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Modeling the optical transmission of crystalline-glass materials composed of densely packed Mie particles

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ABSTRACT

An approximation to the scattering efficiency for a collection of densely packed Mie particles is applied to compute the optical transmission (OT) relevant to glass crystallization. Initially, the shapes and shifts of the OT curves relative to the crystal size scale are computed and reviewed. Numerical simulations are made over the extended range of crystal number densities. The input data link to both forecasting the lithium disilicate glass crystallization as well as prolonging the virtual glass crystallization to higher sample crystallinity. The shape of the OT curves is also revealed at low OT magnitudes, in order to show the nature of the specific interference structure. The positions of the first OT minima linearly relate to the crystal number density. However, such linearity may change due to interparticle interactions that become important at the elevated packing densities of crystals.

1. Introduction

Analysis of the optical behavior of crystalline materials becomes a convenient approach for the characterization of nucleation processes. In general, optical methods are valuable tools to study the kinetics of thermally induced phase transitions in glasses. As the nuclei grow, the fraction of glass occupied by the particles also increases. Under such conditions the glassy material has to be interpreted as a multiply-scattering medium rather than a collection of independently scattering particles [1,2]. The computations made by Okada and Kokhanovsky [3] for particles with various refractive indices imply that dependent scattering needs to be taken into account at concentrations above 1%. Basically, the intensity of the scattered radiation depends on the structure factor, which has an origin in statistical mechanics and is related to the probability distribution function of inter-particle distances, e.g. see the early paper by Andreev [4]. In that work he also analyzed the effects of interparticle interference on light scattering by glasses and concluded that the anomalous character of light scattering can be related to the coherent scattering of radiation by a multiparticle assembly. In a targeted experiment performed on a dense distribution of particles by Ishimaru and Kuga [5], the characteristics of the coherent field were found to be strongly affected by the pair-correlated distributions of scatterers. Even if the incorporation of pairwise correlation functions into a theoretical model might not exactly mimic an anomalous behavior of the scattered or attenuated electromagnetic field [6], a set of well-known approximations are in use. For instance, the Percus–Yevick (P–Y) function appears to be a good approximation at the elevated volume concentrations of scattering particles, but it becomes inaccurate at advanced stages of particle clustering [7]. Under such conditions, rigorous solutions of the Maxwell equations are needed to interpret the measurements accurately [8,9].

In our numerical study the Percus–Yevick-based approximation is used to analyze the specific optical features of crystalline-glass materials composed of densely packed Mie

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particles. Even if the P–Y model involves a set of approximations on the particle system that may not be completely satisfied, it has been proved that the P–Y approximation is applicable in modeling the optical effects of a quasi-monodisperse system of particles. The P–Y approach is of great benefit here, since it allows us to retrieve the basic features of the interference structure of the OT and can be also useful in the rapid detection of early stages of particle clustering i.e. the phases before the aggregated microstructures are formed. There are also some extensions to the P–Y concept that make it more accurate. For instance, Shepilov [10] has shown that the model with exclusion zones is more accurate and appears to be in good agreement with computations made by the discrete dipole approximation.

The computations made in this work are considered to be relevant to inorganic glass crystallization and comprise the theoretical optical transmission (OT). The term OT is also called the optical pattern or the optical dependency in this paper. To determine the OT under evolving crystallinity degree, we extended the solution concept that has been originally introduced in [11,12] and then adopted in [13]. Special attention is paid to the shapes as well as the shifts of OT curves relative to the crystal size axis. Some OT curves drawn on the logarithmic scale demonstrate the optical effects at small OT magnitudes.

