OPTICAL EXTINCTION BY SMALL PARTICLES OF AMORPHOUS SILICON DIOXIDE

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Extinction spectra of amorphous silicon dioxide small particles depending on particle sizes, their concentration, and surrounding medium are investigated in the vicinity of the one phonon states zone.

It is shown that at the particles sizes comparable and larger than the wavelength of incident light the transmission peak is observed in extinction spectra, which corresponds to the equality of refractive indices of particle substance and surrounding medium. At particle sizes smaller than the wavelength of incident light the surface modes of particles are appeared, frequencies of which shift to lower frequencies as the dielectric constant of the surrounding medium increases.

1. Introduction

The substance as particles widely exists both on the Earth and in the interstellar space. We also use many properties of particles in daily life, medicine, cosmetology, and other areas. Rapid development of nanotechnology and nanophysics provides to use very small particles in the most various areas of modern optoelectronics [1] and medicine [2]. One of the actual directions of physics of small particles clearing widespread perspectives of corresponding application in novel areas of photonics, is the study of interaction of electromagnetic radiation with particles. The present work focuses an attention to the establishment of laws of optical absorption and scattering by small particles through ones of silicon dioxide depending on their sizes, concentration, and surrounding medium.

2. Experimental

The pieces of chemically pure amorphous silicon dioxide are used for getting of small particles. After careful crushing in agate mortar with small addition of spirit the obtained powder was passed through the system of sieves with the known sizes of apertures. Such method allows obtaining the fractions of particles with the grain sizes of 160-200 μm, 100-160 μm, 63-100 μm, 50-63 μm, and less than 50 μm. Last fraction was subjected to the subsequent division on sedimentation time in the column with spirit according to expression

$$t = 18h\eta / (\rho_1 - \rho_2)\, g\, d^2,$$

where h - a column height; η – a viscosity factor; ρ_1 and ρ_2 - densities of silicon monoxide and spirit, accordingly; g – free falling acceleration; d - the particle cross-section sizes. The obtained fractions were dried up in a vacuum of 10^{-2} torr at temperature of 50º C within a week. Then they were mixed up with pure powders of TlCl, KBr, KCl и NaCl (Beckman firm) in vibromill within 8 hours. The mixture were pressed by means of an optical vacuum pressform (Beckman firm) in tablets in diameter of 13mm. Force of pressure varied depending on the microhardness of the matrix compound. Besides, the powder was also deposited on the surface of KBr plate.

Extinction spectra were carried out on spectrophotometer Specord 75 IR in the frequency range of 4000-400cm^{-1}. The resolution and an accuracy of frequency definition were not worse than 2cm^{-1}. More precise of the band form and frequencies were carried out by the two-beam spectrophotometer of the model 4260 of Beckman firm. In this case, the resolution and the accuracy of frequency definition reached up to 1cm^{-1}. Radiation represented itself the parallel light beam falling perpendicularly to the tablet plane. For getting of additional information the tablet without the filler was placed in the comparison beam.

The transmission spectra in the visible region were recorded on spectrophotometer of model 557 (Hitachi firm). The refractive indices of pure silicon dioxide in the visible region and matrices in the infrared region were determined on the interference pattern from transmission spectra. High-frequency dielectric constant of silicon dioxide was defined as a square of refractive index in the visible region. Dielectric constants of matrices were determined by similar method. Low-frequency constant of silicon dioxide was measured by the device BM-560 on the frequency of 50Hz.

3. Results and Discussion

When the light propagates in the medium consisting of particles, its intensity decreases according to the expression

$$I = I_0 \exp(-\alpha_{ext} L), \qquad (1)$$

where extinction factor α_{ext} is the additive value. It consists of absorption and scattering factors:

