

## Comparison of refractive indices of amorphous and crystalline $\text{As}_2\text{S}_3$

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Method to calculate refractive index and transparency range dispersion of amorphous  $\text{As}_2\text{S}_3$  is proposed. It is based on effective dielectric permittivity models for porous composite media, comparison of glass and crystal density and use of data on refractive index of the crystal. It is shown that the best agreement of calculated and experimental values of refractive index of glass is obtained within the wavelength interval  $460 \div 670$  nm when using Lorenz-Lorentz formula. It is established that  $\text{As}_2\text{S}_3$  glasses possess pores with filling factor  $q = 0.057$  submerged to isotropic matrix with approximately two times smaller porosity ( $q_M = 0.031$ ).

Предложен способ вычисления показателя преломления и дисперсии в области прозрачности аморфного  $\text{As}_2\text{S}_3$  с помощью моделей эффективной диэлектрической проницаемости пористых композитных сред. Способ основан на сравнении плотностей стекла и кристалла и использовании данных по показателю преломления кристалла. Показано, что наилучшее согласие вычисленных и экспериментальных значений показателя преломления стекла достигается в интервале длин волн  $460 \div 670$  нм при использовании для расчета формулы Лоренц-Лорентца. Установлено, что стекла  $\text{As}_2\text{S}_3$  обладают порами с фактором заполнения  $q = 0.057$ , погруженными в изотропную матрицу с меньшей, приблизительно в два раза, пористостью ( $q_M = 0.031$ ).

Among chalcogenide amorphous semiconductors, glasses of  $\text{As}_2\text{S}_3$  and structurally similar substances got the widest and most diversified practical application. Reviews of investigations in  $\text{As}_2\text{S}_3$  structure and physical properties are presented in [1–4]. The possibility of  $\text{As}_2\text{S}_3$  film photodoping with Ag [5] extended the researches in connection with possible  $\text{As}_2\text{S}_3$  application in diffraction optics, holography, optical recording of information [3, 4]. The changes in refractive index of  $\text{As}_2\text{S}_3$  under various optical and thermal actions [3, 4] is of considerable importance in the photodoping processes and applications.

When studying the microstructure of amorphous  $\text{As}_2\text{S}_3$ , it is compared with structure of arsenic sulphide crystal — auripigment [2, 6]. Auripigment has a monoclinic lattice ( $C_{2h}$  crystal class) with unit cell parameters

$a = 1.147$  nm,  $b = 0.957$  nm,  $c = 0.425$  nm,  $\beta = 90^\circ 23'$  and  $z = 4$ . The crystal structure elements are  $\text{AsS}_3$  pyramids connected with sulphur atom links into a corrugated grid in ( $a, c$ ) plane. The As–S bond is predominantly covalent while the inter-grid bond is predominantly Van der Waals one. This defines the layered crystal structure and easy cleavability along planes containing  $\mathbf{a}$  and  $\mathbf{c}$  axes.

In  $\text{As}_2\text{S}_3$  glasses, the short-range order is retained in first two coordination spheres [2]. Under melting,  $\text{AsS}_3$  structural elements are conserved in  $\text{As}_2\text{S}_3$  without As–S bond length change, but grids are bent and possibly cross the neighboring grids. Grid disintegration to twelve-membered rings is also possible. In other words, amorphous  $\text{As}_2\text{S}_3$  retains some "memories" of the crystalline structure. The glass density  $\rho_{gl} = 3.17$  g/cm<sup>3</sup> is lower than crystal one  $\rho_{cr} = 3.46$  g/cm<sup>3</sup>,

thus indicating its porosity. The existence of pores undoubtedly promotes penetration of metal atoms into the glass at photodoping processes.

