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# Fused Silica As a Composite Nanostructured Material

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**Abstract**—A method for calculating the refractive index of optical fused silica by applying the model of effective permittivity of composite homogeneous media is proposed and realized. The calculation was performed using the tabular data of the refractive index of crystalline α quartz and the ratio of the quartz glass and α quartz densities. It was suggested that fused silica contains nanosized pores with a glass filling number $q$ immersed in a matrix with a density differing from the α quartz density by a factor of $\kappa$, where $\kappa$ is slightly less than unity. It was established that the Maxwell-Garnett model makes it possible to calculate the refractive index of quartz glass and its dispersion in the transparency range ($404\ \text{nm} \le \lambda \le 671\ \text{nm}$) with a deviation less than 0.0002 from the tabular values. The calculated and experimental values coincide at $q = 0.155$ and $\kappa = 0.986$.

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## INTRODUCTION

The need for a detailed study of the optical and other physical properties of materials containing nanoparticles, i.e., particles with a radius $a$ much smaller than the light wavelength $\lambda$ is related to the development of the physics and technology of nanostructures, the formation of composites on their basis, and their practical application. Models of optically homogeneous medium [1, 2] with an effective permittivity (EP) are used to calculate the optical characteristics of materials with nanoparticles. EP and its dispersion depend on the nanoparticle permittivity $\varepsilon_1$, nanoparticle shape, the permittivity $\varepsilon_2$ of the matrix (i.e., the medium are referred nanoparticles), and the filling number of composite with nanoparticles $q = Nv$, where $N$ is the concentration of particles and $v$ is their average volume.

Many studies devoted to various methods of preparation of nanostructures and analysis of their optical properties within EP models have been published recently (see reviews [3, 4]). Transparent media (in particular fused silica and quartz films prepared by various methods) are used as matrices. Nanoparticles in these media are metal or semiconductor particles. It should be noted that the density and refractive index of optically homogeneous fused silica are much smaller than the corresponding parameters of crystalline α quartz, which indicates a high porosity of quartz glass. Both the densities and refractive indices of quartz glass and α quartz have been measured at room temperature with a high accuracy. The aforesaid gives grounds for an exact calculation of the quartz glass refractive index based on the data on the glass and α quartz densities and the refractive index of crystalline quartz within EP models. The present study is devoted to solution of this problem.

## EP MODELS IN USE

The problem of optical properties of nanocomposites is a part of the general problem of properties of mixtures of materials with different permittivities. The interest in the optics of mixtures arose a long time ago. Even Newton proposed the following simple formula to describe the EP of a mixture of two media with different permittivities $\varepsilon_1$ and $\varepsilon_2$:

$$\varepsilon_{\text{ef}} = \varepsilon_1 q + \varepsilon_2(1-q), \tag{1}$$

where $\varepsilon_1 = n_1^2$ and $\varepsilon_2 = n_2^2$, for transparent isotropic media and $n_1$ and $n_2$ are the refraction indices of the media. However, at the end of the 19th century, Clausius and Mossotti proposed a new formula for the dielectric constant of a mixture [5] that was based on the concept of refraction. A similar formula for the optical range was proposed independently by Lorenz and Lorentz as follows [5]:

$$\frac{\varepsilon_{\text{ef}}-1}{\varepsilon_{\text{ef}}+2} = \frac{\varepsilon_1-1}{\varepsilon_1+2}q + \frac{\varepsilon_2-1}{\varepsilon_2+2}(1-q). \tag{2}$$

The derivation of formula (2) is based on the assumption that a molecule located at the center of a hollow sphere is affected by the electric field $E'$, which differs from the field $E$ beyond the sphere

$$E' = E + 4\pi P/3, \tag{3}$$

where $P$ is the polarization of the medium around the molecule, $P = \chi E$, and $\chi$ is the susceptibility. In fact, the sphere is also filled with molecules, but the action of their fields on the central molecule is the same as for a hollow sphere.

For a gas mixture, formula (2) is reduced to (1). Formula (2) is successfully used to determine $\varepsilon_{ef}$ of liquid and solid solutions at a specified molar concentration of mixture.

