Low frequency Raman scattering of densified vitreous B_2O_3

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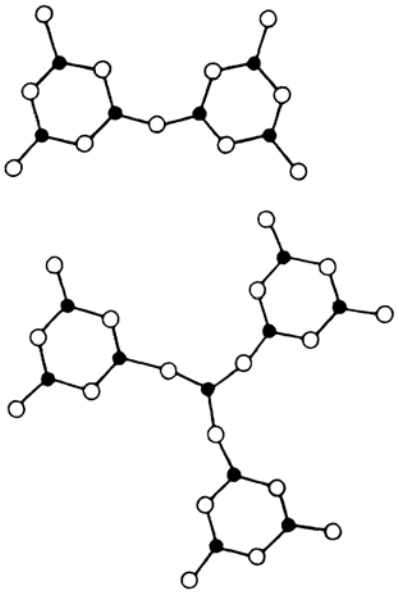
Anomalies in the physical properties of a glass

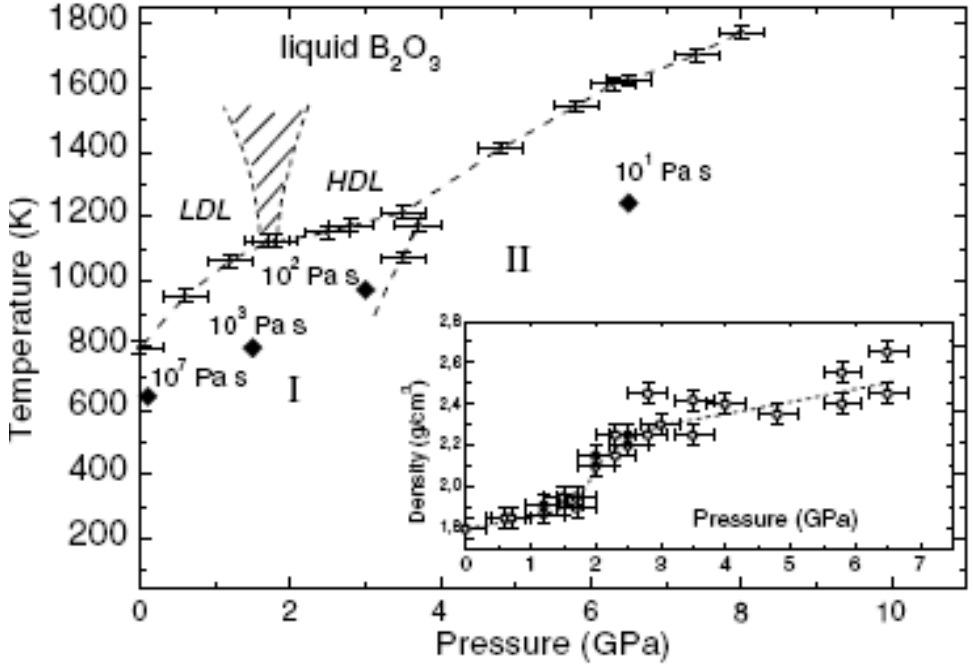
1) An excess specific heat C over the Debye predictions, is observed between 1 and 25 K. It is ascribed to an excess of low energy or soft vibrations which is revealed by inelastic light and neutron scattering. In a plot of $g(\omega)/\omega^2$, the ratio between the density of low energy vibrational states and ω^2, it results a peak usually defined as “Boson peak”.

2) An excess attenuation of acoustic waves over the frequency range from Hz to GHz, associated to structural defects subjected to thermally activated relaxation motions and tunneling effects

