shift in the range of $11-40\,\mu$m was studied for the first time by optical spectroscopy for all five stable germanium isotopes simultaneously. Moreover, for the ^{70}Ge germanium isotope, such a study was performed for the first time.

It was found that for all isotopes there is a clear correspondence between the position of the peak in the IR phonon absorption spectrum and the mass number of the Ge isotope. The obtained experimental dependence can be recommended for use in express analysis of the mass composition of isotopically pure germanium crystals.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] O.I. Podkopaev, A.F. Shimansky, *Vyraschivanie monokristallov germaniya s nizkim soderzhaniem dislokatsiy i primesey* (Sib. feder. un-t, Krasnoyarsk, 2013) (in Russian).

[2] L. Claeys, E. Simoen. *Germanium-based technologies: from materials to devices* (Berlin: Elsevier, 2007). www.sciencedirect.com/science/book/9780080449531

[3] M. Bosi, G. Atolini. Progress in Crystal Growth and Characterization of Materials, **56**, 146–174 (2010). DOI: 10.1016/j.pcrysgrow.2010.09.002

[4] I.A. Kaplunov, V.E. Rogalin, Fotonika, **13** (1), 88–106 (2019) (in Russian). DOI: 10.22184/FRos.2019.13.1.88.106

[5] V.V. Korotaev, G.S. Melnikov, S.V. Mikheev, V.M. Samkov, Yu.I. Soldatov. *Osnovy teplovideniya* (ITMO, SPb., 2012) (in Russian).

[6] E.E. Alekseev, S.Yu. Kazantsev, I.G. Kononov, V.E. Rogalin, K.N. Firsov. Opt. Spectrosc., **124** (6), 821–825 (2018). DOI: 10.1134/S0030400X18060036.

[7] A.V. Gusev, A.M. Gibin, I.A. Andryuschenko, V.A. Gavva, E.A. Kozyrev, FTT, **57** (9), 1868–1870 (2015) (in Russian)

[8] I.Ya. Pomeranchuk, ZhETF, **2**, 245–254 (1942) (in Russian).

[9] V.I. Ozhogin, A.V. Inyushin, A.N. Taldenkob, A.V. Tikhomirov, G.E. Popov, E. Haller, K. Itoh, Pisma v ZhETF, **63** (6), 463–467 (1996) (in Russian).

[10] I.Ya. Pomeranchuk, ZhETF **12**, 419 (1942) (in Russian).

[11] K.M. Itoh, W.L. Hansen, E.E. Haller, J.W. Farmer, V.I. Ozhogin, A. Rudnev, A.V. Tikhomirov. J. Mater. Research., **8** (6), 1341–1347 (1993). DOI: 10.1557/JMR.1993.1341

[12] M. Cardona, M.L.W. Thewalt. Rew. Mod. Phys. **77** (4), 1173–1224 (2005). DOI: 10.1103/RevModPhys.77.1173

[13] *Vusokochistye veschestva*, Eds. M.F. Churbanov, Yu.A. Karpov, P.V. Zlomanov, V.A. Fedorova (Nauchny mir, M., 2018) (in Russian).

[14] V.A. Gavva, O.Yu. Troshin, S.A. Adamchik, A.Yu. Lashkov, N.V. Abrosimov, A.M. Gibin, P.A. Otopkova, A.Yu. Sozin, A.D. Bulanov, Neorganicheskie materialy, **58** (3), 258–263 (2022) (in Russian). DOI: 10.31857/S0002337X22030058

[15] Izotopy: svoystva, poluchenie, primenenie, Eds. V.Yu. Baranov (IzdAt, M., 2000) (in Russian).

[16] M. Sanati, S.K. Estreicher, M. Cardona. Solid State Commun., **131**, 229–233 (2004). DOI: 10.1016/j.ssc.2004.04.043

[17] A.V. Inyushkin. Inorganic Materials, **38** (5), 427–433 (2002). DOI: 10.1002/pssc.200405341.

[18] A.A. Kaminsky, V.G. Ral'chenko, A.P. Bolshakov, A.V. Inyushkin, DAN, **464** (6), 676-678 (2015) (in Russian). DOI: 10.7868/S086956521530009X

[19] A.P. Zhernov, FTT, **41** (7), 1185–1189 (1999) (in Russian).