The next step in the theory of composite homogeneous medium was made by Maxwell-Garnett (1904) in the description of optical properties of colloidal solutions of metals in a dielectric matrix and granular metal films [6]. Maxwell-Garnett proposed the following formula:

$$(\varepsilon_{ef} - \varepsilon_2)/(\varepsilon_{ef} + 2\varepsilon_2) = q(\varepsilon_1 - \varepsilon_2)/(\varepsilon_1 + 2\varepsilon_2). \quad (4)$$

Here, $\varepsilon_1 = \varepsilon_1' - i\varepsilon_1''$ is the complex permittivity of the metal and $\varepsilon_2$ is the matrix permittivity. Formula (4) is obtained based on the assumption that the metal particle is spherical and has a small radius ($a \ll \lambda$). Formula (3) for the field acting on a particle was also used to derive formula (4). The latter was verified experimentally for the first time in [7], where the absorption spectra and structure of thin Ag films were studied by electronic microscopy.

It was noted in [7] that the experimental data on the absorption of Ag films of different thickness are in good qualitative agreement with the calculated frequency dependences of $\varepsilon_{ef}''$ in the entire range of $q$. The main result of these experiments is the detection of the plasma resonance band in the absorption spectrum of the films, whose location and red shift (with an increase in $q$) are predicted by formula (4).

However, the correctness of the application of formula (4) to describe the spectra of thin metal films was questioned in monograph [8] and subsequent studies [9] because this formula was derived for a three-dimensional colloid. In addition, the applicability of formula (4) in the entire range of $q$ is doubtful even in the three-dimensional case because the resonant band calculated according to (4) unwarrantly narrows at $q > 0.8$. Another version of formula (4) was proposed in [10, 11], in which $\varepsilon_1$ and $\varepsilon_2$ were permutated, i.e., at $q > 0.8$, the metal becomes a matrix, while the dielectric forms nanoparticles.

The $q$ range of 0.2–0.8 causes the greatest difficulties in the EP theory (percolation case) because the concept of matrix surrounding nanoparticle becomes meaningless. A number of formulas have been proposed for this case, among which we should note the following formula proposed by Bruggeman [12]:

$$\frac{\varepsilon_1 - \varepsilon_{ef}}{\varepsilon_1 + 2\varepsilon_{ef}} q + \frac{\varepsilon_2 - \varepsilon_{ef}}{\varepsilon_2 + 2\varepsilon_{ef}} (1 - q) = 0. \quad (5)$$

This formula was derived based on the assumption that the mean field acting on a spherical particle is

$$E = qE_1 + (1 - q)E_2,$$

where $E_1$ and $E_2$ are the fields acting on electrons and ions in each particle. Other versions of formulas for $\varepsilon_{eff}$ in the above-mentioned range of $q$ were proposed later [1, 3, 13–15].

Note that all of the above formulas have an interpolation character, i.e., $\varepsilon_{ef} = \varepsilon_2$ at $q = 0$ and $\varepsilon_{ef} = \varepsilon_1$ at $q = 1$. All of the formulas except for (1) contain nonlinear dependences of $\varepsilon_{ef}$ on $q$ of different types. Formulas (4) and (5) were obtained for small spherical particles and similar formulas for spheroidal particles were derived in a number of studies [2, 3]. At radii $a >$ 10 nm, the concept of EP loses meaning, and the experimental study of extinction coefficient should be performed taking into account the contribution of light scattering calculated according to the Mie theory [16].

## APPLICATION OF EP MODELS FOR CALCULATING THE QUARTZ GLASS REFRACTIVE INDEX

Fused and crystalline quartz are widely used in various fields of science and technology; correspondingly, a very large number of studies are also devoted to the physical properties of quartz. The favorable combination of mechanical, thermal, and optical properties of fused silica determined its wide application in spectroscopy, fiber optics, and (recently) in composite fabrication.

The optical constants of quartz have been experimentally found in a wide wavelength range, and the refractive index has been measured with high accuracy in the transparency range of 180 nm to 2.7 μm. The data on the refractive indices of crystalline quartz and quartz glass can be found in various handbooks (see, e.g., [17, 18]). Crystalline quartz has a rhombohedral lattice (crystalline class 32); in birefringence, it behaves as a positive uniaxial crystal with the principal refractive indices $n_e = 1.5534$ and $n_o = 1.5443$ at $\lambda =$ 589.3 nm and room temperature. Quartz glass is optically isotropic and has a much smaller refractive index ($n = 1.4585$) at the same wavelength. Note that the refractive index of glass depends weakly on its preparation technique [19]; according to different estimates, the deviation from the reported value does not exceed 0.0002.

There are several types of quartz glasses that are determined by their preparation technique. Glasses of type KU are most often used in spectroscopy [18, 20]; they lack an absorption band at 240 nm and exhibit a high transparency in the UV range with a transmittance of 90% (1-cm-thick plates) at $\lambda = 200$ nm.

