Вісник ХНУ імені В.Н. Каразіна, серія «Фізика», вип. 30, 2019. с. 24-29

PACS: 81.10.Fq, 61.50.−f, 07.20.Mc

UDC: [548.5:546.47’23]+539.1.074

The possibility to obtain ZnSe crystals with high structural perfection for cryogenic bolometric technics

I.A. Rybalka[1,2], I.A. Tupitsyna[1,2], B.V. Grynyov[1,2], R.V. Vovk[1], M.V. Kislitsa[1], G.Ya. Khadzhai[1], Yu.I. Boyko[1]

1 V.N. Karazin Kharkiv National University, 4 Svobody Sq., 61022 Kharkiv, Ukraine
2 Institute for Scintillation Materials National Academy of Sciences of Ukraine, 60 Nauky ave., 61072 Kharkiv, Ukraine
ruslan.v.vovk@univer.kharkov.ua

ORCID: 0000-0003-1700-0173

DOI: 10.26565/2222-5617-2019-30-03

In this work the samples of ZnSe zinc selenide crystal grown from the melt by Bridgman method from high-purity (chemical and radio) raw materials were studied for further use in experiments on the search for neutrinoless double beta decay. The microstructure of the test samples was studied. Chemical selective etching, first of all, has allowed to determine the nature of distribution and sizes of area twinning, as well as the etch pits along twins boundaries. It is shown the figures found by chemical etching are the dislocation exits to the studied crystal surface. The dislocation density was estimated by counting the dislocation etch pits on the plane perpendicular to the growth direction and was 10^4 cm^{-2}. As a rule, thermophysical conditions of ZnSe crystal growth, as well as high concentration of foreign inclusions and impurities in the crystal significantly affect the formation of twins and growth dislocations and are the cause of the optical, electrical, and mechanical heterogeneity of the material. The optical and electrical characteristics of the samples were measured. The absorption bands observed in the optical transmission spectra of the visible and IR ranges gave important information about the presence of local defects and impurities in the crystal, namely in 470÷550 nm and 580÷650 nm regions – absorption by point defects and in 3÷15 μm region – Fe^{2+}, CSe and CSe_2 absorption. The total transmission level in the visible range reached 60 %, which is lower than the theoretical one and due to scattering by defects. The phonon thermal conductivity of ZnSe sample was measured in the temperature range 5÷298 K. Based on the approximation of obtained temperature dependences of the thermal conductivity, it was shown that the phonon mean free path at low temperatures is comparable with the distance between twins’ boundaries in the sample.

Keywords: ZnSe crystal, twins, dislocations, optical transmission, thermal conductivity.

Можливість отримання кристалів ZnSe з високою структурною досконалістю для кріогенної болометричної техніки

І.А. Рибалка[1,2], І.А. Тупіцина[1,2], Б.В. Гриньов[1,2], Р.В. Вовк[1], М.В. Кислиця[1], Г.Я. Хаджай[1], Ю.І. Бойко[1]

1 Харківський національний університет імені В.Н. Каразіна, м. Свободи 4, 61022, Харків, Україна
2 Інститут сцинтиляційних матеріалів Національної академії наук України, пр-т Науки, 60, Харків 61072, Україна

