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A Raman study of the ring defects in $\text{GeO}_2\text{-SiO}_2$ glasses

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Abstract. The Raman spectra of $\text{GeO}_2\text{-SiO}_2$ glasses have been studied using samples of different GeO_2 contents, which are found to have the general features of the spectrum of vitreous SiO_2 ($v\text{-SiO}_2$). It is demonstrated that substitution of Ge for Si in the $v\text{-SiO}_2$ network prevents the formation of ring structures. A new vibrational band located at $570\text{--}700\text{ cm}^{-1}$ was found in the spectra of high- GeO_2 -content samples (above 5.0 at.% GeO_2). It is also shown that the W_3 vibration of the $v\text{-SiO}_2$ network is reduced in highly GeO_2 doped $\text{GeO}_2\text{-SiO}_2$ glasses.

1. Introduction

The vibrational spectra of amorphous solids consist primarily of broad lines, whose width has been ascribed to disorder in the bond angles (Bell 1982, Galeener 1979), force constants (Martin and Galeener 1981) and breakdown in vibrational rules (Shuker and Gammon 1970). However, attention has been drawn to significantly narrow lines which are also part of the Raman spectra of several glasses (Galeener 1982a, b, Griscom 1978, Lucovsky *et al* 1983, Bridenbaugh *et al* 1979). It has been proposed (Galeener 1982a, b) that these sharp lines in vitreous SiO_2 ($v\text{-SiO}_2$) are due to the highly regular rings in the $v\text{-SiO}_2$ network.

Recently, EXAFS and x-ray scattering experiments were carried out on $\text{GeO}_2\text{-SiO}_2$ glasses (Greeger *et al* 1987) to determine their structures. The analysis indicated a substitutional model in which Ge substitutes randomly for Si in the $v\text{-SiO}_2$ network with little Ge clustering. However, information about the ring structures was not included in the data. In this paper, we present the Raman spectra of the $\text{GeO}_2\text{-SiO}_2$ glasses, from which we investigate certain characteristic properties of the ring defects.

2. Experimental details

Seven samples were employed in this investigation: $v\text{-SiO}_2$; 0.1 at.% $\text{GeO}_2\text{-}99.9$ at.% SiO_2 ; 1.0 at.% $\text{GeO}_2\text{-}99.0$ at.% SiO_2 ; 5.0 at.% $\text{GeO}_2\text{-}95.0$ at.% SiO_2 ; 13.0 at.% $\text{GeO}_2\text{-}87.0$ at.% SiO_2 ; 15.0 at.% $\text{GeO}_2\text{-}85.0$ at.% SiO_2 ; 25.0 at.% $\text{GeO}_2\text{-}75.0$ at.% SiO_2 . These samples were prepared by a vapour-phase oxidation process. (MCVD method) using vapour mixtures of GeCl_4 and SiCl_4 . In this process a porous preform of $v\text{-SiO}_2$ or $\text{GeO}_2\text{-SiO}_2$ glass is prepared by depositing the 'soot' reaction products (from

hydrolysis–oxidation of GeCl_4 – SiCl_4 vapour mixtures by a hydrogen–oxygen flame) onto the inside wall of a bait quartz tube rotating in air. This porous preform is then sintered to a high-quality bubble-free glass rod at 1500 °C. The glass composition is controlled by varying the SiCl_4 and GeCl_4 vapour flows. The GeO_2 content was determined by x-ray energy dispersion techniques as well as deflection rate measurements. A round plate 11.24 mm in diameter and 5.00 mm in thickness was cut from this rod. Samples sectioned from these plates along the diameter were fixed with a clamp. The Raman spectra were obtained from a Jobin–Yvon U-1000 Raman spectrometer in the standard 90° scattering configuration at 200 mW from the 514.5 nm line of an Ar^+ laser.

3. Results and discussion

The Raman spectra obtained in our experiment is shown in figure 1. The broad features are labelled W_1 and W_3 as suggested by Galeener (1979). They have been identified as the vibrations of the ν - SiO_2 network as described by a nearest-neighbour central-force dynamical theory (Galeener 1979, Sen and Thorpe 1977). The defect lines labelled D_1 and D_2 have been interpreted by Galeener 1982a, b) as arising from the symmetric stretch of planar threefold and regular fourfold ring structures, respectively. These rings are embedded in the more irregular glass network that accounts for the broad lines.

It is demonstrated in the figure that the Raman spectra of SiO_2 – GeO_2 glasses containing a relatively small fraction of GeO_2 have the general features of the ν - SiO_2 Raman spectrum. However, the changes in defect lines are obvious. With increasing GeO_2 content, the intensity of the D_1 line decreases sharply, while that of the D_2 line decreases slowly and broadens.

The decrease in the intensities of the D_1 and D_2 lines indicates a decrease in the number of fourfold and threefold ring defects in the GeO_2 – SiO_2 network. This reduction signifies that the substitution of Ge for Si in the ν - SiO_2 network prevents the formation of the ring structures.

According to the results of EXAFS and x-ray scattering (Gregor *et al* 1987) and the fact that the Raman spectra of GeO_2 – SiO_2 glasses have the general features of the ν - SiO_2 Raman spectrum, the structure of GeO_2 – SiO_2 glasses can be considered to be such that there are some GeO_4 tetrahedra in the GeO_2 – SiO_2 glass network, and the number of tetrahedra is determined by the GeO_2 content. In this structure, fewer fourfold and threefold ring defects exist than in ν - SiO_2 .