Crystalline quartz has some modifications [19, 21], which are stable at different temperatures and differ in

**Table 1.** Comparison of refractive indices calculated from crystalline quartz refractive index using (1) Newton, (4) Maxwell-Garnett, (5) Bruggeman, and (2) Lorenz–Lorentz formulas with the tabular values for quartz glass

| $\lambda$, nm | 670.8 | 656.3 | 643.8 | 589.3 | 546.1 | 508.6 | 486.1 | 480.0 | 404.7 |
|---|---|---|---|---|---|---|---|---|---|
| (1) | 1.4669 | 1.4673 | 1.4676 | 1.4694 | 1.4711 | 1.4729 | 1.4742 | 1.4745 | 1.4808 |
| Tabular value | **1.4561** | **1.4564** | **1.4568** | **1.4585** | **1.4602** | **1.4619** | **1.4632** | **1.4636** | **1.4697** |
| (4) | 1.4516 | 1.4519 | 1.4522 | 1.4539 | 1.4555 | 1.4572 | 1.4585 | 1.4588 | 1.4648 |
| (5) | 1.4499 | 1.4503 | 1.4506 | 1.4523 | 1.4539 | 1.4556 | 1.4568 | 1.4571 | 1.4631 |
| (2) | 1.4383 | 1.4386 | 1.4389 | 1.4404 | 1.4419 | 1.4435 | 1.4446 | 1.4449 | 1.4504 |

the densities and lattice point symmetry groups. $\alpha$ quartz with the above-mentioned structure and refractive index is most stable at room temperature. The $\alpha$-quartz density, which is measured with a high accuracy, is 2.6487 g/cm$^3$. Higher temperature stable modifications, e.g., tridymite ($T \geq 870°$C) and cristobalite ($T \geq 1470°$C), have lower densities (2.27 and 2.32 g/cm$^3$, respectively). The quartz glass density (2.202 g/cm$^3$) is lower than the density of crystalline modifications. The dependence of the refractive index of different crystalline modifications and quartz glass on their density was established in [22, 23]; the refractive index monotonically and nonlinearly increases with an increase in density.

The fact that the quartz glass density is below the density of different crystalline quartz modifications indicates the formation of cavities (voids) in the glass. The presence of voids is evidenced by the high glass permeability for light gases (H, Ne, He) [19] and the penetration of noble metal ions into glass under ion [4, 24] or laser [25] implantation. The ratio of the fused and crystalline quartz densities makes it possible to determine independently the glass filling factor by voids, $q$. This filling factor can be used to calculate $\varepsilon_{\text{eff}}$ and the refractive index based on the known EP models and suggested value of $\varepsilon_2$ of the matrix around the voids.

To calculate $q$, we used the densities of glass and $\alpha$ quartz, measured with high accuracy. It was assumed that the matrix density in quartz glass is equal to the crystal density. Then, the glass density $\rho_{\text{gl}} = \rho_{\text{cr}}(1 - q)$, where $\rho_{\text{gl}}$ = 2.202 g/cm$^3$ and $\rho_{\text{cr}}$ = 2.6487 g/cm$^3$; hence, $q = 0.168$. Since quartz glass is isotropic, $\varepsilon_2$ in formulas (1), (2), (4), and (5) can be calculated as the mean of the principal permittivities of crystalline quartz

$$\varepsilon_2 = (2n_o^2 + n_e^2)/3 = 2.3943$$

for $\lambda = 589.3$ nm. Based on this value and $q$ found from the density, we calculated $\varepsilon_{\text{eff}}$ and the refractive index of the glass using different EP models. It was found that formula (4) gives the best agreement with the tabular value of $n_{\text{gl}}$. For example, the calculated value $n_{\text{gl}} = \varepsilon_{\text{ef}}^{1/2} = 1.4539$ for $\lambda = 589.3$ nm, which differs by only 0.0046 from the tabular value (1.4585). Other models give a much larger deviation from the tabular value (Table 1).

A comparison of the calculated and experimental $n_{\text{gl}}$ values shows that a difference of 0.005 exceeds the error in measuring $n_{\text{gl}}$ (0.0002). Thus, we concluded that the above simple assumptions about $\varepsilon_2$ of the matrix and its density should be corrected. It is reasonable to suggest that the matrix density around the voids is somewhat lower than $\rho_{\text{cr}}$ [27] due to the presence of a topological disorder in it [26]; i.e., $\rho_{\text{M}} = \kappa\rho_{\text{cr}}$, where the factor $\kappa$ is smaller than 1. Hence,

$$\rho_{\text{gl}}/\rho_{\text{cr}} = \kappa(1 - q) = 0.832, \quad (6)$$

where the new filling factor of glass with voids differs from the previously calculated value $q = 0.168$. Here,

$$1 - q = \rho_{\text{gl}}/\rho_{\text{M}}, \quad q < 0.168.$$

A decrease in $\rho_{\text{M}}$ leads to a decrease in the refractive index and $\varepsilon_2$ of the matrix. The estimation of the new $\varepsilon_2$ value is somewhat difficult due to the existence of different calculation versions.