В роботі досліджено зразки кристалу селеніду цинку ZnSe, що вирощено з розплаву методом Бріджмена з високочистої (хімічно та радіаційно) сировини, для подальшого використання в експериментах з пошуку безнейтринного подвійного бета-розпаду. Вивчено мікроструктуру досліджуваних зразків. Хімічне вибіркове травлення, в першу чергу, дозволило виявити характер розподілу та розміри двійникових областей, а також фігури травлення вздовж границь двійників. Показано, що виявлені за допомогою хімічного травлення фігури є виходами дислокацій на досліджувану поверхню кристалу. Оцінена щільність дислокацій шляхом підрахунку дислокаційних ямок травлення на площині, перпендикулярній напрямку росту, яка склала 10^4 $см^{-2}$. Як правило, теплофізичні умови вирощування кристалу ZnSe, а також висока концентрація сторонніх включень та домішок у кристалі суттєво впливають на формування двійників і ростових дислокацій та є причиною оптичної, електричної, механічної неоднорідності матеріалу. Проведено вимірювання оптичних та електричних характеристик зразків. Смуги поглинання, що спостерігалися в спектрах оптичного пропускання у видимому та ІЧ діапазонах, дали важливу інформацію про наявність локальних дефектів і домішок в кристалі, а саме, в областях 470÷550 нм й 580÷650 нм – поглинання точковими дефектами, та в області 3÷15 мкм – поглинання Fe^{2+}, CSe и CSe_2. Загальний рівень пропускання у видимому діапазоні досягав 60 %, що нижче теоретичного, й це пов’язано з розсіюванням на дефектах. Проведено вимірювання фононної теплопровідності зразка ZnSe в інтервалі температур 5÷298 К. За результатами апроксимації отриманих температурних залежностей теплопровідності показано, що довжина вільного пробігу фононів при низьких температурах є порівняною з відстанню між границями двійників в зразку.

Ключові слова: кристал ZnSe, двійники, дислокації, оптичне пропускання, теплопровідність.

Возможность получения кристаллов ZnSe с высоким структурным совершенством для криогенной болометрической техники

И.А. Рыбалка[1,2], И.А. Тупицина[1,2], Б.В. Гринёв[1,2], Р.В. Вовк[1], М.В. Кислица[1], Г.Я. Хаджай[1], Ю.И. Бойко[1]

1 Харьковский национальный университет имени В.Н. Каразина, м. Свободы 4, 61022, Харьков, Украина

2 Институт сцинтилляционных материалов Национальной академии наук Украины, пр. Науки, 60, Харьков 61072, Украина

В работе исследованы образцы кристалла селенида цинка ZnSe, выращенного из расплава методом Бриджмена из высокочистого (химически и радиационно) сырья, для дальнейшего использования в экспериментах по поиску безнейтринного двойного бета-распада. Изучена микроструктура исследуемых образцов. Химическое избирательное травление, в первую очередь, позволило выявить характер распределения и размеры двойниковых областей, а также фигуры травления на границах двойников. Показано, что выявленные с помощью химического травления фигуры являются выходами дислокаций на исследуемую поверхность кристалла. Оценена плотность дислокаций путем подсчета дислокационных ямок травления на плоскости, перпендикулярной направлению роста, которая составила 10^4 см$^{-2}$. Как правило, теплофизические условия выращивания кристалла ZnSe, а также высокая концентрация инородных включений и примесей в кристалле существенно влияют на формирование двойников и ростовых дислокаций и являются причиной оптической, электрической, механической неоднородности материала. Проведены измерения оптических и электрических характеристик образцов. Наблюдаемые в спектрах оптического пропускания в видимом и ИК диапазонах полосы поглощения дали важную информацию о наличии локальных дефектов и примесей в кристалле, а именно, в областях 470÷550 нм и 580÷650 нм – поглощение точечными дефектами, и в области 3÷15 мкм – поглощение Fe^{2+}, CSe и CSe_2. Общий уровень пропускания в видимом диапазоне достигал 60 %, что ниже теоретического, и это связано с рассеяниям на дефектах. Проведены измерения фононной теплопроводности образца ZnSe в интервале температур 5÷298 К. По результатам аппроксимации полученных температурных зависимостей теплопроводности показано, что длина свободного пробега фононов при низких температурах сопоставима с расстоянием между границами двойников в образце.

Ключевые слова: кристалл ZnSe, двойники, дислокации, оптическое пропускание, теплопроводность.

