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In situ measurements of the D₁ and D₂ Raman band intensities of vitreous and molten silica in the 77–2150 K temperature range

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Abstract

In situ quantitative Raman spectra of vitreous and molten silica were measured from LN₂ temperatures up to above melting and used to calculate the intensities of the two ‘defect peaks’ D₁ and D₂ associated with the corresponding four- and three-membered ring structures. The D₁ intensity decreases with increasing temperature while the D₂ intensity appears to be invariant to temperature. The data are in disagreement with the quenching/fictive temperature experiments and show definitely no abrupt intensity changes at any temperature.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Over 50 years ago Krishnan obtained the first room temperature Raman spectrum of vitreous silica by using a spectrograph and photographic film [1]. Since then a large number of papers concerning the vibrational spectra of vitreous silica and their interpretation in the framework of a continuous network have been published. A rather thorough list of the most important references in the field is given in a recent publication [2]. One mystifying behavior in the overall Raman spectrum consisting of broad bands is the appearance of the two sharp ‘defect peaks’ D₁ and D₂ at ~ 495 and ~ 610 cm⁻¹, respectively. These bands are totally polarized with a full width at half-maximum much narrower than those of the regular network bands. A combination of experimental, theoretical and simulation methods have convincingly associated these bands to breathing vibrations of the four- and three-membered rings [3–8]. The three-membered rings appear to be planar while the four-membered rings deviate from planarity. Early Raman spectroscopic studies [4] have shown that the population of these rings increases smoothly with increasing quenching rate, indicating

that their formation is favored at high temperatures. A similar conclusion was inferred from high temperature Raman measurements of McMillan *et al* [9]. Furthermore, these studies revealed that the D₁ and D₂ ring frequencies were rather insensitive to temperature, indicating that their vibrational modes are more likely to be decoupled from the rest of the silica network.

Recently, *in situ* Raman spectra of vitreous and molten silica from 77 to 2150 K have shown that the D₁ and D₂ frequencies shift to lower energies with increasing temperature (i.e. decreasing density) but the shift was much weaker relative to the shift of the remaining stretching/bending modes of the SiO₄ tetrahedra participating in the network [2]. High pressure *in situ* Raman studies also show similar but stronger relative shifts with decreasing pressure (density) in the elastic compression region [10]. Another recent *in situ* Raman study of vitreous silica in the temperature range 300–1600 K shows that the D_{*i*} (*i* = 1, 2) intensities remain practically constant in all temperatures studied [11], which is in disagreement with the fictive temperature [4] and the previous high temperature studies [9]. Finally, a careful Raman study of quenched vitreous silica samples shows a reversal of the D_{*i*} intensity

slopes at fictive temperatures near the recently discovered density minimum of vitreous silica [12].

It is noteworthy that the D_i intensity changes in the above studies were estimated experimentally using two different methods: (a) by measuring for each fictive temperature the D_i band intensity (area) relative to the total area of the reduced spectra [4, 12] or (b) by keeping the scattering geometry and spectral conditions rather constant and measuring for each (real) temperature the D_i intensity relative to that of another spectrum measured at room temperature [11]. A smoothly varying background around the D_i bands [4, 12] or Gaussian fittings of the overall spectrum [11] were used to calculate the band intensities.

In the present work *in situ* quantitative Raman spectral measurements in the temperature range 77–2150 K are used to calculate the peak and area intensities of the D_i bands relative both to the total spectral band intensity and to the corresponding room temperature intensity. The percentages of the D_i intensities relative to the intensity of the overall spectrum are measured at each temperature and compared with those measured by the above-mentioned quenching experiments. The results are discussed in terms of the discrepancies found between the *in situ* and the fictive temperature data and the structural peculiarities of vitreous/liquid silica.

2. Experimental details

High purity silicon dioxide rods of 3 and 5 mm in diameter, (Suprasil 300, Heraeus Amersil Inc., Hanau, Germany) were used in the present study. The specified purity in water content was ~ 1 ppm and the metallic impurity concentration ~ 10 ppb. Three different experimental Raman set-ups were utilized to cover the complete temperature range 77–2150 K. A homemade optical Dewar-type cryostat was used for recording and comparing relative Raman intensities in the low temperature (77–300 K) regime with an accuracy less than 1%. In the interval 300–1300 K a homemade water-cooled optical furnace with Kanthal heating wire permitted relative Raman intensity measurements with a maximum error of less than 2% [13]. For measurements at temperatures higher than 1300 K and up to above melting a self-support configuration and CO₂ laser heating were used [2, 14]. This latter set-up permits relative intensity measurements within a spectrum at a chosen temperature but no accurate comparisons can be made with the spectra at other temperatures [2]. Detailed descriptions of the configurations used are given in the above cited references.

