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RESEARCH ARTICLE

Optical scattering in glass-ceramics.

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(October 6, 2008)

The transparency of glass-ceramics with nanocrystals is generally higher than that expected from the theory of Rayleigh scattering. We attribute this ultra-transparency to the spatial correlation of the nanoparticles. The structure factor is calculated for a simple model system, the random sequential addition (RSA) of equal spheres, at different volume filling factor. The spatial correlation given by the constraint that particles cannot superimpose produces a diffraction peak with a low $S(q)$ in its low- q tail, which is relevant for light scattering. The physical mechanism producing high transparency in glass-ceramics is demonstrated to be the low density fluctuation in the number of scatterers. The addition of a size distribution of the spherical particles produces important changes in the q -dependence of the scattering intensity in the region of the diffraction peak, but it has minor effects on the low- q tail.

Keywords: glass-ceramics; transparency; size distribution.

*AMS Subject Classification:*78.20 -Bh; 81.05.Pj;78.35.+c; 61.05.cf

1. Introduction

Glass-ceramics are composite materials formed by a glass matrix containing nanometer sized crystals. Their structure makes them valuable for application in photonics as they combine the spectroscopic properties of crystals with the mechanical properties of glasses [1–5]. A strong optical scattering, highly detrimental for applications, would be expected for these systems on the basis of the presence of particles, which have in general a different refractive index from the amorphous matrix where they are embedded. However many glass-ceramics, in particular those obtained from oxyfluoride glasses, have shown a transparency similar to that of glasses, much higher than that expected from the theory of Rayleigh scattering [2, 3].

In a recent work [6], we have addressed the problem of the origin of such behaviour. The main reason appears to be related to their spatial arrangement and the consequent interference pattern of the scattered field, as suggested firstly by Tick [2]. Different approaches attempted at evaluating it. On one hand Hopper, and then Hendy, considered the long range effects due to a spinodal decomposition which induces a quasi periodicity over some spinodal length, disregarding the short

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range correlation [7, 8]. On the other hand, Shepilov researched the effects of the strict short range correlation induced by the process of nucleation and growth of the nanocrystals, which prevents the formation of contacting particles as expected for a completely random distribution [9].

Here we revise the theory underlying the problem and discuss the effects of the size distribution on the scattering properties.

2. Theoretical background

Let's consider at first the individual fields scattered at any angle (θ) of scattering, or at any exchanged wavevector $q = (4\pi/\lambda) \sin(\theta/2)$ by the particles excited by a homogeneous external field \mathbf{E}_0 [10]:

$$\mathbf{E}_i(\mathbf{q}) = \mathbf{E}_0 A_i(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}_i), \tag{1}$$

where \mathbf{r}_i is the position of the i -th scatterer and A_i the amplitude function which depends on the shape of the particle, exchanged wavevector and state of polarization of the incident wave.

The attenuation coefficient is given by the ratio of the radiation scattered on the whole solid angle by all the particles in a certain volume divided by the incident intensity. In the absence of any spatial correlation, this is simply given by the sum of the Mie scattering cross section of all the particles in the volume unit V :

$$\alpha_S = \frac{1}{V} \sum \sigma_i. \tag{2}$$

For equal particles it reduces to $\alpha_S = \rho_N \sigma_i$ where ρ_N is the particle density.

In presence of spatial correlation, however, interference effects occur and in general the scattered intensity takes the form:

$$I(\mathbf{q}) = \mathbf{E}_0(\mathbf{q})^2 \left| \sum_i \exp(i\mathbf{q}\mathbf{r}_i) A_i(\mathbf{q}) \right|^2, \tag{3}$$

For equal particles ($A_i = A$), it is possible to separate the effect of interference:

$$I(\mathbf{q}) = \mathbf{E}_0(\mathbf{q})^2 |A(\mathbf{q})|^2 \left| \sum_i \exp(i\mathbf{q}\mathbf{r}_i) \right|^2 = N \mathbf{E}_0(\mathbf{q})^2 |A(\mathbf{q})|^2 S(\mathbf{q}), \tag{4}$$

