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Finite size microcrystal's in glasses

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Experiments described in this paper have shown that Raman technique is a particularly sensitive method to determine the presence of microcrystal's in the glassy matrix. Room-temperature polarized Raman scattering spectra of model glass have been collected. Low-frequency peaks were observed in the spectra. A model is proposed for explanation of their appearance. It is shown clearly that the low-frequency Raman spectra allow determining the conditions at the boundaries, sizes as well as concentration of micro-heterogeneities in non-crystalline materials. It was established earlier that for all amorphous (glassy) materials a low-frequency peak, observed in the corresponding spectral region of Raman scattering and called boson peak, is inherent. This peak is absent in crystals of the same chemical composition and is associated with space correlations on the scale of medium-range order $R_c \approx 10$Å. On the contrary, less known is that a boson peak can give important information about the presence of microcrystalline inclusions and heterogeneities in the low-frequency Raman spectra of glasses irrespective to their chemical composition.

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1. Introduction

Relatively great number of studies has been performed to understand the structure of non-crystalline solids from light scattering investigations. The majority have concentrated on spectral features in the optical mode region of the Raman scattering spectra. Recent interest has developed in the low-frequency or acoustic Raman modes region. This interest is a manifestation of theoretical works on the properties of light scattering from acoustic modes in disordered solids [1, 2]. A direct explanation for the universal presence of low-frequency modes in non-crystalline modes was given by Shuker and Gammon [1] and Martin and Brenig [2] (the later authors exemplified it for the case of oxide glasses). Studies appeared on other aspects of Raman scattering as a sensitive probe for the structure of glasses. To the author's best knowledge, Duval [3] was the first who established that Raman spectroscopy is a powerful and sensitive technique to determine the size of the microcrystal's in a glass. It has been shown that, in the case of microcrystal's included in a glassy phase, only the lowest energy vibration eigenmodes (surface modes) are active in the acoustic Raman scattering region [4-6]. Interestingly, the frequency of these surface vibration modes (modes with large amplitudes at the particle surface) are related to the diameter of the microcrystal's.

The low-frequency Raman spectra of glasses with microcrystal's have been investigated in the present paper. It is shown that the spectra permit to determine conditions at the boundaries, sizes and concentrations of structural microinhomogeneities in disordered materials.

2. Experimental

Model glasses ($K_2O \cdot Al_2O_3 \cdot 6GeO_2$, Photochromic glasses, chalcogenides glasses) were chosen as samples for these studies for several reasons. These materials can be prepared as well characterized high optical quality bulk glasses. Optical quality is important to minimize the spectral component due to elastically scattered light which masks low frequency Raman spectral features. In addition, both glasses can be easily prepared and crystallized. Fortuitously, one can study properties aroused from differences in structure (caused by thermal treatment) in detail.

Right angle Raman spectra were measured using a double monochromator with a spectral slit width of 1 cm^{-1}, and exciting wavelength of 647 nm. Raman measurements were performed in the usual VV and HV polarizations.

3. Results

Fig. 1 shows Raman spectra for the not-annealed and annealed photochromic glass samples. A low-frequency (the so-called boson peak, typical of the spectra of any vitreous material) is observed at the frequency $\omega \approx 60$ cm^{-1}.

Annealing of samples caused a change of the spectra in the frequency range $\omega < 20$ cm^{-1}; the peak with $\omega_{max} \sim 10$ cm^{-1}appears (Fig. 2). The latter corresponds to vibrational spectrum of microcrystals which grow during annealing.

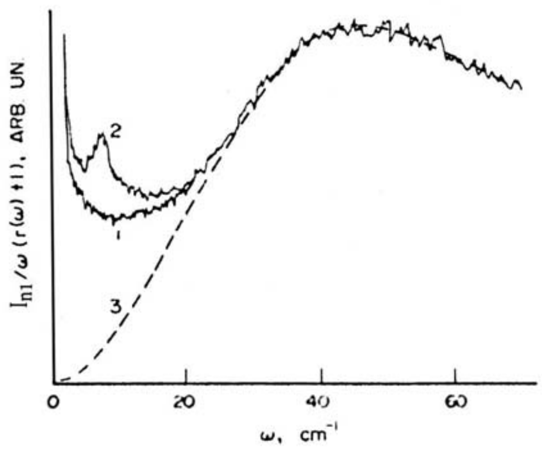

Fig. 1. The low-frequency Raman spectra of the not-annealed (1) and annealed (2) samples; (3) – the calculated spectrum [7] for the contribution from acoustic vibrational excitation.