Verifying these versions, we found that the calculation based on the decrease in the extraordinary ray refractive index in the matrix in comparison with $n_e$ of crystalline quartz is in best agreement with the expreimental data. Within this approximation, the $\kappa$ and $\varepsilon_2$ values are found from the equations

$$(n_e'^2 - 1)/(n_e^2 - 1) = \kappa, \quad (7)$$

$$\varepsilon_2 = (2n_o^2 + n_e'^2)/3. \quad (8)$$

Since the extraordinary wave refractive index changes in the range $n_e \leq n_e' \leq n_o$, one can vary $n_e'$ in this range to find $\kappa$ and $\varepsilon_2$ and derive a new value of $q$ from formula (6). For example, at $n_e' = n_o$, we have $\kappa = 0.9801$ and $\varepsilon_2 = n_o^2$. Formula (6) gives $q = 0.1517$ and Eq. (4) yields the refractive index of glass $n_{\text{gl}} = 1.4606$ ($\lambda$ = 589.3 nm), which exceeds the tabular value by 0.0021. The best results were obtained at $\kappa = 0.9862$, $\varepsilon_2$ = 2.3876, and $n_e' = 1.5452$. In this case, $q = 0.1564$. The Maxwell-Garnett formula at $\lambda = 589.3$ nm gives $n_{\text{gl}} =$

**Table 2.** Comparison of the refractive indices calculated from crystalline quartz refractive index using formula (4) and different κ values with tabular values for quartz glass

| λ, nm | 670.8 | 656.3 | 643.8 | 589.3 | 546.1 | 508.6 | 486.1 | 480.0 | 404.7 |
|---|---|---|---|---|---|---|---|---|---|
| κ = 0.98 | 1.4582 | 1.4585 | 1.4590 | 1.4606 | 1.4622 | 1.4641 | 1.4654 | 1.4657 | 1.4718 |
| Tabular value | **1.4561** | **1.4564** | **1.4568** | **1.4585** | **1.4602** | **1.4619** | **1.4632** | **1.4636** | **1.4697** |
| κ = 0.986 | 1.4561 | 1.4564 | 1.4569 | 1.4585 | 1.4601 | 1.4619 | 1.4632 | 1.4635 | 1.4696 |
| κ = 1 | 1.4516 | 1.4519 | 1.4522 | 1.4539 | 1.4555 | 1.4572 | 1.4585 | 1.4588 | 1.4648 |

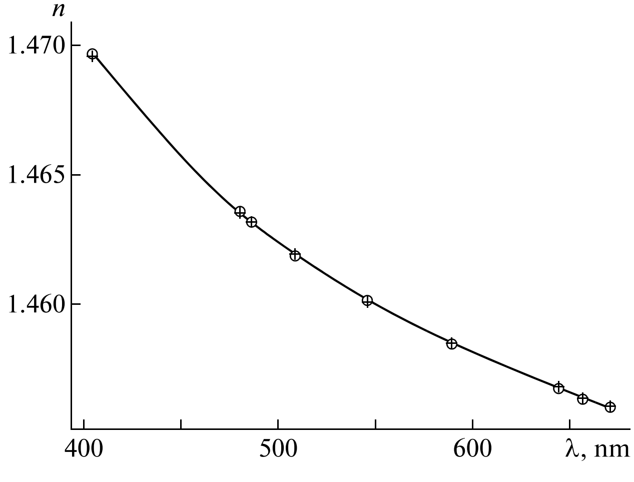
1.4585, which is in good agreement with the tabular value within the errors. This consistency was verified in the calculation of $n_{gl}$ for all wavelengths in the range $404 \leq \lambda \leq 671$ nm taking into account the dispersion of the refractive indices $n_o$ and $n_e$ of crystalline quartz. It can be seen from Table 2 and the figure that the calculated and experimental results are in good agreement in the entire range of λ. This indicates that the constants κ and $q$ are independent of λ.