Introduction

One of fundamental problems of high-energy physics today is study of rare events processes (double beta decay and other rare nuclear decay events). Whatever of the nature of such processes, the general conditions for their experimental proof are: development of the conditions for obtaining detectors which guarantee an extremely low (ideally zero) radiation background; creation of detectors with extremely high sensitivity. For the construction of new highly sensitive detectors, very often crystals are used as for the cryogenic bolometric technique. The cryogenic bolometric technique is one of the promising experimental approaches in neutrinoless double beta decay (0νDBD) experiments because of the achievable excellent energy resolution and high detection efficiency [1]. The crystals what used in this case, in addition to low concentration of radioactive impurities must have a perfect crystal structure to provide high sensitivity of the detector.

In recent years, zinc selenide ZnSe has been considered as the most promising material for use in scintillation bolometers in double beta decay experiments [2]. Today, the first part of the obtained ZnSe enriched crystals with ^{82}Se selenium isotope is successfully undergoing bolometric tests in the underground Laboratori Nazionali del Gran Sasso (Italy) [3] as part of LUCIFER project [4], that opens up prospects for the further widespread use of this material as scintillation detector in 0νDBD experiments. However, the questions of influence of defect various types in these crystals on phonon and scintillation signals at low temperatures remain unexplored. The solution of these problems will optimize the technology for producing crystals and increase the cryogenic detectors sensitivity.

This article reports on the possibility to obtain high purity ZnSe crystals with high degree of structural perfection for use in scintillation bolometers and study of neutrinoless double beta decay.

Experimental methodology

ZnSe crystals were grown from the melt using the vertical Bridgman technique in the graphite crucibles with a diameter of 50 mm under inert gas of argon at a pressure up to $15 \cdot 10^6$ Pa; the crystallization speed was 1 mm/h; the temperature in the melt zone – up to 1850 K; the melt overheating value ΔT was varied in 30÷200 K range. The crystals were grown from stoichiometric ZnSe powder, which we synthesized in [3] by gas-phase synthesis from elemental Zn and Se with high chemical and radio purity. Chemical purity and radio-purity analysis of Zn and Se elements and ZnSe crystal were performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and High-resolution gamma-ray spectrometry with cooled hyperpure germanium (HPGe) at Istituto Nazionale di Fisica Nucleare (Italy) and at Laboratori Nazionali del Gran Sasso (Italy) and were shown in the work [3]. Chemical purity of ZnSe crystal was 9,5 ppm, radio purity was 14,56 mBq/kg.

Microstructure defects were studied with an optical microscope. The fine structure of the crystal was investigated using chemical selective etching method. The effect of various etchants on the test ZnSe crystals was

studied. The composition solution: HNO_3 (1 part), CrO_3 (2 parts) and H_2O (3 parts) under the etching mode T = 368 K and t = 10 min, was optimal for chemical polishing; and the composition solution: HCl (2 parts) and CrO_3 (1 part) under the etching mode T = 293 K and t = 10 min – the most effective etchant for dislocation detecting.

The transmission spectrum in the visible region was measured using Shimadzu UV mini-1240 spectrophotometer operating in the range 200÷1100 nm with 1 nm resolution. The transmission spectrum in the IR region was measured using Shimadzu Fourier Transform Infrared spectrophotometer IR Affinity-1 operating in the range 7800÷350 cm^{-1} (1,3÷28,5 μm) with 2 cm^{-1} resolution. ZnSe sample with size 10×10×2 mm was optically polished on parallel planes 10×10 mm.

The electric resistivity of ZnSe sample with 10×10×2 mm dimensions were measured by classic 4 probes method. The current and the voltage were measured with a V7-35 electronic voltmeter at the room temperature. The electric resistivity value was calculated by the formula: $\rho = 2\pi sU/I$, where s is the distance between sensitive contacts. ZnSe electric resistivity was measured in the range from 10 Ω·cm to 10^{12} Ω·cm at the supply voltage of the current circuit from 5 V to 300 V and at the sensitivity of the V7-35 voltmeter of the current 1 nA and the voltage 1 μV.

The thermal conductivity of a sample 60×3×3 mm in size was measured by the stationary uniaxial heat flow method in the temperature range 5÷298 K. The heat flow was directed along the crystallographic direction [100].