$$\alpha_{ext} = NC_{ext} = NC_{abs} + NC_{scat}, \qquad (2)$$

where N – the number of particles in the volume unit; C_{ext}, C_{abs} and C_{scat} – extinction, absorption, and scattering cross-sections, accordingly. According to Mie theory, the scattering processes dominate at the particles sizes comparable and larger than the wavelength of incident light. Thus, if the refraction index of environment medium differs from one of particle substance then the sample strongly scatters. But the refractive indices can be equalized near the resonant band of the particle substance where its refractive index sharply changes. At that case, the sample becomes optically homogeneous near the corresponding frequencies and the scattering decreases. This effect we observe in fig.1. The extinction spectra of silicon dioxide small particles with weigh concentration of 2 % and the sizes more than 50μm imbedded in KBr are presented in this figure. As seen, the transmission maximum on the frequency of 1336cm^{-1} and the absorption bands with maxima on the frequencies of 475cm^{-1}, 805 cm^{-1}, and 1092 cm^{-1} are observed. The latter has the greatest intensity and halfwidth. The transmission increases with increasing of the particle sizes but the contrast of the transmission band is deteriorated. Using (1-2) it is easy to show that the transmission intensity is inversely proportional to the particle sizes. The transmission band is more precisely observed at particle sizes of 50-63 μm and has the form close to Gauss one.

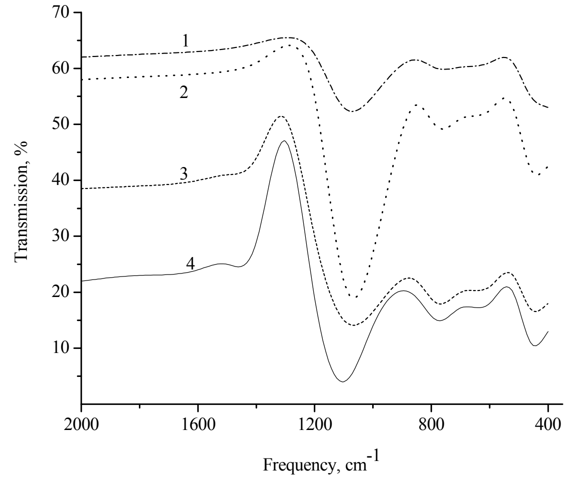

Fig.1. Extinction spectra of silicon dioxide particles in the KBr matrix for different fractions: 1- 160-200 μm, 2- 100--160 μm, 3- 63-100 μm, 4- 50-63 μm.

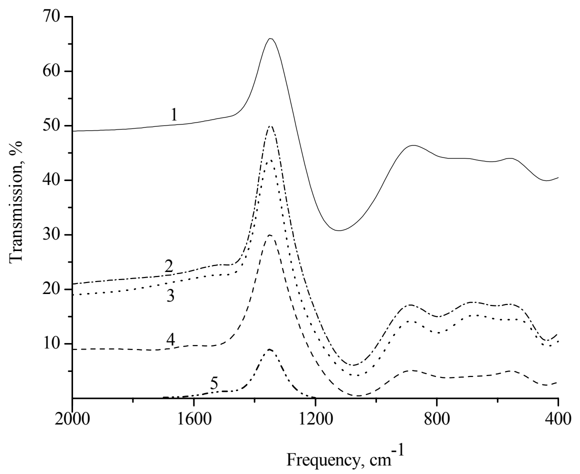

Fig.2. Extinction spectra of silicon dioxide particles with sizes of 50-63 μm in the KBr matrix for different concentrations: 1-1 %, 2-2 %, 3- 3 %, 4- 4 %, 5 – 6 %.

The extinction spectra of silicon dioxide particles with sizes of 50-63μm at various concentrations in KBr are presented in fig.2. One can see that the frequency of transmission maximum at 1336cm^{-1} remains invariable but with increasing of filler concentration the transmission intensity decreases and the ratio between the transmission maximum and common background is improved. Obviously, the transmission maximum corresponds to those values of refractive indices of silicon dioxide which coincide with ones of the matrix. Analogical extinction spectra of silicon dioxide small particles are observed when matrix is KCl or NaCl, and also at precipitation on the KBr surface. At that case the frequency of transmission maximum changes while the frequencies of absorption maxima remain invariable. The greatest frequency of transmission maximum is observed when the filler is KBr, and the least – at the powder precipitated on the KBr surface. Any transmission maxima are not observed for the samples with the TlCl matrix. Apparently, that given fact connects with disjointness dispersion curves of filler and matrix for these samples. Accordingly the sample scatters light the same manner for all frequencies in the measured spectral region. Being based on the above-stated arguments and using dispersion curves of matrices a set of refractive indices at various frequencies can be determined. The obtained values are results in Table 1.