The static structure factor $S(\mathbf{q}) = \left| \sum_i \exp(i\mathbf{q}\mathbf{r}_i) \right|^2 / N$ modulates the scattered intensity at all angles and polarizations, accounting for all the effects of the destructive and constructive interference. If the distribution of particle is isotropic (as we will assume in the following), the static structure factor depends only on the modulus of \mathbf{q} . The attenuation at a certain λ will be obtained by integration of Eq. (4) for all q between 0 and $4\pi/\lambda$. In glass-ceramics, the average distance between nanocrystals ($\sim d$) is much less than the wavelength of light, which are the wavelengths of interest while speaking of attenuation. Therefore the relative q are much apart from the interference peak, which is placed at about $2\pi/d$, while they are in the low- q tail of the structure factor where its value is nearly constant (S_0). In these conditions, the ratio of the attenuation between correlated and uncorrelated equal particles is given by S_0 .

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3. Results and discussion

In order to evidence the effects of correlation on the glass-ceramic transparency, we have numerically studied a system of equal spherical hard particles with the minimum and unavoidable degree of correlation given by the impossibility of interpenetration [6]. The system was generated by the random sequential addition (RSA), where the n -th particle is placed randomly within a cubic box with periodic boundary condition only if it finds the space left free from the previous $n - 1$ particles [11]. The filling factor $\phi = 4/3\pi R^3 \rho_N$ is the only parameter characterizing the system. It resulted that as ϕ increases also the correlation increases: the diffraction peak located at $q_p \simeq 2\pi/2R$ becomes more and more well defined, while S_0 decreases. For the maximum attainable $\phi \sim 0.3828$, S_0 is about 0.05 [11].

If the size of the particle is much smaller than the wavelength of the light, as it happens for glass-ceramics, Rayleigh scattering occurs. The cross section for Rayleigh scattering by a not absorbing spherical particle of radius R and refractive index n_p , embedded in a not absorbing medium of refractive index n_m , is given by [10]:

$$\sigma_{Ray} = \frac{8}{3} \pi k^4 R^6 \left(\frac{m^2 - 1}{m^2 + 2} \right)^2, \tag{5}$$

where $m = n_p/n_m$, $k = 2\pi/\lambda = 2\pi n_m/\lambda_0$ is the wave vector of the light of wavelength λ in the medium and λ_0 in vacuum.

The dependency on the volume of the scattered field is typical of such limiting case, and it is not respected in the general Mie approach. Notably, this dependency is found also in the other limiting case of very low wavelengths, i.e. for X-ray. In this condition the interaction is between the X-photon and the electron cloud of any atom. The resulting scattered field is proportional to the number of atoms, and henceforth to the volume of the particle v_i , and to its form factor $f(q, R_i)$, which takes into account the internal effects of interference.

$$\mathbf{E}_i(\mathbf{q}) \propto \mathbf{E}_0(\mathbf{q}) v_i f(q, R_i) \exp(i\mathbf{q}\mathbf{r}_i), \tag{6}$$

We have exploited the previous equation, with the explicit dependency on the volume, to calculate the interference properties of the scattered radiation by a system where the embedded spherical particles present a size distribution, when Eq. (4) holds no more. In these conditions, $S(q)$ does not represent any more the interference effects.

The RSA model can be easily modified in order to account for such a size distribution, considering to place particles with a radius randomly chosen from a pre-defined distribution. In particular we assumed a log-normal distribution of the particle size:

$$D(r) \sim \exp\left(-\frac{[\ln(R/R_0)]^2}{2\sigma^2}\right)/R. \tag{7}$$

The inset of figure 1 reports the size distribution for different values of the parameter σ . As a matter of fact, this distribution is often found when analyzing system of particles of nanometric size [12].