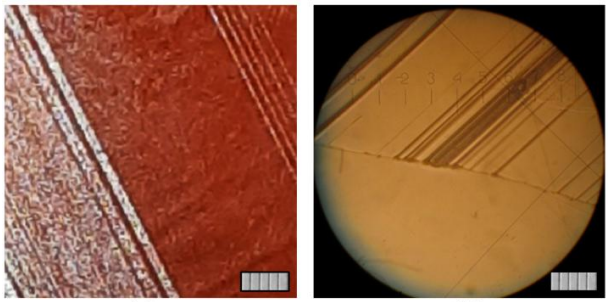
Results and discussion

In this work we have studied samples cut from a ZnSe undoped crystal ∅50 mm and l = 100 mm in size, obtained by the technology described in [3]. The crystal structure was a single crystal ingot with the presence of large twin regions oriented at 45° angle to the growth axis.

It is known [5] that ZnSe is a compound with tetrahedral atomic coordination, which may have the structure of sphalerite (S) or/and wurtzite (W). The type of structure for ZnSe is determined by many factors: crystallometric stability criterion [5] and degree of ionicity [6], deviations from stoichiometry [7] and equilibrium crystallization conditions [8], and the doping of controlled impurities [9, 10]. It is known [11] that during the growth of undoped ZnSe crystals from the melt a wurtzite-sphalerite (W→S) phase transition proceeds, which temperature is 1693 K at heating and 1683 K at cooling. Due to the incompleteness of the W→S phase transition one-dimensional disordering of the crystal lattice S occurs, which leads to the formation of the twins and packing defects of twinning type.

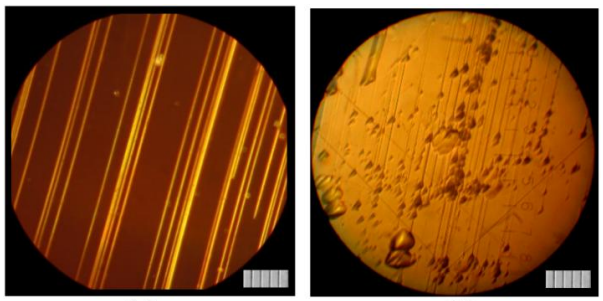
Obvious evidence of the presence of twins in the studied crystals associated with the polymorphic transformation in the solid phase, first of all, is the presence of characteristic inclined bands on the side surface of the grown ingots [12]. This is explained by the different orientations of the reflective surfaces (110) and microcavities due to thermal etching. Such bands, which we have observed by an optical microscope at low magnification, are shown in Fig. 1a during thermal etching of the side surface and in Fig. 1b during chemical etching of the cross section crystal. The width of a single band can be from 1 μm to several millimeters.

Chemical selective etching, first of all, has allowed to determine the nature of distribution and sizes of area twinning. In Fig. 1b and Fig. 2a the microstructure of sections perpendicular to the growth direction of ZnSe crystal are shown, on which a clear block twin structure is visible. The bands of the twins are characterized by change in the contrast of the image, since the reorientation of the crystal lattice in the twin (and the possible change in the density of atoms on its surfaces) causes the deviate of the light beam reflected from the crystal surface in microscope. The boundaries of twins are areas of segregation of chemical impurities, which in turn lead to generator of new structural defects. So, we have observed the formation of etching figures along the boundaries of twins, as shown in Fig. 2b.



(a) (b)

Fig. 1. Twinning bands – boundaries of twin blocks in ZnSe: a – during thermal etching on the side surface of the crystal (1 mm); b – during chemical etching on the cross section crystal (50 μm).



(a) (b)

Fig. 2. Structural defects on the cross section ZnSe crystal, detected by chemical selective etching method (50 μm): a – during chemical polishing; b – during chemical etching of dislocations.