The principal refractive indices (RI) of crystalline  $\text{As}_2\text{S}_3$  were measured in transparency region (visible and near IR range) [6]. A large number of works is aimed at amorphous glass RI measurements both in bulk and film state, and at various treatments [4, 7, 8]. Optical constants of crystalline and amorphous  $\text{As}_2\text{S}_3$  are presented in [9]. In consideration of  $\text{As}_2\text{S}_3$  optical isotropy in the glassy state and the ratio of crystal density to glass one, comparison of RI in two states is of interest. The absence of noticeable light scattering in the glass indicates small pore radii in comparison with light wavelength  $\lambda$ , i.e. pores are of nanometer size. This fact permits the effective dielectric permittivity  $\varepsilon_{eff}$  (EDP) models to be applied when analyzing the glass RI. These models are used successfully in studies of optical properties of composite materials containing nanoparticles [10, 11]. In this study, we compared the RI of  $\text{As}_2\text{S}_3$  crystal and glass, basing on  $\varepsilon_{eff}$  models assuming the pores with  $\varepsilon_n = 1$  to be "nanoparticles".

For a medium being mixture of two substances with dielectric permittivities  $\varepsilon_1$  and  $\varepsilon_2$ , the filling factor  $q$  is introduced. That is the specific volume filled by substance with  $\varepsilon_1$ , correspondingly,  $q' = 1 - q$  for substance with  $\varepsilon_2$ . If the mixtures are optically homogeneous and light scattering is absent (except for Rayleigh scattering), then EDP model is applicable thereto.

The simplest model is that proposed by Newton:

$$\varepsilon_{eff} = \varepsilon_1 q + \varepsilon_2 (1 - q). \quad (1)$$

For transparent and optically isotropic mixtures,  $\varepsilon_1 = n_1^2$  and  $\varepsilon_2 = n_2^2$ , where  $n_1$  and  $n_2$  are the respective RI. However, at the end of XIX century, Clausius and Mossotti have proposed a new formula for static dielectric permittivity derived under assumption of difference between field  $E' = E + (4\pi/3)P$  acting on a molecule situated in center of empty sphere, and field  $E$  in surrounding medium [12]. Here  $P = N\alpha E'$  is the polarization of substance with  $\varepsilon_1$ ,  $N$  and  $\alpha$  are molecular concentration and polarizability.

A similar formula was proposed independently by Lorenz and Lorentz for optical frequency range:

$$\frac{\varepsilon_{eff} - 1}{\varepsilon_{eff} + 2} = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} q + \frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} (1 - q). \quad (2)$$

Formula (2) is used successfully to determine RI of liquid and solid solutions. Results of  $n = \sqrt{\varepsilon_{eff}}$  determination obtained with (2) are better than those from (1). For gaseous mixtures, formula (2) is reduced to (1). Application of (2) for composite nanostructured media was discussed also in [13, 14].

The next step in theory of composite medium was taken by Maxwell and Garnett (1904 [15]) in connection with description of optical properties of metal colloidal solutions in dielectric matrices and description of granular metal film spectra. The formula proposed in [15] has the form:

$$\frac{\varepsilon_{eff} - \varepsilon_2}{\varepsilon_{eff} + 2\varepsilon_2} = q \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}. \quad (3)$$

Here  $\varepsilon_1 = \varepsilon_1' - i\varepsilon_1''$  is the complex dielectric permittivity of a spherical metal particle;  $\varepsilon_2$ , permittivity of dielectric medium surrounding the particles. For solutions, formula (3) predicts existence of a narrow plasma resonance band in absorption spectrum of noble metals and dependence of that spectral band position on factor  $q$ . Results of calculations using (3) are in agreement with many experimental data [16]. But in accordance with modern concepts [11], formula (3) is applicable to describe the optical properties of composite media at small  $q$  ( $q < 1/3$ ). At larger  $q$ , the concept of matrix surrounding particles is not adequate anymore (percolation case), and a number of interpolation formulae is proposed to describe optical properties of optically homogeneous composite media (see [10, 11, 16]). When studying the optical characteristics of solid solutions of nanoparticles, a problem of filling factor  $q$  determination. Recently, the Rutherford backscattering technique is used to determine  $q$  [17]. But the determination accuracy of the mean  $q$  value is not good enough (about 10 % error). Determination of  $q$  becomes simpler when comparing optical characteristics of crystals and amorphous media, because their densities are known as a rule with a high accuracy. The density ratio provides the filling factor value of amorphous material with pores.