Pressure–temperature phase diagram of B_2O_3

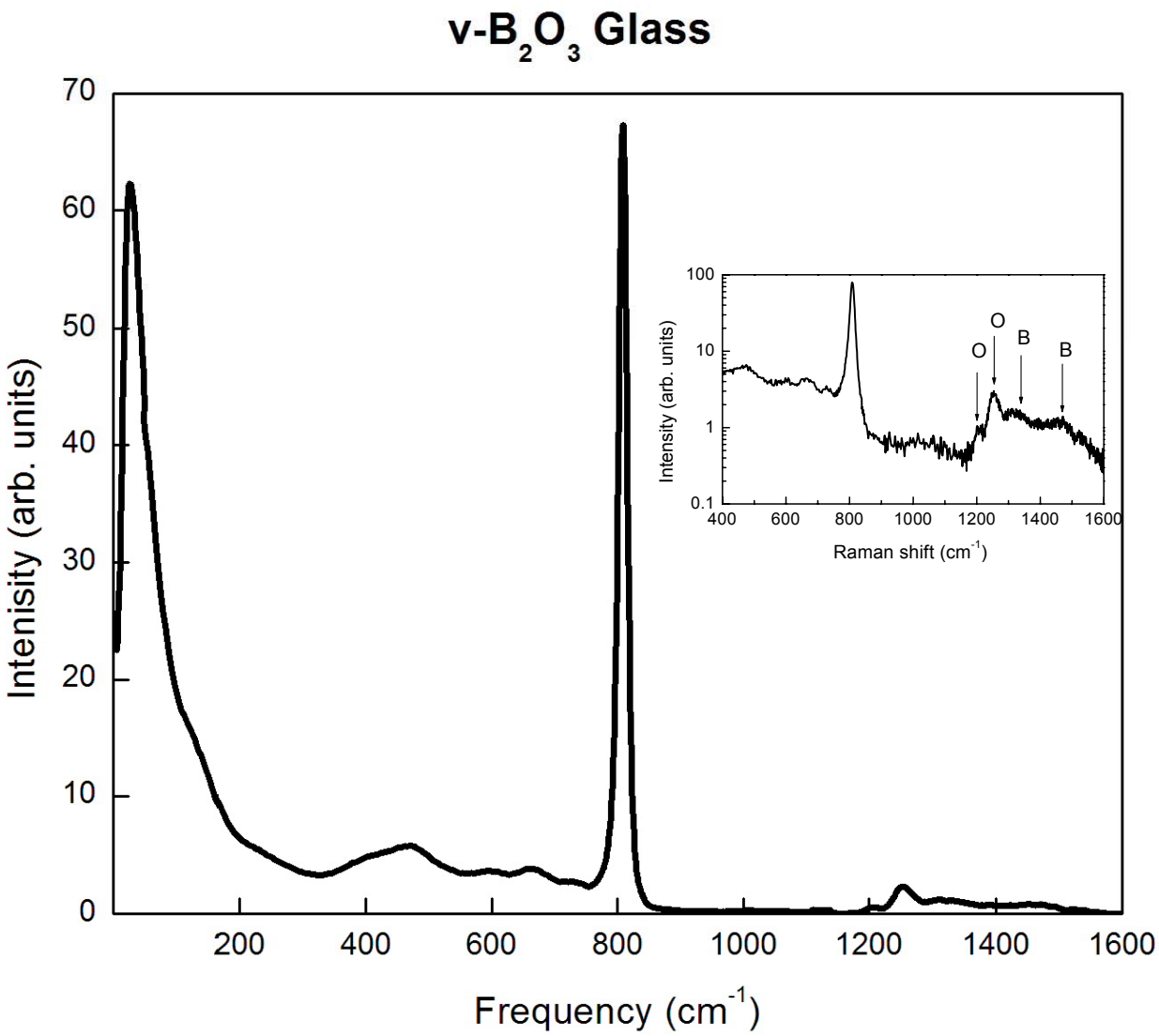
Structure of normal v-B_2O_3



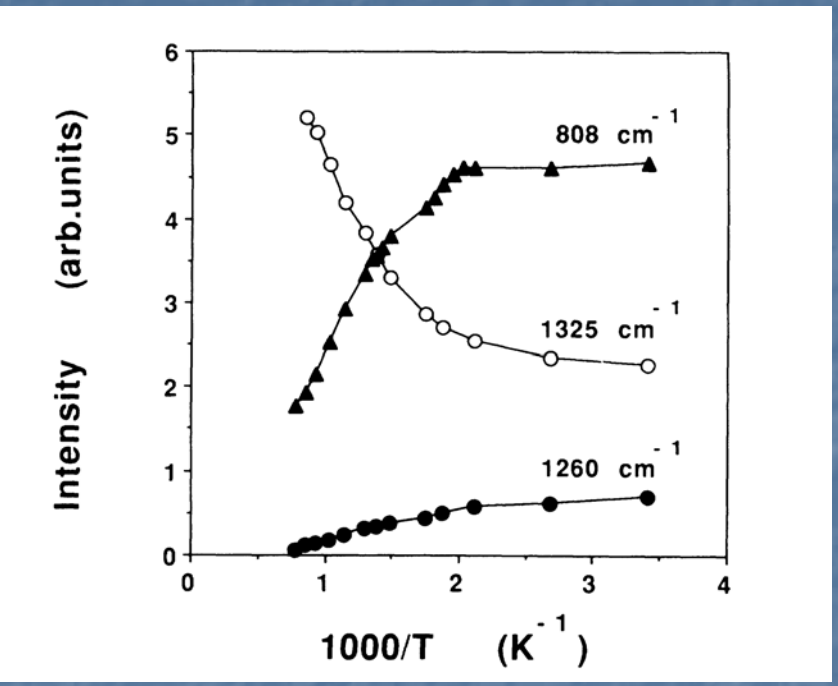


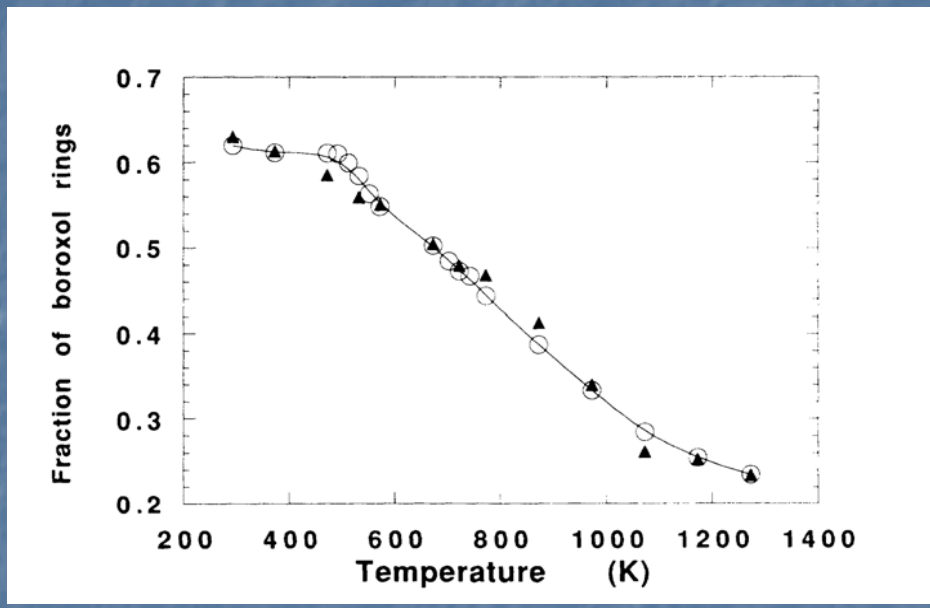
The room pressure density vs the pressure of quenching dependence for the pressure-synthesized glasses shows the existence of a transformation between low-density and high-density liquids (LDL and HDL)

Raman spectra of normal v-B_2O_3 Glass



Structural Changes of B_2O_3 over the liquid-glass transition range by Raman Scattering (Hassan, Torell et al PRB 1992)





$$N_{rings}+N_{chains}+N_{network}=1$$

The Glasses

Glass cylinders of B_2O_3 were encapsulated in a Pt-foil and then inserted into a graphite heater element. An MgO octahedron was used as a pressure transmitting medium in order to obtain hydrostatic pressure. Glasses were quenched from melts compressed to pressures of 2 GPa (1423 K) and 4 GPa (1473 K) in a HT-HP multi-anvil apparatus. The final products were homogeneous and permanently densified ingots having both diameter and length of about 5 mm and a reasonably good optical quality.