The room temperature spectrum was taken as the basis for the relative intensity measurements. By matching the room temperature spectrum measured for the silica rod sample in the cryostat to that measured in the Kanthal furnace, relative intensity values could be established from 77 to 1300 K with an estimated maximum error of $\sim 2\%$. At higher temperatures, faster integration times and different iris diaphragm apertures in the Raman collection optics were used and thus intensity comparison with the room temperature spectrum could not be made accurately.

3. Results and discussion

Raman spectra of silica were measured at 20 different temperatures from LN2 to above melting. From the raw data intensities in polarized (I_{VV}) and depolarized (I_{VH}) configurations the reduced isotropic (R_{Iso}) and anisotropic (R_{Aniso}) representations were calculated [2, 15]. A selection of spectra at four characteristic temperatures is shown in figure 1. Cycling the temperature without quenching did not show any changes in intensities. The band assignments, the appearance of new bands in the Si–O stretching region (800–1000 cm⁻¹) at high temperatures and the preservation of the boson peak (~ 60 cm⁻¹) in the high temperature glass and the melt have been discussed elsewhere [2, 16].

The dotted lines below the D_1 and D_2 bands in the reduced spectra are examples of the typical baselines used to measure the peak intensity and the area under these bands. The overlap between the D_1 and the 450 cm⁻¹ band does not permit intensity measurements at temperatures above 1200 K. On the other hand, the D_2 intensities could be measured in the complete temperature range but, as discussed previously, the intensity values above 1300 K could not be easily correlated to the values measured below this temperature due to the different experimental set-ups used. However, it seems that in the normalized data (figure 2) both regions, above and below 1300 K, follow the same trends on a line with a small negative slope. The estimated errors in measuring the D_1 intensities were higher than those of D_2 and increased with increasing temperatures. The peak/area intensities relative to the corresponding values at room temperature, including the estimated error bars, are shown in figure 2. To extend the comparison of the D_i area intensities in the full temperature range (77–2150 K) the areas were normalized with respect to the overall spectral intensity. Thus, the areas of the reduced isotropic spectra were measured and the percentages of the D_i areas were calculated and plotted in figure 3. The depolarized intensity ($I_{VH} = I_{Aniso}$) is much lower than the polarized part (I_{VV}), which implies that there are some small differences between the reduced polarized (R_{VV}) and the reduced isotropic (R_{Iso}) intensities; this is reflected in the percentage areas of the D_i bands giving somewhat lower values (and higher slopes) by using the R_{VV} instead of the R_{Iso} representation (see figure 3). Both figures 2 and 3 contain for comparison corresponding data taken from the literature cited in the figure captions.

It appears from figure 2 that the *in situ* data give D_i intensities which do not change drastically with temperature, having small negative slopes. The present data are in excellent agreement with the data presented in [11] for a narrower temperature range and where the intensities are measured from curve fitting of the data in contrast to the baseline method used in the present work. On the other hand, measurements of the D_i intensities after quenching [17] give positive slopes on a fictive temperature plot. Irrefutable differences are seen in the percentage normalization (figure 3) where the *in situ* measurements indicate smooth changes and negative slopes while the quenching/fictive temperature results of two investigations [4, 12] almost coincide at temperatures above 1200 K with marked positive slopes. Extension of the