Table 1.
The frequencies of transmission maxima of samples and the magnitudes of refractive indices of silicon dioxide for different frequencies.

Matrix	frequency of transmission maxima (cm^{-1})	refractive index
KBr	1336	1.532
NaCl	1320	1.508
KCl	1312	1.464
Air	1211	1.000

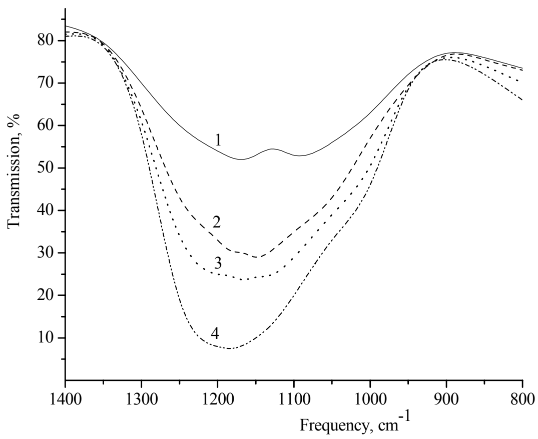

Fig.3. Extinction spectra of silicon dioxide particles with sizes less than wavelength of incident light in the KBr matrix: 1-3.5-4.0μm, 2- 0.5-0.7μm, 3- 0.3-0.5μm, 4- less than 0.3μm.

The transmission spectra of silicon dioxide particles at its sizes smaller than the wavelength of incident light result in fig. 3. For the largest particles (3.5-4.0μm) the spectrum is characterized by two bands of approximately equal intensity: the low-frequency band closed to the frequency (1082cm^{-1}) of transverse optical phonon [3] and more high-frequency band. A diminution of particle sizes results in reduction of low-frequency band and at sizes less than 0.5μm to its full disappearance. Position of high-frequency band is shifted to high frequencies and reaches 1181cm^{-1} at particle sizes of d<0.3μm. Similar dependences are observed when surrounding medium is TlCl, KCl, NaCl, or an air. The experimental results of values of frequencies of absorption maxima for particles with d< 0,3 μm are collected in Table 2. Apparently, the frequencies of absorption maxima shift to lower frequencies as the dielectric constant of the surrounding medium increases.

Table2.
The frequencies of main absorption band maxima of silicon dioxide particles depending on surrounding medium.

surrounding medium	dielectric constant	experimental frequency (cm^{-1})	calculated frequency (cm^{-1})
TlCl	5.10	1139	1136
KBr	2.33	1181	1176
NaCl	2.25	1183	1178
KCl	2.13	1188	1182
air	1.00	1225	1228

It is known that lattice dynamics on the particle surface depends on the surrounding medium and differs from bulk vibrations. At decreasing of particle sizes surface vibrations increase their contribution to experimental spectra. They are radiation modes and shown in absorption and emission spectra. The condition of appreciable display of surface modes is $\omega_t R/c$<1 [4] for spherical particles, where ω_t-the frequency of transverse phonon, *R*- radius of the particle, and *c* – the light velocity. The surface modes are located in the frequency range in which $\varepsilon(\omega)$<0 that corresponds to frequencies between ones of transverse and longitudinal phonons of the bulk sample. They are defined for spherical particles from the following expression

$$\varepsilon (\omega) = -(n + 1)\, \varepsilon_m/n, \tag{3}$$

where ε and ε_m – dielectric constants of particles and surrounding medium, respectively; *n*- natural numbers. The most intensive mode with *n*=1 called the Frohlich one is uniformly polarized, and its frequency is given by

$$\omega_f = \omega_t\, [(\varepsilon_0 + 2\, \varepsilon_m)/ (\varepsilon_\infty +2\varepsilon_m)]^{1/2}, \tag{4}$$

where ω_t- the frequency of transverse optical phonon; ε_0 and ε_∞ are the low- and high-frequency dielectric constants respectively.

