Comment on "Medium-Range Order in Permanently Densified SiO_2 and GeO_2 Glass"

The origin of the low-frequency Boson band and the first sharp diffraction feature in glasses has been the subject of extended debate [1–3]. Specifically, it has been proposed that these features contain detailed information on intermediate-range order, phonon localization, and transport properties in disordered systems. To address these issues, Sugai and Onodera [4] performed Raman scattering and x-ray diffraction measurements on densified SiO_2 and GeO_2 glasses recovered from high-pressure conditions, documenting irreversible shifts in the Boson and first sharp diffraction peaks. They concluded that the data were indicative of structural changes in the compacted glasses. They noted, however, that *in situ* Raman measurements would be preferable for identifying pressure effects on the Boson peak, but this is complicated in diamond-anvil cell studies by the strong central peak and luminescence from the anvils. Here we point out that such Raman measurements have in fact been performed on SiO_2 glass with low-fluorescence diamonds and with sufficient sensitivity that the Boson peak can be observed [5]. Analysis of the spectra revealed a remarkably large pressure shift over moderate pressures [6]. These results combined with *in situ* high-pressure x-ray diffraction of the glass [7] reveal significant correlations not evident from study of the pressure-quenched densified material.

Figure 1 shows the shift in the maximum of the Boson peak ν_m and the first sharp diffraction peak Q_1 of SiO_2 glass obtained at high pressure [5–7] and from pressure-quenched samples [4]. The shifts for both features measured *in situ* are significant at low pressures, well below the pressure onset for densification (10 GPa) [5]. By contrast, the largest changes reported for the pressure-quenched samples are considerably smaller. Sugai and Onodera [4] interpret their results in terms of the pressure-induced four- to sixfold coordination change in Si. However, the changes observed *in situ* begin well below the pressure of the coordination increase [6,7]. Moreover, spectroscopic and x-ray studies have demonstrated that the coordination changes in such glasses can be examined only through *in situ* measurements (see [6]). Hence, other mechanisms for the origin of features observed both at high pressure and on pressure quenching must be considered.

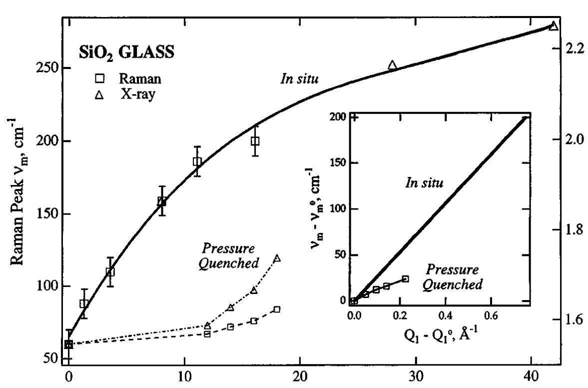

FIG. 1. Pressure dependence of the maximum of the low-frequency Boson band ν_m and the first sharp diffraction peak Q_1 for SiO_2 glass measured *in situ* [5–7] and at zero pressure following quenching from the indicated pressures [4]. The thick line is a single polynomial fit through both sets of data. The inset shows the relative shifts plotted against each other, where ν_m^0 and Q_1^0 are the initial zero-pressure values.

A linear correlation between pressure shift of ν_m and Q_1 [2] is observed in Fig. 1, with the data for the pressure-quenched densified glass falling on a distinctly lower trend (Fig. 1, inset). Sugai and Onodera [4] focus instead on a possible relation between ν_m and the width of the diffraction peak ΔQ_1, because for some glasses $\nu_m \sim v_t \Delta Q_1$, where v_t is the transverse sound velocity [3]. However, this does not hold at high pressure: ΔQ_1 remains essentially constant (to at least 42 GPa [7]) despite the large shift in ν_m, and *in situ* measurements of v_t show that it actually *drops* from 3.8 km/sec at zero pressure to 3.3 km/sec at 8 GPa [8]; hence, $v_t \Delta Q_1$ in fact decreases rather than increases (as predicted by this model) to this pressure. It has also been proposed that the intensity of Q_1 should decrease with pressure as a result of decreasing free volume in the glass [1]. Like ΔQ_1, however, the intensity is also unaffected by pressure to 8 GPa despite the volume reduction by ~10% over this range [8]. The intensity decreases only at much higher pressure where densification and the gradual Si coordination changes begin, as expected if Q_1 is a signature of a tetrahedral framework [7]. These results show that major changes in structure and dynamics given by pressure-induced effects on the Boson and diffraction peaks are not associated with the coordination change and are not apparent upon pressure quenching.

Russell J. Hemley, Charles Meade, and Ho-kwang Mao
Geophysical Laboratory
Carnegie Institution of Washington
Washington, D.C. 20015

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