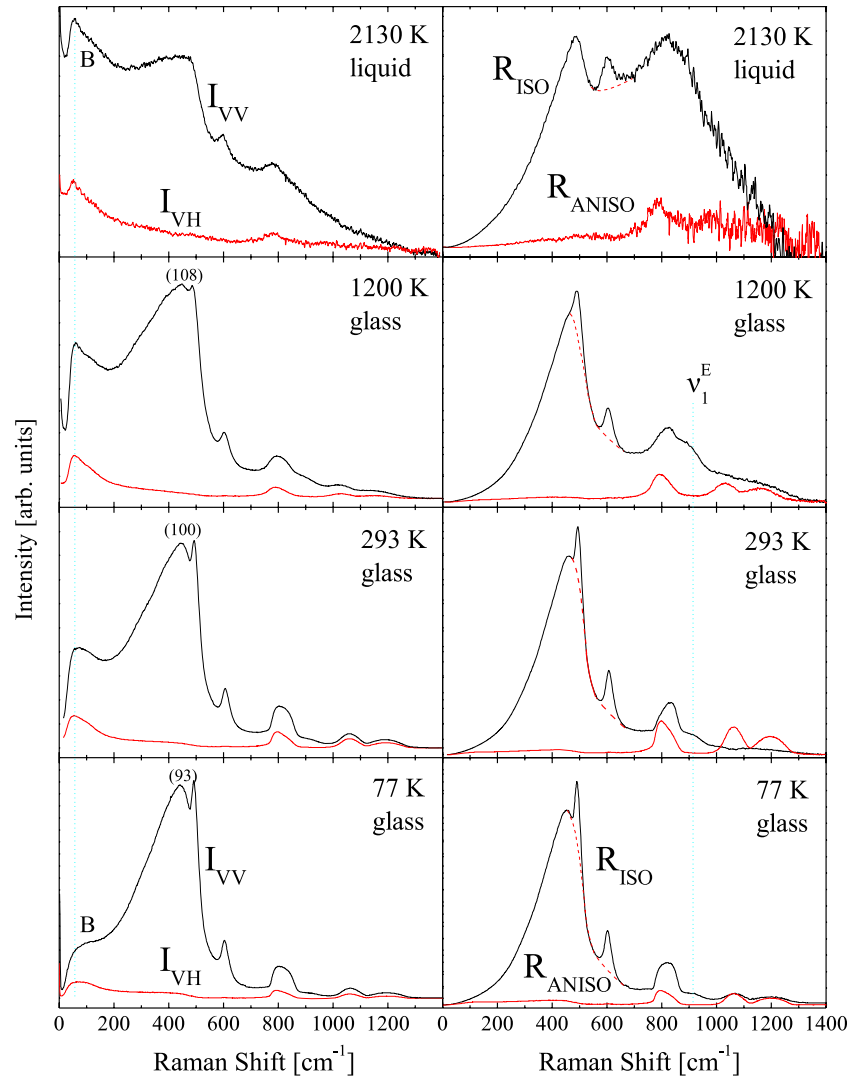


Figure 1. Raman spectra of vitreous and molten silica at selected temperatures. *Left panel:* raw data are shown in the I_{VV} and $I_{VH}(=I_{Aniso})$ polarizations. Numbers in parentheses indicate the peak intensity of the $\sim 450\text{ cm}^{-1}$ band relative to that at room temperature having an arbitrary value of 100. For the liquid spectra and all spectra obtained above 1400 K and used in the present work a correction for black-body radiation was made; for details see [2, 14]. The B marks the boson peak [2, 16]. *Right panel:* calculated reduced isotropic spectra (R_{ISO}); the dashed lines indicate the background used for calculating the D_i band peak and area intensities. The ν_I^E marks the frequency associated with edge bridged tetrahedra [2]. *Spectral conditions:* resolution 2 cm^{-1} (CCD detector), laser power 400 mW, laser line 488 or 514.5 nm for measurements above or below room temperature, respectively.

quenching experiments down to 1100 K reverses the slopes and shallow minima appear which are correlated to the presence of a density minimum of vitreous silica in the same temperature range [12, 18].

The *in situ* data clearly show that, when vitreous silica is heated/cooled slowly, there are no abrupt intensity changes of the D_i bands. The association of these bands with the four- and three-membered rings implies smooth variation of the population of the rings. Increasing temperature does not affect much the relative intensities (figure 2) and it seems that the population of both the three- and four-membered rings decreases slightly. A more pronounced population decrease with increasing temperature is noticeable by the measurements of the percentage area measurements (figure 3), especially in the case of the four-membered rings while the three-membered rings are practically unaffected. The D_2 band intensities of

the quenched samples are lower than those of the *in situ* experiments at temperatures below T_g , but the situation appears to be reversed at temperatures above T_g (figure 3). To a certain extent the behavior of the D_1 band intensities (figure 3) is similar since the extrapolated line of the *in situ* D_1 data meets and splits the bulk of the quenched data values above and below this line at temperatures above and below the T_g region, respectively.