2. Theoretical considerations

If a beam of monochromatic radiation with the wavelength λ propagates through a slab containing the particles from top to bottom, the intensity decays in accordance to the Bouger–Lambert–Beer law

$$F_\lambda(\tau_\lambda) = F_\lambda(0)\exp\left\{-\frac{\tau_\lambda}{\cos z}\right\}, \tag{1}$$

where z is the angle of incidence (measured from normal direction to the slab), $F_\lambda(\tau_\lambda)$ and $F_\lambda(0)$ are flux densities of the radiation at the bottom and upper interfaces of the slab, respectively. In Eq. (1), τ_λ is the optical thickness determining the optical transmission of a scattering medium

$$OT_\lambda = \exp\{-\tau_\lambda\}. \tag{2}$$

Assuming the size distribution of scattering particles is quite narrow, the optical thickness is linearly proportional to the product of the slab thickness L and the number density of crystals N. Such a relation can be expressed through the scattering cross-section $C^D_{ext,\lambda}(n,r)$ of a single particle situated in a densely packed environment, i.e.

$$\tau_\lambda = L\, C^D_{ext,\lambda}(n,r)\, N, \tag{3}$$

with r being the particle radius and $n=n_p/n_m$ being the refractive index of the particles (p) measured relative to the surrounding medium (m). By introducing the so-called structure factor $S_{str,\lambda}$ [14], the cross section $C^D_{ext,\lambda}(n,r)$ can be expressed as

$$C^D_{ext,\lambda}(n,r) = C_{abs,\lambda}(n,r) + \frac{\lambda^2}{2\pi}\int_{\theta=0}^{\pi} S_{11,\lambda}(n,r,\theta)\, S_{str,\lambda}(\theta)\sin\theta\, d\theta, \tag{4}$$

where θ is the scattering angle, $C_{abs,\lambda}(n,r)$ is the absorption cross section computed using conventional the Mie theory, and $S_{11,\lambda}(n, r, \theta)$ is the first element of the Stokes scattering matrix [15].

The data serving as an input to numerical computations include the parameters L, N, r, λ, and the difference in refractive indices of the crystalline and glassy phases, i.e. $\delta n = n_p - n_m$.

3. An overview of the computed OT curve patterns

The total optical thickness of the random media is a non-trivial function of δn, λ, r, so these parameters cannot be evaluated independently. The optical density of disperse media is known to increase when N, r or δn grow, or when λ decreases (here δn is assumed to be much smaller than unity). Under high optical density conditions, the OT decreases steeply with growing crystal sizes. Consequently, the OT approaches zero at a very low virtual glass-ceramics degree of crystallinity.

In the present computations, the parameter N has been changed over several orders of magnitude ranging from 3×10^{12} up to $1\times10^{16}\,\mathrm{m}^{-3}$. Some profoundly nucleated silicate glasses, e.g. the $2Na_2O\cdot CaO\cdot 3SiO_2$ glass [16] or lithium disilicate glass nucleated heterogeneously [17], can even exceed the range of N treated here. The particle radius (r) is varied on a large scale, while the parameter δn is considered to be either 0.01 or 0.02 depending on both the refractive index of disilicate glass [18] and the two refractive indices of the crystalline lithium disilicate [19].

Since the computed OT dependencies are interrelated with crystallization of the lithium disilicate glass through the specific values of δn, only λ and L remain as free-choice parameters. In our numerical experiments λ is set to 0.7 μm, while L is 0.3 mm. If these parameters are set to their respective values of 0.8 μm and 0.011 mm, the optical thickness changes only moderately. This makes it possible to conduct the glass virtual crystallization to a higher degree of crystallinity α that is otherwise called a degree of conversion in kinetic studies. In the optics of densely packed systems this parameter is equivalent to the filling factor [11]

$$\alpha = \frac{4}{3}\,\pi\, r^3 N. \tag{5}$$

3.1. OT dependencies computed for $\delta n = 0.01$

The computed OT intensity in Fig. 1 is drawn on a relative scale as a function of the crystal size. The common features identified in Fig. 1 are two OT minima originating presumably from the efficiency factor for extinction $Q^D_{ext,\lambda} = C^D_{ext,\lambda}/(\pi r^2)$ that shows an oscillatory behavior for slightly absorbing or non-absorbing crystals evaluated in this study. The first OT minima appear at relatively high OT values and all of them correspond to almost the same computed sample crystallinity $\alpha = 0.24$. By decreasing N, the positions of OT minima shift to higher values of r. Curves 1–3 exhibit the customary shapes of the descending/reverse sigmoidals only to the points of the first OT minima. The course of the OT curves could be obtained to some reliability by fitting the computed curve simultaneously by an equation of the reverse sigmoidal and the Gaussian