## DISCUSSION OF THE RESULTS OF CALCULATION OF THE QUARTZ GLASS REFRACTIVE INDEX

It follows from the above calculation of the glass refractive index that the EP model proposed by Maxwell-Garnett (formula (4)) adequately describes its difference from the crystal refractive index. It should be noted that the Bruggeman model (formula (5)) also gives $n_{gl}$ values that are close to the experimental values. This result is not unexpected because, with $\varepsilon_{eff}$ expanded in a power series in $q$, at small $q$, both formulas give the same result in the linear approximation as follows:

$$\varepsilon_{ef} = \varepsilon_2[1 - 3q(\varepsilon_2 - \varepsilon_1)/(2\varepsilon_2 + \varepsilon_1)].$$

The small difference of the results of calculations based on these two formulas is determined by the difference in the higher order expansion terms.



Dispersion of the fused silica refractive index: (solid line) tabular values, (circles) experimental results, and (crosses) values calculated from formula (4) at κ = 0.986.

The applicability of the above-mentioned models to the calculation of $n_{gl}$ suggests that there are two different types of voids in fused silica, i.e., relatively large voids with a filling number $q$ and several nanometers in size (much smaller than λ) and much smaller voids in the matrix, about 1 Å in size, as is evidenced by the proximity of the parameter κ to 1. In other words, quartz glass can be considered to be a peculiar uniform nanostructured medium, where large voids with $\varepsilon_1 = 1$ play the role of nanoparticles.

Note also that the difference between the matrix and crystal densities should be taken into account in the analysis of the spectral position and shape of plasma resonance bands arising in the particle spectra as a result of implantation of noble metal ions into quartz glass by different methods, since the band peak frequencies depend strongly not only on the optical constants of metal in nanoparticles [28] but also on $q$ and $\varepsilon_2$ of the matrix.

The assumptions about the quartz glass structure are somewhat contradictory with the widely cited [26, 29] model of its structure (Zachariasen model [30]). According to [30], quartz glass is a disordered network of $SiO_4^{2-}$ tetrahedra, with the bond lengths and angles in the tetrahedra identical to those in the crystalline state. Unlike crystals, where α is constant, tetrahedra are connected by oxygen bridges, but the angles α between the Si–O–Si bonds of neighboring tetrahedra vary within 120°–180°. This model also assumes the presence of voids of different radii; however, their values form a continuous series. This model is inconsistent with our conclusion about the sharp difference in the radii of large and small voids in the quartz glass matrix. The quartz glass structure was debated in later studies [19]. The diffraction measurements indicate the conservation of short-range order in the arrangement of neighboring tetrahedra and, according to some data, of medium-range order [29]. Thus, the model developed in [30] should be further corrected.

A possible reason for the discrepancy of the glass structure within the Zachariasen model is in the certain important role that cristobalite plays in the glass formation from melt [19, 21]. As was mentioned above, cristobalite is the highest temperature stable modification at normal pressure. Apparently, the cristobalite phase is formed upon slow heating of pure quartz to melting. It is possible that, due to the high melt viscosity, the glass structure retains its memory about the cristobalite structure upon cooling to glass formation. This memorization was evidenced in the early experiments on glass crystallization upon heating to 1000°C [21]. In all cases, crystallization leads to cristobalite formation. It was also established that the crystallization temperature and rate depend on the presence of impurities in fused silica. The diffraction analysis of fused silica samples prepared by the sol–gel method in later studies [31, 32] revealed that the glass crystallization into α cristobalite (cubic phase) occurs in the presence of Ag nanoparticles [31] at 500°C, a temperature at which cristobalite is unstable. The same result on crystallization was obtained by introducing copper into glass [32] and cristobalite is only transformed into conventional crystalline α quartz at 800°C α. All of the aforesaid indicates the proximity of the structure of quartz glass to that of α cristobalite.

## CONCLUSIONS

Based on the calculation of the quartz glass refractive index using the exact data on the refractive index of crystalline α quartz and the ratio of crystal and glass densities, we have calculated the refractive index of fused silica in the range of λ of 404–671 nm using the Maxwell-Garnett formula and obtained deviation from the experimental data not larger than 0.0002. Two parameters were used in the calculations, including $q$, the glass filling factor by nanovoids, and $\kappa$, the coefficient that determines the deviation of the isotropic matrix density around the voids from the α-quartz density. The calculation shows that the quartz glass is a nanostructure in which quasi-spherical voids play the role of nanoparticles. It is desirable to perform similar calculations of the glass refractive index using cristobalite as a crystal, but they should be performed based on more exact data on the cristobalite refractive index, density, and structure at room temperature.

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