[20] A.V. Inyushkin, A.N. Taldenkov, V.I. Ozhogin, K.M. Itoh, E.E. Haller. Phys. Rev. B., **68**, 153203 (2003). DOI: 10.1103/PhysRevB.68.153203

[21] I.G. Kuleev, I.I. Kuleev, A.V. Inyushkin, V.I. Ozogin. J. Exp. Theor. Phys., **101** (2), 322–330 (2005). DOI: 10.1134/1.204779

[22] K.A. Valiev. Physics-Uspekhi, **48** (1), 1–36 (2005). DOI: 10.1070/PU2005v048n01ABEH002024.

[23] B.E. Kane. Nature, **393**, 33–137 (1998). DOI: 10.1038/30156

[24] R.M. Jock, A.M. Tyryshkin, J.W. Beeman, E.E. Haller, K.M. Itoh, S.A. Lyon. Phys. Rev. Lett., **115**, 247601 (2015). DOI: 10.1103/PhysRevLett.115.247601

[25] S. Schoenert. Nucl. Phys. Proc. Suppl., **145** (1), 242–245 (2005). DOI: 10.1016/j.nuclphysbps.2005.04.014

[26] C. Aalseth, D. Anderson, R. Arthur et. al. Nucl. Phys. Proc. Suppl., **138** (1), 217–220 (2005). DOI: 10.1016/j.nuclphysbps.2004.11.052

[27] H. Simka, M. Hierlemann, M. Utz, K.F. Jensen. J. Electrochem. Soc., **143**, 2646–2654 (1996). DOI: 10.1149/1.1837063

[28] M.F. Churbanov, A.D. Bulanov, V.A. Gavva, E.A. Kozyrev, I.A. Andryuschenko, V.A. Lipsky, S.M. Zyryanov. *Method for obtaining isotope variety of elementary germanium with high isotope and chemical purity.* Patent RU 2641126 (2016).

[29] Yu. Purans, V.I. Ozhogin, S.I. Tyutyunnikov, Perspektivnye materialy, **8**, 395–399 (2010) (in Russian).

[30] A.M. Potapov, P.A. Otopkova, A.D. Bulanov, In: *Tezisy dokladov Tretiego sezda analitikov Rossii* (GEOHI RAN, Moscow, 2017), p. 97 (in Russian).

[31] V.E. Rogalin, I.S. Tsenina, I.A. Kaplunov, Nauchno-tekh. vedomosti SPb. Gos. politekh. un-ta, **4–1** (183), 353–358 (2013) (in Russian).

[32] I.A. Kaplunov, V.E. Rogalin, M.Yu. Gavalyan. Opt. Spectrosc., **118** (2), 240–246 (2015). DOI: 10.1134/S0030400X15020083.

[33] A.V. Gusev, A.D. Bulanov, S.V. Filimonov, S.M. Zyryanov, D.G. Arefyev, M.F. Churbanov, I.A. Andryuschenko, A.M. Potapov, V.A. Gavva, S.A. Adamchik, Perspektivnye materialy, **10**, 17–20 (2011) (in Russian).

[34] M.F. Churbanov, V.A. Gavva, A.D. Bulanov, N.V. Abrosimov, E.A. Kozyrev, I.A. Andryushchenko, V.A. Lipskii, S.A. Adamchik, O.Yu. Troshin, A.Yu. Lashkov, A.V. Gusev. Cryst. Res. Technol., **52** (4), 1700026(6) (2017). DOI: 10.1002/crat.201700026

[35] GOST 3520-92. *Materialy opticheskie. Metody opredeleniya pokazateley oslableniya.* Vved. 1993-07-01 (Izd-vo standartov, M., 1992).

[36] Yu.M. Smirnov, I.A. Kaplunov. Materialovedeniye, **5**, 48–52 (2004) (in Russian).

[37] Yu.I. Ukhanov, Opticheskie svoistva poluprovodnikov (Nauka, M. 1977) (in Russian).

[38] V.A. Lipskiy, V.O. Nazaryants, T.V. Kotereva, A.D. Bulanov, V.A. Gavva, V.V. Koltashev, M.F. Churbanov, V.G. Plotnichenko. Appl. Opt., **58**, 7489–7496 (2019). DOI: 10.1364/AO.58.007489

[39] H.D. Fuchs, C.H. Grein, M. Bauer, M. Cardona. Phys. Rev. B., **45** (8), 4065 (1992). DOI: 10.1103/PhysRevB.45.4065

[40] K.M. Iton, W.L. Hansen, E.E. Haller, J.W. Farmer, V.I. Ozhogin, A. Rudnev, A. Tikhomirov. J. Mater. Res., **8**, 1341–1347 (1993). DOI: 10.1557/JMR.1993.1341

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