	Density	
Normal	1.826	g cm^{-3}
2 GPa	2.05	g cm^{-3}
4 GPa	2.38	g cm^{-3}

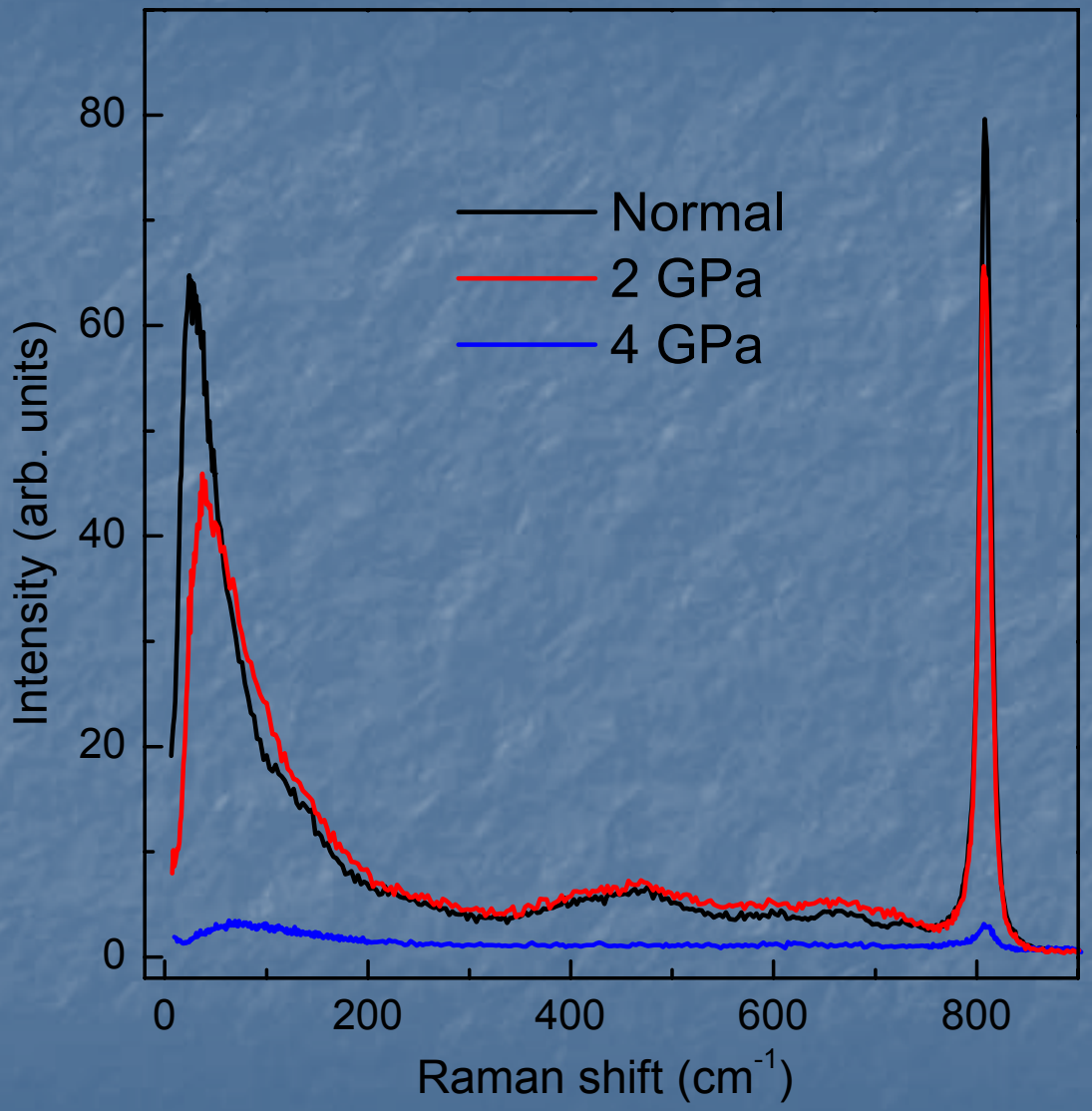
“Hot” densification of glasses

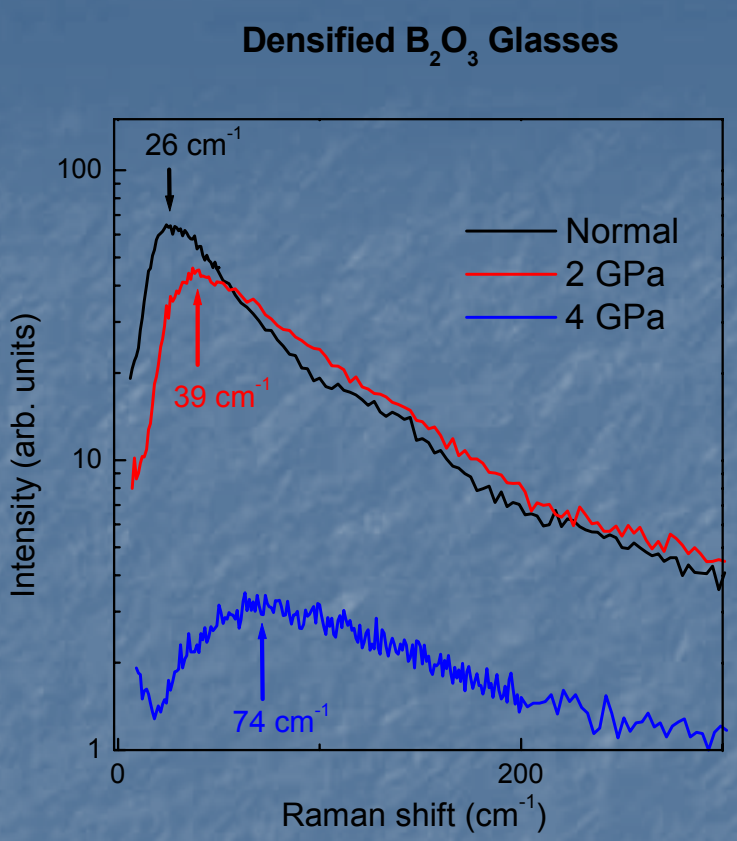
Glasses quenched from melts compressed to pressures of up to 8 GPa in a HT and HP multi-anvil apparatus