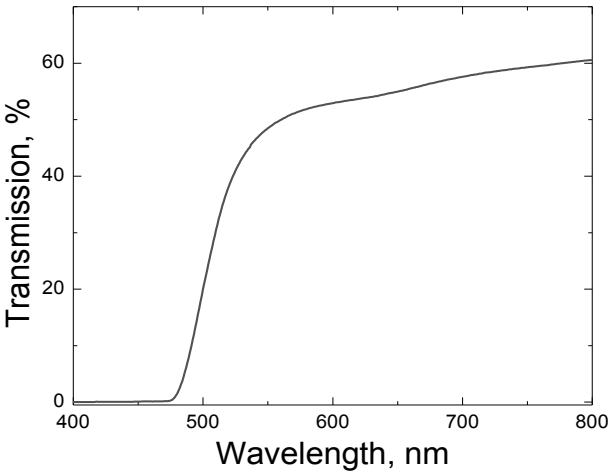
The figures found by chemical etching are the dislocation exits to the studied crystal surface [13]. Dislocation etching is based on change in the local chemical potential near structural inhomogeneities caused by crystal lattice deformation. Significant internal stresses appearing in the crystal bulk near the inclusions of excess phases can be a source of generation of such dislocations.

In Fig. 2b it is seen that the dislocation etch pits have a triangular shape. The dislocation density, estimated by counting the dislocation etch pits on the plane perpendicular to the growth direction, is 10^4 cm^{-2} and substantially depends on the concentration of foreign inclusions and impurities in the crystal, as well as on thermophysical growth conditions. In the places of the greatest accumulation of dislocations their density reaches $\sim 2 \cdot 10^6$ cm^{-2}. As a rule, defects of this type in ZnSe crystals are the cause of the optical, electrical and mechanical heterogeneity of the material.

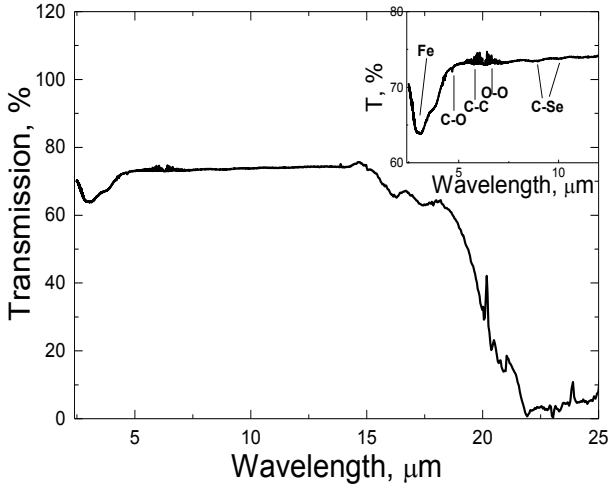
For each scintillation crystal, the optical transmission is fundamental to minimize the reabsorption of scintillation light and, as a result, increase the overall light output. In the case of ZnSe scintillation bolometer the transmission in combination with the luminescence spectrum [14] can be used as an indicator for bolometric and scintillation characteristics. Also, the study of optical characteristics will help to optimize the growth conditions and obtain crystals with higher structural perfection. The possible absorption bands observed in the transmission spectra can give important information about the presence of local defects and impurities in the crystal.

In Fig. 3a it is shown the transmission spectrum of ZnSe crystal in the visible region, measured along the twinning plane. In the region of fundamental absorption band edge of 470÷550 nm as well as in the range of 580÷650 nm the absorption bands due to point defects are observed. In the range of 650÷800 nm there are no obvious absorption bands associated with defects that form local trapping centers in the band gap. The total transmission level in this range reaches 60 %, which is lower than the theoretical one and due to scattering by defects.

