Modeling of the Raman spectrum of vitreous silica

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We calculated the Raman spectrum of vitreous silica using a bond-polarizability model of which the parameters are derived from first-principles results on crystalline polymorphs of SiO_2. By comparison with the experimental spectrum, we could give an estimate for the concentration of three- and four-membered rings[1].

We used a periodic model for vitreous silica consisting of corner-sharing tetrahedra, for which the vibrational properties were determined previously using a first-principles approach[2]. The use of a bond polarizability model as a simple schema for calculating Raman intensities in tetrahedrally bonded SiO_2 systems has been previously validated by comparison with first-principles results for the first order Raman intensities in α-quartz[3]. The parameters of the bond polarizability model used in the present study were derived from first principles results for the derivatives of the polarizability tensors with respect to atomic displacements for a series of crystobalite polymorphs. Using crystobalite polymorphs under different compressive and tensile pressures, we could evaluate the dependence of the bond polarizability parameters as a function of the Si-O-Si bond angle. Application to the reduced HH Raman spectrum of vitreous silica shows that the calculated spectrum reproduces most of the features found in the experimental spectrum (Fig. 1). However, the large concentrations of three- and four-membered rings in our model sample[4] significantly enhance the intensities of the D_1 and D_2 defect lines at 497 and 609 cm^{-1}, respectively. By comparing theoretical and experimental intensities of these two lines, we estimate that $\sim 0.5\%$ and $\sim 2\%$ of the oxygen atoms belong to three- and four-membered rings, respectively.
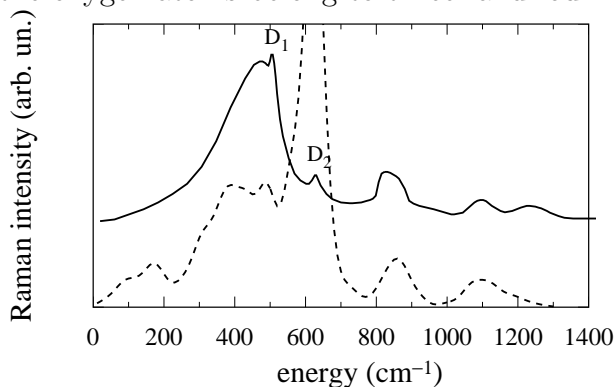

FIG. 1. Calculated (dashed) and measured (solid) reduced HH Raman spectrum of vitreous silica.

[1] F.L. Galeener, *Solid State Commun.* **44**, 1037 (1982).
[2] J. Sarnthein, A. Pasquarello, and R. Car, *Science* **275**, 1925 (1997).
[3] P. Umari, A. Pasquarello, and A. Dal Corso, *Phys. Rev. B* **63**, 94305 (2001).
[4] A. Pasquarello and R. Car, *Phys. Rev. Lett* **80**, 5145 (1998).