When calculating the RI of amorphous  $\text{As}_2\text{S}_3$ , principal refractive indices of biaxial  $\text{As}_2\text{S}_3$  crystal were used, as well as the glass/crystal density ratio. To find the fac-

for  $q$  from densities, we have proposed the formula:

$$\frac{\rho_{gl}}{\rho_{cr}} = \kappa(1 - q), \quad (4)$$

where  $\rho_{gl}$  and  $\rho_{cr}$  are densities of glass and crystal, respectively;  $q$ , the filling factor of amorphous material with pores;  $\kappa = \rho_m/\rho_{cr}$ , density ratio of matrix surrounding the pores to crystal. The  $\kappa$  value may be greater or smaller than 1, depending on whether the matrix is denser than crystal or not. When writing formula (4), a significant radii difference between pores with  $q$  factor and pores in matrix with  $\kappa < 1$  is assumed. Here we believe the term "matrix" to be applicable when  $q < 1/3$ , as it was mentioned. It will be shown below that this condition is accomplished for amorphous  $As_2S_3$ . According to different sources,  $\rho_{cr} = 3.42$  g/cm<sup>3</sup> [18], 3.49 g/cm<sup>3</sup> [7] or 3.46 g/cm<sup>3</sup> [2], and  $\rho_{gl} = 3.17$  g/cm<sup>3</sup>. We used data from [2] in our calculations. Therefore,  $\rho_{gl}/\rho_{cr} = 0.916$ . The matrix density  $\rho_m$  and  $\kappa$  value are fitting parameters. Taking into account the short-range order preservation in amorphous  $As_2S_3$ , one may assume small difference of  $\kappa$  from 1.

The  $n_a$  and  $n_c$  principal values were measured in [6] using the light interference in thin crystal plates. Those are accurate to within 0.01. The  $n_{a,c}(\lambda)$  measurements were done for  $\lambda > 0.46$  nm due to edge absorption. As the crystal is a mica-type layered crystal, the direct  $n_b$  measurements are impossible. To measure  $n_b$  and the angle between optical axes, the authors [6] used the birefringence measurements proceeding from conoscopic figures in polarized light observed at various angles of incidence onto thin plates. The RI of bulk amorphous  $As_2S_3$  were measured in [19] by means of prism technique, accurate to within  $10^{-6}$ . But due to edge absorption, the  $n_{gl}(\lambda)$  measurements were bound by wavelengths  $\lambda \geq 0.56$  nm; at  $\lambda < 0.56$  nm,  $n_{gl}(\lambda)$  measurements were carried out using interference technique on thin  $As_2S_3$  films of various thickness [7]. These measurements are summarized in [9]. The RI measurement results in thin  $As_2S_3$  films prepared by various ways are given in [4, 8] also. The data from the mentioned works have been used in our calculations.

We have pre-checked the formulae (1–4) applicability to compare RI of glass and crystal at  $\lambda = 625$  nm admitting  $n_a = 3.19$ ,  $n_b = 2.53$ ,  $n_c = 2.84$  and  $n_{gl} = 2.62$  [9]. It was taken into account that glass is optically isotropic, the matrix density was supposed to be equal to one of crystal ( $\kappa = 1$ ). The filling factor was taken to be  $q = 0.084$  and mean dielectric permittivity of matrix

$$\varepsilon_2 = \frac{n_a^2 + n_b^2 + n_c^2}{3} = 8.23. \quad (5)$$

As  $\varepsilon_1 = 1$  for pores, formulae (1), (2), and (3) are reduced to the following:

$$\varepsilon_{eff} = \varepsilon_2 - q(\varepsilon_2 - 1), \quad (6)$$

$$\varepsilon_{eff} = \frac{3\varepsilon_2 - 2q(\varepsilon_2 - 1)}{3 + q(\varepsilon_2 - 1)}, \quad (7)$$

$$\varepsilon_{eff} = \frac{\varepsilon_2[2\varepsilon_2 + 1 - 2q(\varepsilon_2 - 1)]}{2\varepsilon_2 + 1 + q(\varepsilon_2 - 1)}. \quad (8)$$