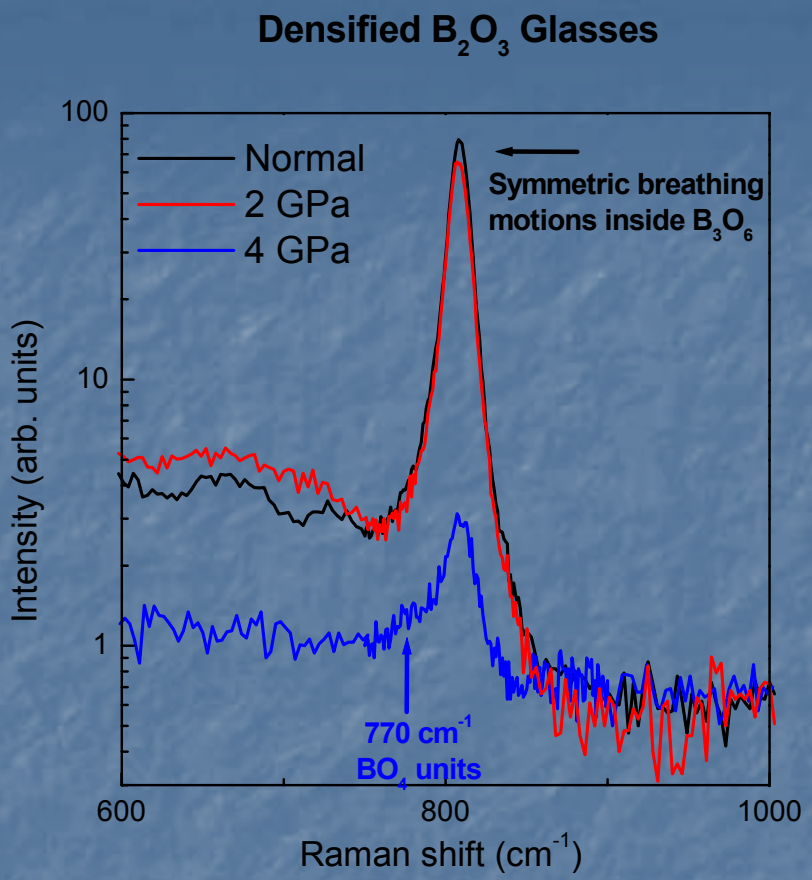
1. **Differently from “cold” densified glasses, which do not undergo glass transition at high pressure, the structures of “hot” densified glasses represent those of supercooled liquids at high pressure at T_g**

2. **“Hot” irreversible compaction of a glass produces substantial modification of the atomic packing and of the coordination number characterizing the network. The structural modifications can be performed in a controlled way by increasing pressure.**

Densified B_2O_3 Glasses







Low Frequency Raman scattering in glasses (below ~150 cm^{-1})

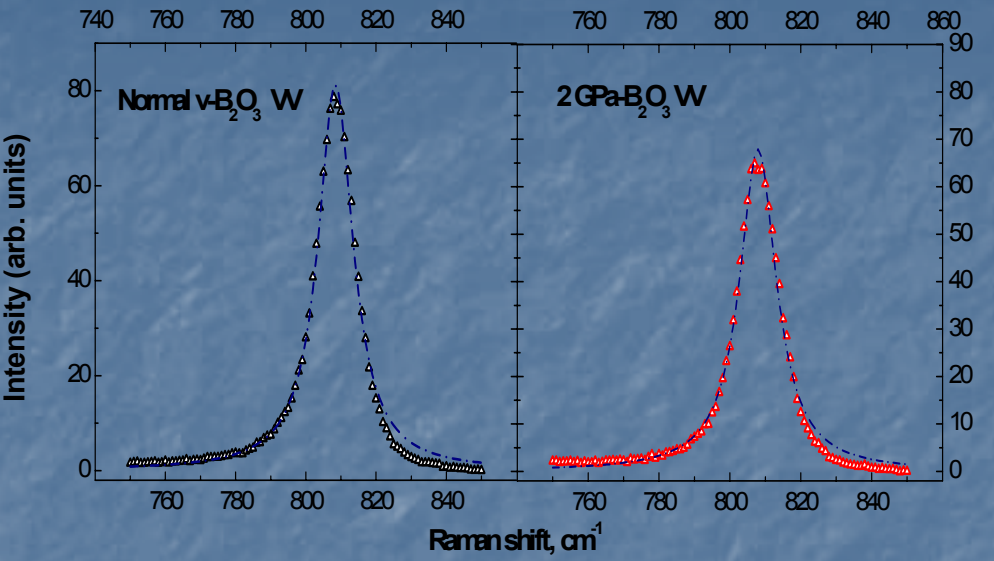
(Shuker and Gammon, PRL 1972)