Study of optical characteristics of the test sample in the IR spectral region has showed the presence of an absorption band of uncontrolled iron impurity in the range 2,5÷5 μm (Fig. 3b). This is due to the contamination of the crystal with furnace construction materials when grown from the melt. The iron impurity is easily included in Zn sublattice (Fe^{2+} and Zn^{2+} have close radiuses) and, as shown in [3], degrades ZnSe bolometric signal due to strong resonance phonon scattering by Fe^{2+} ions [15]. The maximum Fe concentration in the crystal should not exceed 1 ppm to provide satisfactory bolometric characteristics. Also, impurity defects, such as carbon and oxygen compounds, can affect ZnSe bolometric characteristics and their presence in the crystal can be determined from the oscillatory absorption bands in the IR spectra. In Fig. 3b (insert), they are given harmonic atomic bond frequencies, characteristic of ZnSe crystal [16], for the main impurity defects: C-O – 2138 cm^{-1} (4,68 μm), C-C – 1641 cm^{-1} (6,09 μm), O-O – 1580 cm^{-1} (6,33 μm), C-Se – 1036 cm^{-1} (9,65 μm).



(a)



(b)

Fig. 3. Optical transmission spectra of ZnSe crystal in the visible (a) and IR (b) spectral ranges.

The presence of impurities in the crystal can be a source of free charge carriers, which, in turn, can degrade the bolometric signal. Based on the IR transmission spectrum of the test sample the absorption by free electrons was not observed. An indirect estimate of the free charge carriers concentration in ZnSe sample was carried out by the value of the measured electrical resistivity, which was about 10^{10} Ω·cm. Note that optimum bolometric characteristics were obtained for crystals with electrical resistivity of the order of 10^8 Ω·cm [3].

In order to obtain a more complete understanding of the mechanisms of phonon scattering in ZnSe the phonon thermal conductivity of ZnSe crystal was measured in the temperature range 5÷298 K. The temperature dependence of the thermal conductivity (λ) of ZnSe test sample is shown in Fig. 4. The temperature dependence of λ was measured along the twinning plane (110) and is consistent with the data of [17].

The experimental data were approximated using an equation, which describe low- and high-temperature mechanisms of phonon scattering [18]

$$\lambda^{-1}(T) = \frac{A_0}{A_1} T^{-3} + A_2 T^{-2} e^{-A_3/T}. \qquad (1)$$

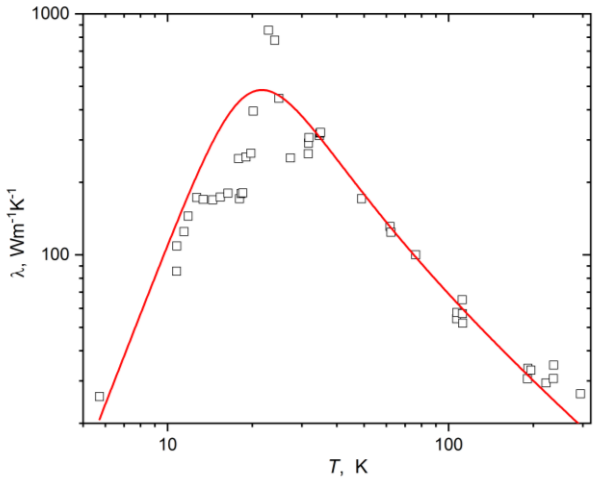


Fig. 4. The temperature dependence of the thermal conductivity of ZnSe crystal measured along the twinning plane (110). Points – experiment, line – approximation by formula (1)..

When fitting the coefficients A_1-A_3 were varied. The first term describes phonon scattering at the boundaries, and parameter A_1 has the physical meaning of the mean free path of the phonons at the lowest temperatures, where phonons with long wavelengths predominate [19]. The second term describes phonon-phonon scattering in the high temperature region [20]. According to the results of approximation of the obtained temperature dependences of λ, the mean free path of the phonons at the low temperatures is about 20 μm, which is comparable with the distance between twins' boundaries in the crystal.

Conclusion

1. The paper shows the possibility to obtain a large-block ZnSe crystal from the melt from high-purity (chemical and radio) raw materials synthesized by the gas-phase method. It is shown that the crystal structure is a single crystal ingot with the presence of large twin regions oriented at 45° angle to the growth axis. The width of a single band can be from 1 μm to several millimeters.