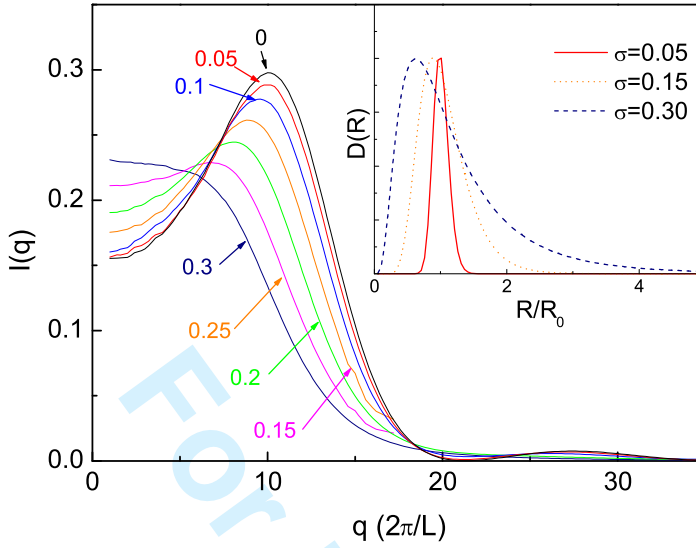


Figure 1. Scattered intensity, calculated by Eq. (1), for a RSA system with a volume filling factor $\phi = 0.2$ and a log-normal size distribution with σ given by the labels. Inset: evolution with σ of the log normal distribution of particles: $\sigma = 0.05$ (solid line) $\sigma = 0.15$ (dotted line) $\sigma = 0.30$ (dashed line)

We have calculated

$$I(q) = \frac{|\sum_i \exp(i\mathbf{q}\mathbf{r}_i) v_i f(q, r_i)|^2}{\sum_i v_i^2}, \tag{8}$$

normalizing the scattered intensity by $\sum_i v_i^2$. In this way, in the limit of small q -values ($qR \ll 1$), when $-f(q, R) = 1$, and for equal particles ($v_i = cost$), $I(q) \propto S(q) = |\sum_i \exp(i\mathbf{q}\mathbf{r}_i)|^2/N$. We set the proportionality constant equal to 1.

The particle density and the occupied volume are kept fixed as the width of the distribution changes. Therefore the mean particle size slightly decreases with sigma, since the mean particle volume is constant. Figure 1 shows the dependence of the scattered intensity on the width of the size distribution for a fixed volume filling factor, $\phi = 0.2$. The diffraction peak broadens and shift towards lower q -values as the size distribution increases in width. The shape of the peak changes dramatically, but the low- q limit of the intensity does not. Note that, in this limit, $S_0 = I(0)$, since the structure factor is 1 for any particle size, $f(q, r) = 1$, as figure 2 also shows for $\phi = 0.2$. Broadening the size distribution to $\sigma = 0.3$, we observe that $I(0)$ increases from about 0.155 to about 0.23. This change is comparable to the change produced by a change of the filling factor from $\phi = 0.2$ ($S_0 = 0.155$) to $\phi = 0.25$ ($S_0 = 0.25$). The volume filling factor is indeed the more important parameter in determining $I(0)$, the size distribution having a minor effect in increasing the low- q scattering.

In reference [6], we have evidenced that S_0 was fundamentally related to the fluctuations of the number of scatterers M within spheres of radius l according to the relation [13]:

$$\frac{\langle M^2 \rangle - \langle M \rangle^2}{\langle M \rangle} = 1 + 4\pi\rho_N \int_0^l dr r^2 (g(r) - 1) \rightarrow S_0, \tag{9}$$

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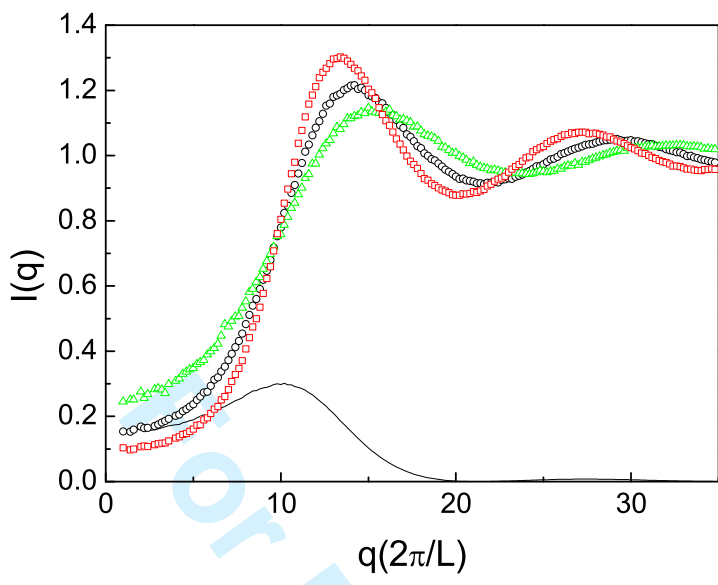