Calculation of  $n_{gl} = \sqrt{\varepsilon_{eff}}$  using formulae (6–8) results in the following:  $n_{gl} = 2.76$  by Newton formula (6),  $n_{gl} = 2.55$  by Lorenz-Lorentz formula (7) and  $n_{gl} = 2.72$  by Maxwell-Garnet formula (8). These pre-check result in the following conclusions:

1. The amorphous  $As_2S_3$  RI found are substantially lower than mean crystal RI  $\bar{n}_{cr} = \sqrt{\varepsilon_2} = 2.87$  (5), thus indicating the crystal porosity.

2. Calculated values of  $n_{gl}$  are deviated from experimental value  $n_{gl} = 2.62$ . There is  $\Delta n = 0.14$  by (6),  $\Delta n = -0.07$  by (7) and  $\Delta n = 0.1$  by (8). The deviation is minimal when using Lorenz-Lorentz formula.

3. Values of deviations and their signs evidence a difference between  $\kappa$  and 1, and if  $\Delta n > 0$ , then,  $\kappa > 1$  meaning matrix is denser. In contrast,  $\Delta n < 0$  means  $\kappa < 1$  and a less dense matrix. The small value  $q = 0.084$  indicates applicability of concept of matrix surrounding pores.

Formula (7) is in the best agreement with experiment and indicates that the matrix is porous. This is not surprising because bridge bonds between  $AsS_3$  pyramids in layers break when the crystal is transformed to amorphous material [1, 2, 6]. Assuming  $\kappa < 1$ , we carried out further calculations of  $\varepsilon_{eff}$  by (7) at varying  $\kappa$  within limits  $0.95 \leq \kappa < 1$ . The  $\kappa$  value affects the  $\varepsilon_2$

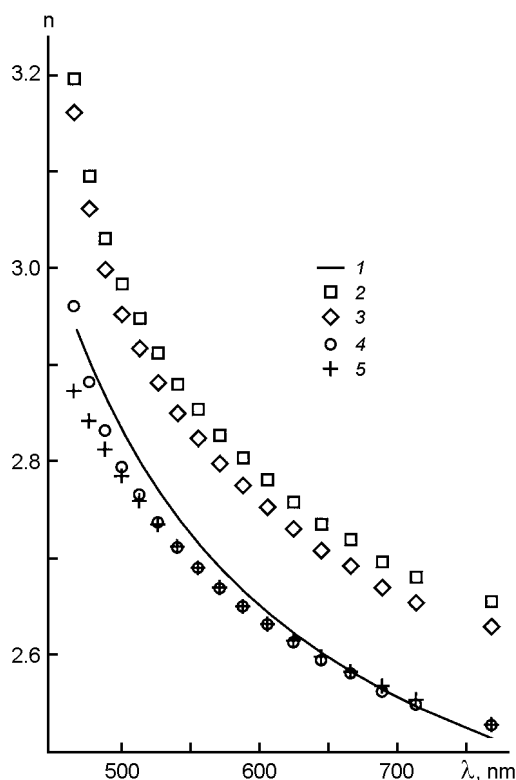


Fig. 1. Comparison of tabular data on amorphous  $As_2S_3$  refractive index and values calculated using  $As_2S_3$  crystal refractive indices and Newton formula (6), Maxwell-Garnett formula (8), Lorenz-Lorentz formula (7) and Wemple formula (10) at  $\kappa = 0.972$ ,  $q = 0.0574$ . Curves 1 - experiment; 2 - Newton; 3 - Maxwell Garnett; 4 - Lorenz-Lorentz; 5 - Wemple

value of matrix, and, unlike (5), to find new  $\varepsilon_2'$  value, one should use the formula

$$\frac{\varepsilon_2' - 1}{\varepsilon_2 - 1} = \kappa. \tag{9}$$

Use of formulae (1, 7, 9) makes it possible to find  $n_{gl}$  consistent with tabular value to within 0.002. In this case,  $\kappa = 0.972$ ,  $q = 0.0574$ , i.e. the matrix porosity is approximately a half of porosity specified by large pores. Using these data, we have calculated  $n_{gl}(\lambda)$  in visible range from 465.2 nm to 762.2 nm with  $\varepsilon_2$  replaced by  $\varepsilon_2'$  in (6-8). As it is seen in Fig. 1, the best agreement of calculated  $n_{gl}$  values with reference data is obtained when using the Lorenz-Lorentz formula. The best agreement with experiment is attained at  $\lambda > 570$  nm: deviation from data in [9] is about 0.01. This is within the error of  $n_{cr}$  determination specified by interference