There are basically two ways by which the temperature influences the vibrational spectra of vitreous silica. First, higher vibrational states are occupied and the amplitudes of vibration of all species involved increase with increasing temperature. The effect presumably facilitates structural transformations and is more likely reversible; thus for a quenched species the amplitudes of vibration would not be much different than those of the same species in an

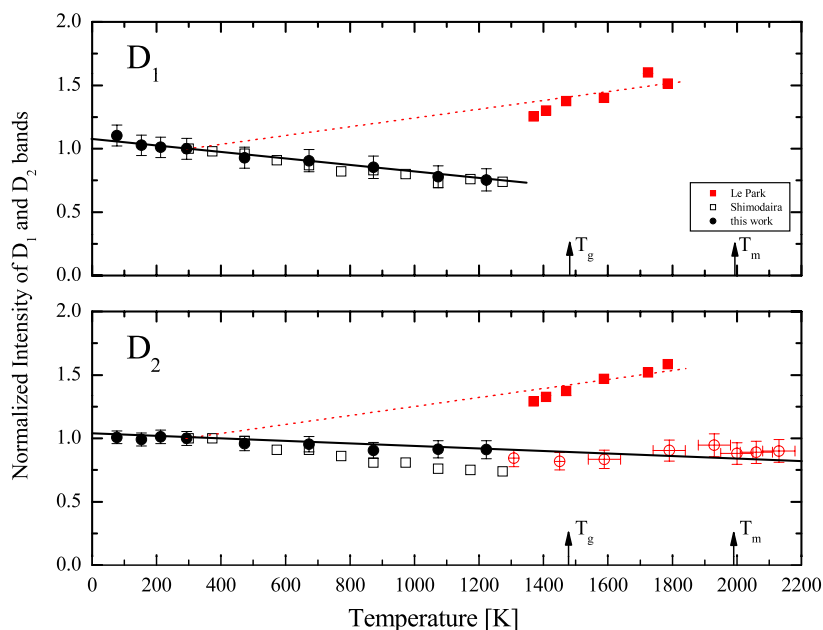


Figure 2. Temperature dependence of the D_1 and D_2 band intensities relative to the corresponding room temperature intensities; peak or area intensity measurements gave identical results. The D_2 intensities above 1300 K cannot be accurately correlated to the 77–1200 K intensities due to the different set-ups used (see text) and different symbols (\bullet and \circ) mark the data in these two regions; however, the points can be approximately connected with a common line and slope. Vertical error bars are estimated errors in measuring the intensities. Horizontal error bars indicate temperature uncertainties in the region above 1400 K while for the region below 1400 K the temperature uncertainties are rather small (<5 K; see [2] for details). A comparison with the literature data of Shimodaira *et al* [11] and Le Park *et al* [17] was possible as follows: (a) the Shimodaira's *in situ* peak intensities of the D_i bands were normalized to the corresponding room temperature intensity, giving values overlapping with the present data, (b) the LePark quenching area intensities of the D_i bands were normalized to the corresponding intensity with the lowest fictive temperature (~ 1300 K); a slope of the line fitting the data was established and the line was moved in a parallel way and extrapolated so as to intercept the room temperature point of the present data. Comparison between the *in situ* and fictive temperature data can be made only vis-à-vis the sign of the established slopes and not the magnitude of the normalized values.

equilibrium glass cooled slowly to room temperature. Second, structural changes and rearrangements of the network occur with increasing temperature which alter the populations of the species involved, give rise to new bands and modify the band intensities. A series of *in situ* measurements in a variety of high temperature melts and glasses have shown that reversible Raman intensity changes with temperature are associated with either species in equilibrium or with continuous but reversible structural distortions of the species involved [2, 15]. It seems that the temperature dependence of the silica spectra reflect mainly species in equilibrium showing 'vertical' intensity changes which involve most bands present including the D_i bands [2]. The planar three-membered rings are formed with bond strain of the SiO_4 tetrahedra and most probably have a higher activation energy than that of the four-(or higher-) membered rings consisting of unstrained SiO_4 bridged tetrahedral structures similar to those of the remaining network. Thus, when silica is equilibrated at a certain temperature (as in the *in situ* experiments) structural transformation (or dissociation) of the D_1 rings is easier relative to that of the D_2 rings and this is presumably reflected in the D_1 and D_2 slope differences seen in figures 2 and 3.

