Phonon propagation scale and nanoscale order in vitreous silica from Raman spectroscopy

Vitaly I Korepanov©

Institute of Microelectronics Technology and High Purity Materials RAS, Chernogolovka, Russia

E-mail: korepanov@iptm.ru

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Abstract
For nanoscale systems such as nanoparticles and 3D-bonded networks, the range of spatial coherence is well reflected in the Raman spectral pattern. For confined, or localized, phonons, the range of \( q \)-points contributing to the spectrum depends on the phonon confinement length, which makes it possible to derive size information from the spectra. In this work, the Raman spectrum of vitreous silica is described as localized phonons of an \( \text{SiO}_2 \) network. The convergence of the spectral pattern with the confinement size is studied. It is shown that the phonon propagation scale in vitreous silica is within the 0.5–2 nm range.

Keywords: phonon confinement, Boson peak, glasses, Raman spectroscopy

1. Introduction
Glasses possess a certain degree of local order as evidenced, in particular, by x-ray diffraction \([1, 2]\) and computational studies \([3–7]\). How to quantify the local order, and how to link the experimental data with understanding of the structure are disputable questions of high interest.

The estimates of the correlation length can be based on either static (in particular x-ray diffraction) or dynamic (vibrational spectroscopy) properties \([8]\). In the diffraction experiments of fused silica, the first sharp diffraction peak was assigned to the scale of about 2 nm \([8]\). Structure factor in the neutron diffraction studies also shows peaks in the range 0.8–2 nm interpreted as medium-range order \([9, 10]\).

Vibrational spectroscopy, especially Raman scattering, is sensitive to the nanoscale order and can give information on the coherence range \([11]\). It is argued that the bands in Raman spectra of such systems as fused silica and water represent the phonon modes localized by the disorder \([12–14]\). However, to link the degree of this disorder to the experimental spectral pattern is a non-trivial task.

A number of works suggest that the medium-range order is expressed in Raman spectra as a boson peak, a low-wave-number feature in the range 30–100 cm\(^{-1}\) \([7, 11, 13, 15, 16]\). This peak was also observed in inelastic neutron scattering and hyper-Raman spectroscopy \([17]\). An early attempt to interpret this peak quantitatively was done in terms of the elastic sphere model (frequency of the Raman peak is inversely proportional to the nanocrystal size) and gave the value of 2.5 nm \([8]\). Later, molecular dynamics simulation suggested that the boson peak should be interpreted as lowest optic states hybridized with acoustic states due to the disorder \([13]\). Low-energy modes were also analyzed within simplified model with locally distorted potentials; a coherence range was estimated to be from 1.5 to ~100 nm depending on the phonon energy \([16]\). Although computational studies allow simulation of the Raman spectra \([6, 18]\), physically consistent interpretation of the spectral pattern in terms of local order is still a challenge.

When the vibrations in the continuous network are localized by the disorder, the propagation scale of these phonon-like modes reflects the degree of the dynamic order \([14, 19]\). Raman spectral pattern for nanoscale systems is a reflection of this coherence \([11, 20]\). For the localized (confined) phonons, the Raman spectrum is not limited to the near Brillouin zone (BZ) center modes. The contribution of different \( k \)-points depends on the size, and can be found from Fourier decomposition of the confined phonons into the original bulk wavefunctions \([20]\):
\[ I(\omega) \approx \frac{\Gamma_0(\sigma) \cdot |C(q_0, q)|^2}{(\omega - \omega(q))^2 + (\Gamma_0(\sigma)/2)^2} d^3q. \]  

where \( \omega \) is the wavenumber, \( \sigma \) is the confinement size, \( \Gamma_0 \) is the natural linewidth, \( C(q_0, q) \) is the Fourier coefficient for a given confinement shape and size at a given wave vector \( q \). The scattering intensity at \( q_0 \) depends on the phonon propagation direction, and can be calculated from Raman tensor \([18]\). This gives additional intensity factor \( A_i(q, \varphi, \theta) \) for scattering angles \( \varphi \) and \( \theta \) \([21]\). The intensities should be integrated (numerically) over the scattering directions in polar coordinates and summed up over band index \( i \):

\[ I(\omega) \approx \sum_i \iiint \frac{A_i(q_0, \varphi, \theta) \cdot \Gamma_{0i} \cdot |C(q_0, q)|^2 \cdot q^2}{(\omega - \omega_i(q))^2 + (\Gamma_{0i}(\sigma)/2)^2} dq d\varphi d\theta. \]  

Within such approach, the acoustic phonons should have no contribution, because the intensity factors are zero. However, in disordered systems, the Raman intensity for acoustic phonon range should be described a different way. It was shown that there is an additional wavenumber dependence, referred to as light-to-vibration coupling coefficient \( C_{av}(\omega) \) \([22]\). Experimental studies showed that this dependence is close to linear \( C_{av}(\omega) \sim \omega \) \([23, 24]\).

The phonon confinement model formulated in this way was recently applied to hydrogen-bond network of water, it was shown that experimental Raman spectra of liquid water contain highly important information on the size of ice-like structure fragments \([14]\). The equation (2) links the Raman spectral pattern with the coherence range of the confined phonons. The present study aims at interpretation of the Raman spectra of silica in terms of phonons propagation scale of the SiO\(_2\) network.