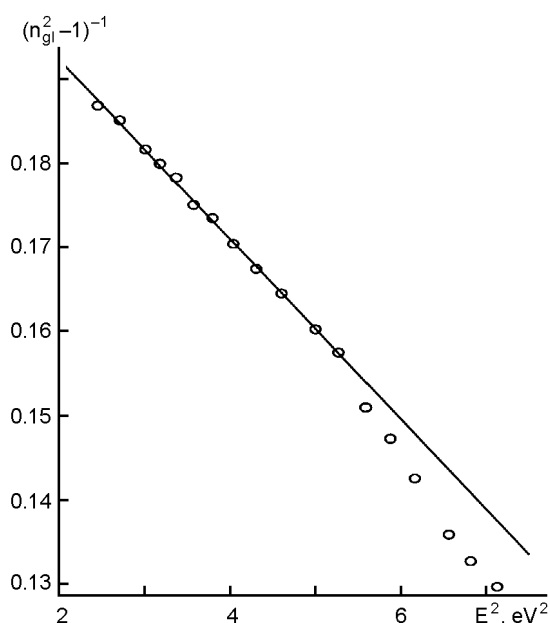


Fig. 2. Linear section in  $(n_{gl}^2 - 1)^{-1}$  dependence on  $E^2$  for  $As_2S_3$ .

curves of the layered crystal transmission. A larger deviation (about 0.03) is observed at  $\lambda < 570$  nm. Perhaps it is associated with additional error in  $n_{gl}$  determination. Results of calculations with other interpolational formulae (6) and (8) agree worse with experiment.

The common way to determine RI and its dispersion in the transparency region is based on the classical Drude-Sellmeier formula under assumption of  $\hbar\omega < E_g$  where  $E_g$  is the band gap width. It is shown in [18] that the  $n(\omega)$  dependence for amorphous materials can be described using model of single oscillator:

$$n_{gl}^2 - 1 = \frac{E_d E_0}{E_0^2 - E^2}, \tag{10}$$

where  $E = \hbar\omega$ ;  $E_0$  and  $E_d$ , parameters determined from experiment. The energy  $E_0$  has sense of the mean position in spectral absorption band.  $E_0 = bE_g$  and, according to estimation in [18],  $b \approx 2$ . The  $E_d$  parameter depends on the amorphous material density and interatomic bond type therein. As is shown in a number of researches on chalcogenide glasses, the formula (10) is linearized in coordinates  $(n_{gl}^2 - 1)^{-1}$  vs  $E^2$  in a wide spectral range. This justifies its applicability and allows determination of  $E_0$  and  $E_d$ .

We used the tabular data from [9] on  $\text{As}_2\text{S}_3$  glass in  $n_{gl}(\lambda)$  calculation with (10). It was found that linear dependence  $(n_{gl}^2 - 1)^{-1}$  vs  $E^2$  is well valid at  $\lambda > 570$  nm,  $E_0 = 4.49$  eV and  $E_d = 21.1$  eV in that case. The latter value agrees rather well with data for annealed  $\text{As}_2\text{S}_3$  films [4, 8]:  $E_0 = 4.5$  eV and  $E_d = 20.7$  eV. But at  $\lambda < 570$  nm, a deviation from linearity is observed that increases when  $\lambda$  decreases (see Fig. 2). The same deviation is observed also in calculations using EDP method (4, 7, 9). Values of  $n_{gl}(\lambda)$  calculated using two methods deviate from the tabular data towards lower values. Both calculations result in almost coincident values.