For interpretation of experimental results we take the frequency of transverse optical phonon equaled 1082cm^{-1}, ε_0=3.75 and ε_∞=2.46. Calculated values of Frohlich frequencies are collected in Table 2. As it is seen, the good agreement between experimental and calculated frequencies is observed. The most intensive band is wide. Obviously, the given fact is connected with the amorphous state of particles and, correspondingly, high extinction factor of surface phonons [4]. On the other hand, the form of particles strongly influences on the distribution of surface charge and, accordingly, on the frequencies and the band form of surface modes. Observation under the optical microscope has shown that particles have an irregular form. According to [5], in that case the band of surface mode should occupy all area between the frequencies of transverse and longitudinal optical phonons.

In summary, at the particles sizes comparable and larger than the wavelength of incident light the transmission peak is shown in extinction spectra, which corresponds to the equality of refractive indices of particle substance and surrounding medium.

The surface vibrations of particles are appeared at particle sizes smaller than the wavelength of incident light. The frequencies of surface modes shift to lower frequencies as the dielectric constant of the surrounding medium increases. The surface mode band in the absorption spectra becomes stronger as the size of the particle decreases.

[1] *N.N.Ledentsov, V.M.Ustinov, V.A.Shchukin, P.S.Kop'ev, Zh.I.Alferov, D.Bimberg*. Semiconductors. 1998, v.,32, n. 4, p.343.

[2] *Bruce A.Holm, Earl J.Bergey, Tapas De, David J. Rodman, Rakesh Kapoor, Laurent Levy, Christopher S. Friend and Paras N. Prasad.* Molecular Crystals and Liquid Crystals.2002, v. 374, p. 589.

[3] *M. Nakamura, Y. Mochizuki, K.Usami, Y. Itoh, T. Nozaki*. Solid State Communications, 1984, v.50, n.12, p. 1079.

[4] Shinji Hayashi. Japanese Journal of Applied Physics. 1984, v.23, n. 6, p. 665.

[5] *C.F.Bohren, D.R.Huffman*. Absorption and Scattering of Light by Small Particles. John Wiley & Sons. Chichester, N.Y. 1983. 450 p.

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AMORF SİLİSİUM DİOKSİD KİÇİK ZƏRRƏCİKLƏRİN OPTİK EKSTİNSİYASI

Amorf silisium dioksid kiçik zərrəciklərinin birfononlu hallar zonası ətrafında ekstinsiya spektrlərinin zərrəciklərin ölçüsü, konsentrasiyası və ətraf mühitdən asılılığı tədqiq edilmişdir.

Göstərilmişdir ki, zərrəciklərin ölçüləri işığın dalğa uzunluğundan böyük olduqda ətraf mühitin və zərrəcik maddəsinin işığın sınma əmsalları bərabərliyinə müvafiq şəffaflıq piki müşahidə olunur. Zərrəciklərin ölçüsü işığın dalğa uzunluğundan kiçik olduqda isə tezlikləri mühitin dielektrik nüfuzluğu artması ilə kiçik tezliklər oblastına sürüşən səthi modalar özünü biruzə verir.

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ОПТИЧЕСКАЯ ЭКСТИНЦИЯ МАЛЫХ ЧАСТИЦ АМОРФНОЙ ДВУОКИСИ КРЕМНИЯ

Исследованы спектры экстинции малых частиц аморфной двуокиси кремния в окрестности зоны однофононных состояний в зависимости от размера частиц, их концентрации и среды нахождения.

Показано, что при размерах частиц больших длин волн падающего света наблюдается пик пропускания, соответствующий равенству коэффициентов преломления вещества частиц и среды нахождения. При размерах частиц меньших длины волны падающего излучения проявляют себя поверхностные моды, частоты которых смещаются в низкочастотную область с увеличением диэлектрической проницаемости среды.

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