2. It is determined that the dislocation density, estimated by counting the dislocation etch pits on the plane perpendicular to the growth direction, is 10^4 cm^{-2} and substantially depends on the content of foreign inclusions and impurities in the crystal, as well as on the thermophysical growth conditions.

3. Optical and electrical characteristics of the samples were studied. It is shown that in the region of fundamental absorption band edge of 470÷550 nm as well as in the range of 580÷650 nm the absorption bands due to point defects are observed. While, in the range of 650÷800 nm the transmission level reaches 60 %, which is lower than the theoretical one and due to scattering by defects. It is shown that in the IR spectrum of optical transmission there are absorption bands of uncontrolled impurities (Fe^{2+}, CSe, and CSe_2) in the range of 3÷15 μm, which impair the bolometric characteristics of ZnSe.

4. Phonon thermal conductivity of ZnSe sample was measured in the temperature range 5÷298 K. Based on the approximation of obtained temperature dependences of the thermal conductivity, it was shown that the phonon mean free path at low temperatures is comparable with the distance between twins' boundaries in the crystal.

References

1. C. Enss, D. McCammon. J. Low Temp. Phys., 151, 5 (2008).
2. S. Pirro, C. Arnaboldi, S. Capelli, et al. Astroparticle Physics, 34, 344 (2011).
3. I. Dafinei, S. Nagorny, S. Pirro, et al. Journal of Crystal Growth, 475, 158 (2017).
4. F. Ferroni. IL NUOVO CIMENTO C, 33, 5, 27 (2010) DOI 10.1393/ncc/i2011-10696-1.
5. L.V. Atroshchenko, L.A. Sysoev. Kristallographiya, 5-6, 16, 1026 (1971) [in Russian].
6. V.M. Koshkin, L.A. Sysoev. Sbornik trudov "Monokristally i tekhnika", VNII monokristallov, Kharkov v. 2, s. 57 (1970).
7. M.G. Mil'vidskii, B.V. Osvenskii. Strukturnye gefekty monokristallov poluprovodnikov, Metallurgiya, M. (1984), 256 s.
8. M.P. Kulakov, V.D. Kulakovskii, A.V. Fadeev. Neorganicheskie Materialy, 12, 10, 1867 (1976).
9. R. Triboulet. Semiconductor Science and Technology, 6, 9, A18 (1991).
10. M. Shone, B. Greenberg, M. Kaczenski. Journal of Crystal Growth, 86, 1-4, 132 (1990).
11. E.E. Lakin, I.V. Krasnopol'skii, V.P. Kuznetsov. Sbornik nauchnyh trudov "Scintillyatsionnye materialy", VNII monokristallov, Kharkov v. 20, s. 16 (1987).
12. L.V. Atroshchenko, L.P. Gal'chinetskii, I.A. Rybalka, et al. Functional Materials, 12, 4, 610 (2005).

13. A.A. Chernov, E.I. Givargizov, Kh.S. Bagdasarov. Sovremennaya kristallographiya (Tom 3. Obrazovanie kristallov), Nauka, M. (1980), 407 s.
14. Ioan Dafinei, Mauro Fasoli, Fernando Ferroni, et al. IEEE Trans. Nucl. Sci., 57(3), 1470 (2010).
15. A.T. Lonchakov, V.I. Sokolov, N.B. Gruzdev. FTT, 47, 8, 1504 (2005).
16. Kazuo Nakamoto. Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry, 6th Edition, John Wiley & Sons, New York. (2009), 424 p.
17. Glen A. Slack. Phys. Rev. B, 6, 10, 3791 (1972).
18. R. Berman. Teploprovodnost' tverdyh tel, per. s angl. L.G. Aslamazova, pod red. V.Z. Kresina, Mir, M. (1979), 286 s.
19. G. Zahn, B.A. Merisov, G. Kloss, et al. Cryst. Res. Technol., 23, 6, 509 (1988).
20. M.V. Kislitsa, G.Ya. Khadzhai, E.S. Gevorkyan, and R.V. Vovk. Low Temp. Phys., 45, 419 (2019).