The reason for divergence of the values obtained with (10) and experimental data on  $n_{gl}(\lambda)$  is more or less clear. When approaching absorption edge  $\lambda_g = 518$  nm ( $E_g = 2.4$  eV [1]), we should use more precise Drude-Sellmeier formula to calculate  $n_{gl}(\lambda)$ . Unlike (10), in the right side of Drude-Sellmeier equation, there is sum of type (10) summands with different  $E_{oi}$  and  $E_{di}$  values [20].

Even more precise  $n_{gl}(\lambda)$  value can be obtained from Kramers-Kronig dispersion relation. But imaginary part of dielectric permittivity should be known in all the frequency range [21]. Interpretation of divergence between calculated and experimental  $n_{gl}(\lambda)$  values is more difficult in our model, since the  $n_{gl}(\lambda)$  calculation at  $\lambda$  close to absorption edge depends on  $f$  determination accuracy of crystal principal RI within that range. The deviation of calculated  $n_{gl}(\lambda)$  values towards lower values may be associated with larger forbidden gap of auripigment ( $E_g \approx 2.6$  eV for direct interband transitions [16]) than that of glass. However, the  $n_{gl}(\lambda)$  calculation approach proposed by us gives additional information on the amorphous  $\text{As}_2\text{S}_3$  structure. The calculation is based on conventional RI determination method for a porous medium. In first approximation, RI of the matrix is supposed to coincide with that of non-porous material. For  $\text{As}_2\text{S}_3$  glass, we have supposed the amorphous material matrix to be low-porous, too. Such an assumption is natural because auripigment transformation to amorphous isotropic material is accompanied by breaking of bridge bonds between  $\text{AsS}_3$  pyramids, as mentioned above. The assumption of large and small pores allows to explain a substantial change of  $n_{gl}$  in sputtered  $\text{As}_2\text{S}_3$  films at their various treatment

(annealing, photostructural transformations, etc.),  $n_{gl}$  change at doping  $\text{As}_2\text{S}_3$  films by silver and other metals. When meeting such challenges, one should use data on bulk  $\text{As}_2\text{S}_3$  glass, which density and RI are known at a relatively high accuracy.

The EDP model application is most attractive when considering the optical properties of amorphous films doped with various metals, due to wide practical application thereof. It is well-known that Ag dissolution in  $\text{As}_2\text{S}_3$  films increases substantially its RI and leads to long-wave shift of absorption edge [22]. The silver-doped  $\text{As}_2\text{S}_3$  films reveal waveguide properties under laser irradiation (633 nm) [23], and waveguide TE-mode propagation has an explanation at  $n_{gl} = 2.80$  larger than  $n_{gl} = 2.62$  of bulk  $\text{As}_2\text{S}_3$ . According to recent ideas, silver penetrated into  $\text{As}_2\text{S}_3$  forms chemical bonds with  $\text{As}_2\text{S}_3$  forming compounds such that  $\text{Ag}_2\text{S}$ ,  $\text{Ag}_3\text{AsS}_3$ , etc. [4]. Such compounds seem to be formed mainly in large pores. The  $n_{gl}$  calculation approach proposed by us along with absorption spectra measurements, makes it possible to reveal a particular type of the compound. Solution of such a difficult task needs an additional study.

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## Порівняння показників заломлення кристалічного та аморфного $As_2S_3$

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Запропоновано спосіб обчислення показника заломлення та дисперсії в області прозорості аморфного  $As_2S_3$  за допомогою моделей ефективної діелектричної проникності пористих композитних середовищ. Спосіб ґрунтується на порівнянні густини скла та кристала і на використанні даних про показник заломлення кристала. Показано, що найкраще узгодження обчислених та експериментальних значень показника заломлення скла досягається в інтервалі хвиль 460–670 нм при використанні для обчислення формули Лоренц-Лорентца. Встановлено, що стекла  $As_2S_3$  мають пори з фактором заповнення  $q = 0.057$ , занурені в ізотропну матрицю з меншою приблизно удвічі пористістю ( $q_M = 0.031$ ).