The liquid or supercooled liquid quenching experiments 'freeze' the configurational motions and trap the rings and all structural domains of the network with high dissociation activation energies. Thus, the room temperature spectra are characterized by the low amplitude vibrational modes of

all these species, plus the modes of the remaining network domains which, due to their lower activation energies, may exhibit structural alterations relative to the high temperature liquid. Upon quenching the high temperature D_i areas and the normalization area (i.e. the area of the remaining spectrum) 'shrink' due to the diminishing amplitudes of vibration at room temperature. At the same time the *in situ* data show that the D_i intensities are constant or have negative slope with increasing temperature, while positive slopes have been found for the fictive temperature data (figures 2 and 3). This would require that the 'shrinkage' of the band areas upon quenching is not proportional to the original areas of the high temperature glass/liquid spectra. Furthermore, the positive slopes would imply that the higher the quenching temperature the smaller the normalization area and/or the higher the D_i areas at ambient temperatures. Such a behavior could probably be related to the fact that at high fictive temperature the network is to a small extent partially broken relative to that of a lower fictive temperature; a broken network would involve less inter-related vibrations, less bridging modes and more terminal modes, leading consequently to narrower Raman bands in the quenched glass. Alternatively it might be that the quenching processes enhance the D_i ring populations (areas), the effect being more pronounced at high fictive temperatures. So, the trapping by quenching rings may increase in part their population from transformations of other low activation energy species participating in the network. Such a process is also

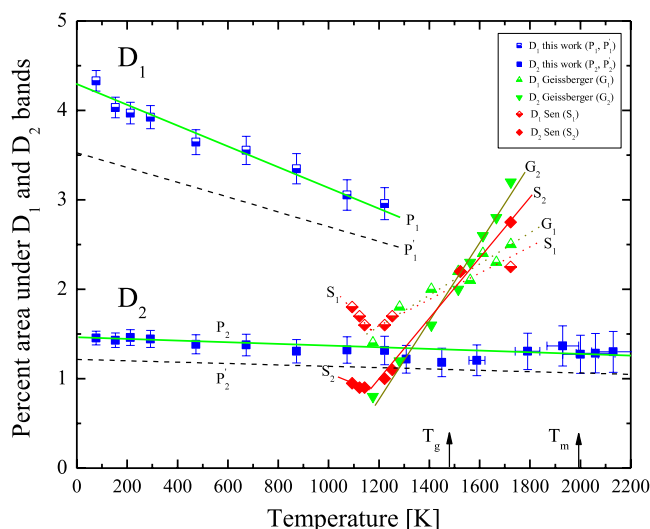


Figure 3. The percentage population of the D_1 and D_2 rings in vitreous and molten silica in a wide temperature range calculated from the *in situ* measurements. The data points and the straight lines through them were calculated from the reduced isotropic spectra (R_{iso}). The dashed lines (no points are shown to aid the clarity of the figure) are the result of the calculations based on the reduced polarized spectra (R_{V}). Error bars are as in figure 2. A direct comparison with the quenching data of Geissberger *et al* [4] and Sen [12] in the fictive temperature range (~ 1000 – 1700 K) is shown. Both sets of data give similar values and positive slopes at fictive temperatures above 1000 K; the slopes are reversed in the Sen data at lower temperatures.

compatible with the view suggesting that the D_i rings are not embedded in the network but are located on surfaces of clusters participating in the overall glass structure [19]. Thus, it might be that, upon quenching to room temperature, the clusters alter their size and increase the D_i population on their surface. In other words the glass structure relaxation processes continue in part at temperatures below T_g and down to ambient temperatures, which is a rather unusual process to happen for a glass with very high T_g originating from a strong (non-fragile) liquid.

Finally, it should be pointed out that a molecular dynamics simulations study has questioned the proportionality relation between the D_i intensities and the population of the corresponding rings in vitreous silica [8]. This is in contrast to the views accepted by all the studies on the D_i bands used and quoted in this paper. Nevertheless, the present quantitative treatment of the *in situ* measurements and the discrepancies found with the quenching experiments are irrelevant to the association or not of the D_i areas with the ring populations.

4. Concluding remarks

The *in situ* Raman spectral measurements show that the D_1 and D_2 ‘defect’ band intensities of silica vary smoothly with temperature in the region studied from 77 to 2150 K. No abrupt

or unusual intensity changes are observed, including the 1100–1300 K region where a density minimum in vitreous silica has been reported. The percentage of the four-membered rings is estimated to be over 4% at LN_2 temperatures and diminishes to $\sim 3\%$ at 1200 K. A smaller percentage of $\sim 1.5\%$ has been measured for the three-membered rings and found to be practically constant from LN_2 temperature up to above melting. The present data show that the vitreous/liquid structure and the ring populations associated with a fictive temperature in the quenching experiments do not reflect by any means the ‘equilibrium’ structure at that temperature. It seems that it is rather risky to extract conclusions on the properties of vitreous materials at high temperatures by quenching experiments; in this respect, previous interpretations of results and views based on such experiments should be treated with skepticism.

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