In the ν - SiO_2 network, a ring structure (fourfold or threefold ring defect) occupies more volume than does an SiO_4 tetrahedroid. For an Si–O bond length a of 1.62 Å, an O–Si–O bridge angle θ of 144° and an Si atomic radius r of 1.172 Å, we can estimate the volumes of an SiO_4 tetrahedroid, a threefold ring and a fourfold ring as $V_T = 2.18 \text{ \AA}^3$, $V_3 = 7.99 \text{ \AA}^3$ and $V_4 = 14.85 \text{ \AA}^3$, respectively. The volumes of the two-atom structure –Si–O– in the threefold and fourfold ring structures are $V'_3 = 2.66 \text{ \AA}^3$ and $V'_4 = 3.71 \text{ \AA}^3$, respectively, which are larger than the volume of an SiO_4 tetrahedroid. When Ge substitutes for Si in the ν - SiO_2 network, each GeO_4 tetrahedroid causes an increment in volume because of the larger Ge–O bond length, $b = 1.68$ – 1.72 Å (Gregor *et al* 1987). For $b = 1.70$ Å, $\Delta V/V = 3(a - b)/a = 15\%$. This results in distortion and strain in the glass network, and therefore an increase in internal energy. The break-up of the ring defects in GeO_2 – SiO_2 glass formation process releases the distortion and strain and lowers the internal energy. The decrease in the intensities of the D_1 and D_2 lines in the spectra can be attributed to this break-up. Because the threefold ring defect

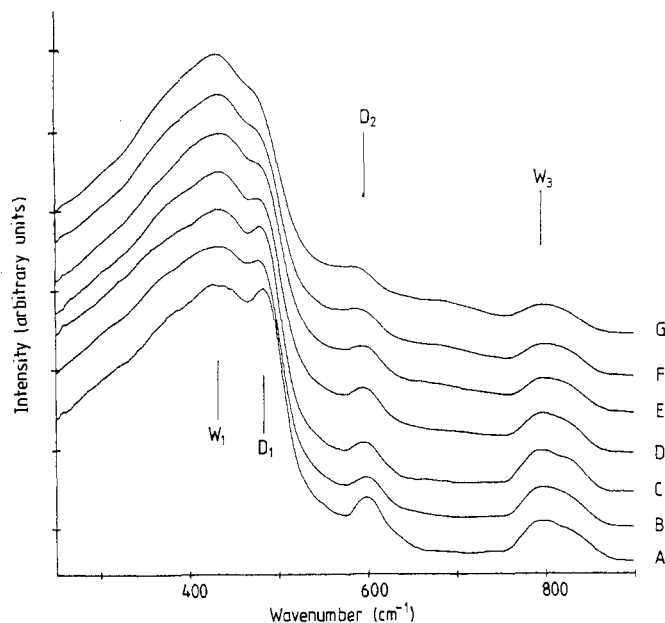


Figure 1. The Raman spectra of $v\text{-SiO}_2$ (curve A), 0.1 at. % $\text{GeO}_2\text{-99.9 at. % SiO}_2$ (curve B), 1.0 at. % $\text{GeO}_2\text{-99.0 at. % SiO}_2$ (curve C), 5.0 at. % $\text{GeO}_2\text{-95.0 at. % SiO}_2$ (curve D), 13.0 at. % $\text{GeO}_2\text{-87.0 at. % SiO}_2$ (curve E), 15.0 at. % $\text{GeO}_2\text{-85.0 at. % SiO}_2$ (curve F), and 25.0 at. % $\text{GeO}_2\text{-75.0 at. % SiO}_2$ (curve G).

has a higher activation energy (Geissberger and Galeener 1983) and smaller volume than does the fourfold ring, we can expect there to be fewer fourfold ring defects than threefold ring defects in $\text{GeO}_2\text{-SiO}_2$ glasses. These differences explain the fact that there is a sharp decrease in D_1 line intensity but a relatively small decrease in the D_2 line intensity.

It is also noticeable in the Raman spectra that the D_2 line becomes a broad feature for a GeO_2 content above 5.0 at. % and a band-like feature at around 700 cm^{-1} appears for a GeO_2 content above 13.0 at. %. Peng and Tian (1989) suggested that these features are due to a new peak which is characteristic of Ge doping in the range $570\text{--}700\text{ cm}^{-1}$ of the VDOS spectra of the glasses. This new peak can be accounted for by superposition of the local densities of the states of SiO_4 and GeO_4 tetrahedra with different weights.

From the Raman spectra (figure 1), it is also shown that the W_3 vibration of the $v\text{-SiO}_2$ network decreases in the GeO_2 content range from 5.0 to 15.0 at. %. This decrease cannot be understood by simply considering the local densities of states of SiO_4 and GeO_4 tetrahedra (Peng and Tian 1989) and requires further work on the more basic process of electronic interactions in these glasses.

4. Conclusions

It was found that the Raman spectra of $\text{GeO}_2\text{-SiO}_2$ glasses obtained in this investigation supports the model that there are some GeO_4 tetrahedra in the $\text{GeO}_2\text{-SiO}_2$ glass network in which fewer fourfold and threefold ring structures exist than in $v\text{-SiO}_2$. It is demonstrated that the substitution of Ge for Si prevents the formation of ring structures

in the network. The different responses of threefold and fourfold ring defects to this substitution can be understood from the differences in their activation energies and volumes. A new vibrational band in the range 570–700 cm^{-1} due to Ge doping was found in the spectra of the high- GeO_2 -content (above 5.0 at.%) samples. It was also found that the W_3 vibration of the $v\text{-SiO}_2$ network decreased in highly GeO_2 doped $\text{GeO}_2\text{-SiO}_2$ glasses.

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