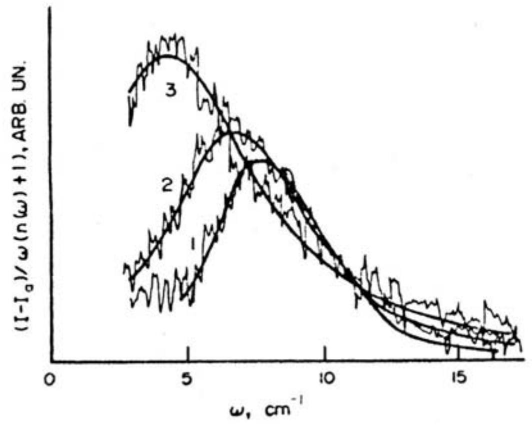

Fig. 2. The difference between spectrum of not-annealed sample and spectra of samples: annealed during 2 h at: 550^o C (1), 573^o C (2) and 600^o C (3).

Clearly, the amplitude of the low-frequency peak increases while $\omega_{\max}$ decreases with annealing temperature.

In general, the annealed samples contain inhomogeneities of two types. The first corresponds to inhomogeneities of matrix itself. The second is associated with microcrystals.

4. Phenomenological approach

The results obtained can be interpreted in terms of phenomenological model. Let us consider homogeneous medium. The density-of-states, $g(\omega)$, is described by the Debye's law

$$g_0(\omega) = 3\omega^2 2\upsilon^3\pi^2 , \tag{1}$$

where $\upsilon = (\upsilon_t^{-1} 2/3 + \upsilon_l^{-1}/3)^{-1}$, with υ_t and υ_l being transverse and longitudal sound velocities, respectively. The presence of microcrystals in glassy matrix changes the Debye density-of-states. There appear additional low-frequency modes due to surface vibrations of microcrystals. These modes are localized at $\omega \approx \upsilon / D$. To describe their contribution to the density-of-states, a simple phenomenological model is used.

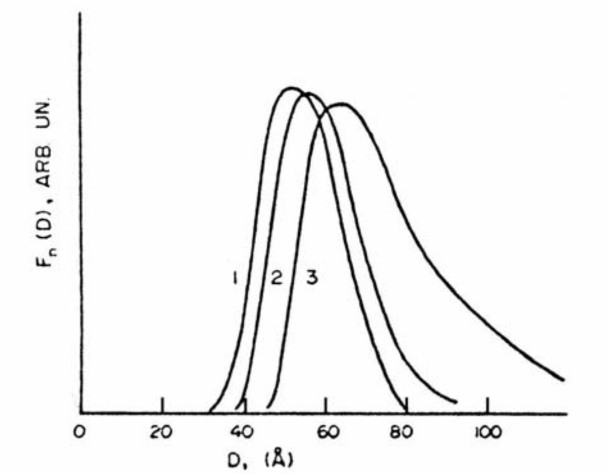

Fig. 3. Microcrystals size distribution of in the samples. Numeration of the curves is the same as in Fig. 2.

The form of the microcrystals is assumed to be close to spherical ones of D_0 in diameter. The density of vibrational states, with account of the contribution from low-frequency modes of a sphere vibrations ω, can be written in the form:

$$g(\omega) = g_0(\omega) + N\delta(\omega - \omega_0) . \tag{2}$$

Both the finite lifetime and the scatter in sizes and shapes of microcrystals results in the broadening of vibrational modes. We can express the Lorentz distribution of width Γ in the form:

$$g(\omega) = 3\omega^2 / 2\upsilon^3\pi^2 + N\Gamma((\omega-\omega_0)^2 + \Gamma^2)^{-1}/\pi . \tag{3}$$

As evident from Eq. (3), there is the resonant peak at $\omega = \omega_0$, superimposed on the smooth Debay density of states.