2. Modeling and experimental details

Based on the similarities between cristobalite and fused silica glass in terms of structure and Raman spectra \([3, 7, 25, 26]\), cristobalite is taken as the structure motif at the nanometer
The phonon dispersion $\omega(q)$ was calculated with the Quantum Espresso package [27, 28]. The PBEsol functional was taken with high-throughput ultrashort pseudopotentials [29] with cut-off for wavefunctions/charge density of 56/320 Ry. The 12-atom unit cell was taken. The geometry and cell parameters were optimized with $8 \times 8 \times 6$ $k$-point grid; phonon dispersion was calculated with the $8 \times 8 \times 6$ grid. Raman tensor was calculated with LDA (PZ) functional with norm-conserving pseudopotentials [30] with the cut-off of 112/448 Ry with the same geometrical parameters. Although the Raman tensor can be calculated with PBEsol functional numerically using the finite-fields/finite-differences approach, it was found in our work [14] and in the literature [31] that Raman intensities estimated by GGA and LDA are in a very good agreement with each other. GGA-level computations are at least 3 times more expensive in terms of the machine time, therefore it was decided to use LDA for this simulation.

The intensity factors $A_i(q, \varphi, \theta)$ were calculated from Raman tensor for the vibrational forms for each $\varphi$ and $\theta$. The Sortphon algorithm was used to exclude the band index permutation [32]. For each band, the intensity factors were scaled according to the experimental spectra of bulk cristobalite. Scaling of the phonon energies was done to match the computed Raman spectral pattern of cristobalite with the experimental data by multiplying the whole dispersion function of the given band $\omega(q)$ by the scaling factor [33]. The scaling factors were in the range (0.96... 1.06). Calculated phonon dispersion is in good agreement with recent ab initio studies [7], where single scaling factor (1.039) was applied.

For the form-factor calculation, spherical confinement was assumed; the Fourier coefficients $C(q, \sigma)$ for this case have an analytic form of Bessel-like function [33]. The integration in equation (2) is done within [0,2] range of the reduced wavevector (i.e. not limited to the 1st BZ [34]).

The Raman spectra of the localized phonons were calculated with equation (2). For the natural linewidth, the inverse size dependence was assumed $\Gamma_i(\sigma) = \Gamma_i(\infty)(1 + g_i/\sigma)$, which reflects the different lifetimes of the localized phonons [11, 35, 36]. $\Gamma_i(\infty)$ is the linewidth for the bulk crystal. $g_i(\infty)$ and $g_i$ values were determined from experimental data for bulk crystal and fused silica correspondingly.

The Raman measurements were carried out with a laboratory built spectroscopic system described elsewhere [37]. Excitation wavelength was 532 nm with laser power of 12 mW at the sample point; 20 × objective was used. Eight spectra were averaged with acquisition time of 30 s. The measured spectra were reduced with the Boltzmann factor and corrected for the $\nu^3$ frequency dependence [37, 38]. For the correct comparison with the calculated spectra, the latter should also be divided by $\omega$ according to the Placzek’s expression [39].

3. Results and discussions

The calculated Raman spectral patterns for different propagation lengths are shown in figure 1. The bands of the bulk cristobalite broaden asymmetrically upon confinement in accordance with the dispersion functions. The most pronounced size dependence is seen in the low-wavenumber region (LWR). Similar size sensitivity can be found in nanoparticles [21,40] and hydrogen-bonded network of water [14], both experimentally and theoretically.

For the size below 2 nm, the calculated spectrum converges to the asymptotic pattern (figure 1). From the Fourier coefficients, $C(q,\sigma)$ it can be seen that the $q$-vectors are effectively spread through the whole BZ for sub-2 nm confinement (figure 2).

From comparison of experimental Raman spectra with the calculations (figure 3), it is clear that the observed spectrum corresponds to the ‘converged’ spectral pattern, in which phonons from the whole BZ are allowed. For the acoustic phonons considered separately, the calculated band maximum is highly sensitive to the size in the few-nm range (figure 4). It arrives to asymptote of ~70 cm$^{-1}$ by the sub-1 nm confinement, which corresponds to 2 unit cells. The corresponding cluster of this size is shown in figure 4 (right).

For small coherence length, the expected spectral patterns show close similarity (figure 3). Below ~2 nm, the positions of the localized acoustic modes vary only within ~10 cm$^{-1}$ (figure 4). It is reasonable to assume that the experimental Raman spectra include contributions from multiple modes with localization scale in the range 0.5–2 nm. This interpretation is in good
agreement with the assignment of the x-ray and neutron diffraction data, which also show certain degree of coherence of the same size scale [8–10]. This result is more consistent than an early interpretation of the boson peak with elastic sphere model which suggested a size scale of ~2.5 nm [8].

4. Conclusions

The phonon confinement model allows one to link the Raman spectral pattern to the degree of medium-range order. It is shown that the Raman spectral pattern of vitreous silica can be well described as confined phonons of SiO2 networks. The LWR of the spectrum has a pronounced dependence on the phonon propagation scale. Upon the confinement, the Raman spectrum converges by the 2 nm size to the spectral pattern, in which q-points from the whole BZ are effectively allowed. Unlike the hydrogen-bonded network of water, the structure of vitreous silica is characterized by a high degree of uniformity. The size scale of the medium-range order estimated from Raman spectroscopy is in good agreement with the x-ray and neutron diffraction data, which also show the coherence in the 0.5–2 nm range. The present approach can be used to analyze not only nanoparticles, but also systems with different degrees of medium-range order, in particular amorphous systems at early stages of crystallization.

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ORCID iDs

Vitaly I Korepanov https://orcid.org/0000-0001-5761-137X

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