Figure 2. The scattered intensity for $\phi = 0.2$ and $\sigma = 0$ (solid line); structure factor, $S(q)$, for $\sigma = 0$ and $\phi = 0.15$ (triangles), $\phi = 0.2$ (circles), and $\phi = 0.25$ squares.

where $g(r)$ is the pair correlation function of the (equal) particles and the limiting value is approached when $l \rightarrow \infty$. The observed effect on S_0 of the ϕ increase was therefore only indirect: as the filling factor is raised, the need of occupying any free space reduces the fluctuations in the number of scatterers per a given volume.

The presence of size distribution does not modify greatly this view. The dependency on the volume of the scattered field reduces the effect of the higher fluctuation in the number of particles due to the size variability, i.e. the possibility that in a free space one large particles or several smaller ones may fit. For low q values, the contributions of near particles are always in phase and the total occupied volume in a certain region becomes the only relevant factor. This explains the weak dependency of S_0 on the broadening of the size distribution.

These considerations can be easily extended to real glass-ceramic materials, with the number of the basic constituents of the particles playing the role of the available space. The growth of nanosized particles, in fact, usually occurs by diffusion within limited spatial regions of the nucleating atoms, which act as building blocks for the particles. Therefore, the original quantity of the building blocks in the region will dictate the total volume of the scatterers in that region, regardless of the size of the single particles.

4. Conclusions

RSA of hard spheres provides useful model systems to study the effects of correlation on the optical scattering of glass-ceramics. The minimum degree of correlation given by the impossibility of interpenetration induces an important decrease in the low- q limit of $S(q)$, which is proportional to the attenuation coefficient. Considering a size distribution of the scatterers does not affect greatly the scattering properties in the visible region. As a matter of fact, the volume dependency of the scattered field attenuates the increased fluctuation in the number of scatterers due to the

size distribution.

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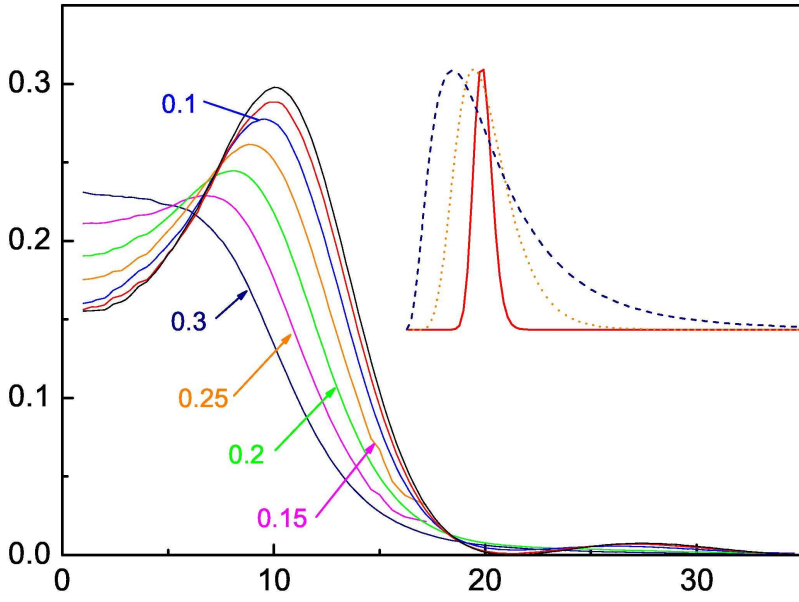
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