In disordered materials, the Raman intensity $I_0(\omega)$ is proportional to the density of vibrational states $g(\omega)$ [1]

$$I_0(\omega) \sim C_{ij}(\omega) g(\omega)(n(\omega)+1)/\omega , \tag{4}$$

where C_{ij} is the square of matrix element of light interaction with vibrational excitation, $n(\omega)+1$ is the bose-factor.

In the low-frequency range, for the acoustic vibrations

$$C(\omega) \sim \omega^2 , \tag{5}$$

And the factor of proportionality depends on elasto-optic constants P_{ij} of the material [8]. Assuming Eq. 5 for simplicity, we have

$$I/\omega(n(\omega)+1) \sim g(\omega) . \tag{6}$$

The frequency of a spherical mode, $I = 0$, is related to the sphere diameter D_0 as follows:

$$\omega_0 \cong 0.7\upsilon_c / cD_0 , \tag{7}$$

where c is the light velocity. Spherical and torsional modes have the frequency

$$\omega^l = \omega^t \cong 0.85\upsilon_t / cD_0 . \tag{8}$$

Therefore, the Raman intensity is of the form:

$$I(\omega_0)/\omega_0(n(\omega_0)+1) \approx (P_{ij}{}^g)^2 3\omega_0{}^2 / 2\upsilon^3\pi^2 + P_{ij}{}^m N/\pi\Gamma \tag{9}$$

Here $P_{ij}{}^g$ and $P_{ij}{}^m$ are elasto-optic constants of the glass and microcrystal, respectively. In Eq. (9), the first term corresponds to the scattering on acoustic phonons of the glass I^{ac} , while the second is the contribution of vibrations localized on microcrystals I^{loc} . Therefore, one can estimate: a) microcrystal sizes using the position of the localized mode in Raman spectrum ω_0 ; b) the microcrystal concentration for Γ and I^{loc}/I^{ac} given

$$N \cong (I^{loc}/I^{ac})(P_{ij}{}^g / P_{ij}{}^m)^2 3\omega_0{}^2\Gamma / 2\upsilon^3\pi \tag{10}$$

The model predicts the lowest surface modes to be localized at $\omega_{\max} = \beta / D_0$, where $\beta \approx 10^{-6}$.

It seemed that the appearance of spherical or torsional modes is determined by interaction between the microcrystal surface and the surrounding glassy matrix: spherical modes if the glass matrix is softer than the microcrystal; torsional for the case of weak coupling between the microcrystal surface and the environment.

In addition to D_0 , the Raman spectrum allows to estimate the microcrystal concentration for I^{loc}/I^{ac} given. It is well-known [9] that a central peak make considerable contribution to the intensity of light scattered at room temperature in the range ω < 20 cm^{-1}. Contribution from acoustic vibrations can be separated via approximation of the boson peak. Taking all factors into account, one obtains N ≈ 10^{17} cm^{-3}.

Finally, the low-frequency Raman scattering appears to be a sensitive method for the investigation of the initial stage of nucleation in multi- and mono-component systems [9]. In the case of the mono-component systems, when the crystalline nuclei do not have an acoustic mismatch as compared to the amorphous matrix, we cannot observe their surface vibrations, but we can make use of the fact that in nucleation there is a jump in a structure correlation length. This results in a sharp decrease in contribution to the density of the acoustic vibration states because of decreasing the concentration of structural correlations on which acoustic phonons are localized. In addition, low-frequency Raman spectroscopy may be useful in the research into the phase transformation in materials for phase-change memories. From the fact that the 17 cm^{-1} band is the only observed in a-Se, does not contain microcrystalline-related features which shift in frequency or increase in intensity with thermal treatment, it may be deduced that all our Raman spectra correspond to the advanced stages of crystallization. That means Raman spectra do not show the formation of the very small microcrystals or nuclei but only reflect the more advanced crystal growth process.

5. Concluding remarks

In our opinion, the very low-frequency region of the Raman scattering could be an important source of information on the structure of disordered solids on the scale ~ 10-100 Å. It should be stressed on that the above method is efficient in distinguishing of micro-inhomogeneities with $\omega_{\max} \sim D$.

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