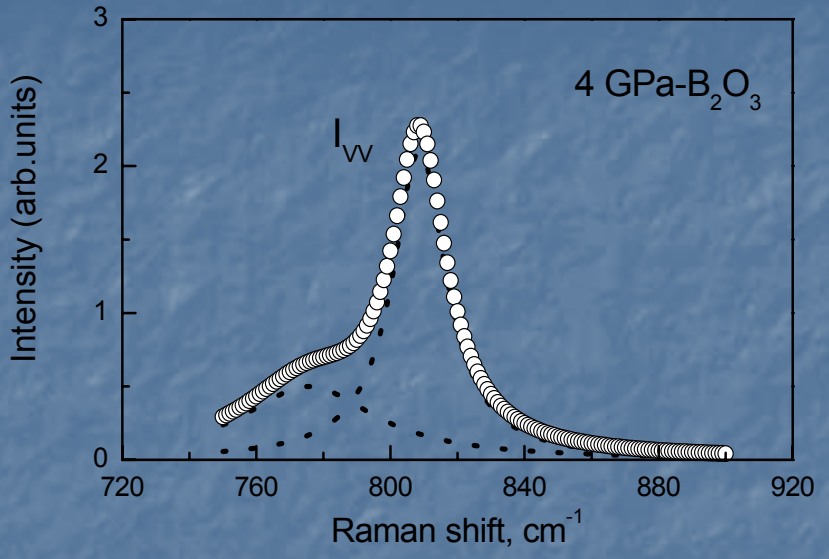
$$I_R = I(\omega)\,\omega / [n(\omega) + 1] = C(\omega)\,g(\omega)$$

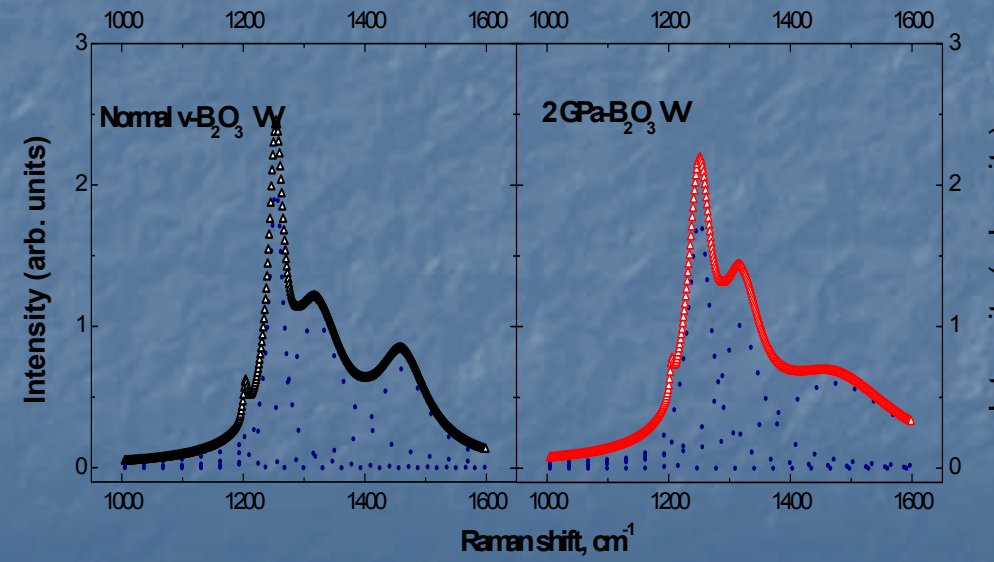
Problem: C(ω) is pressure dependent!

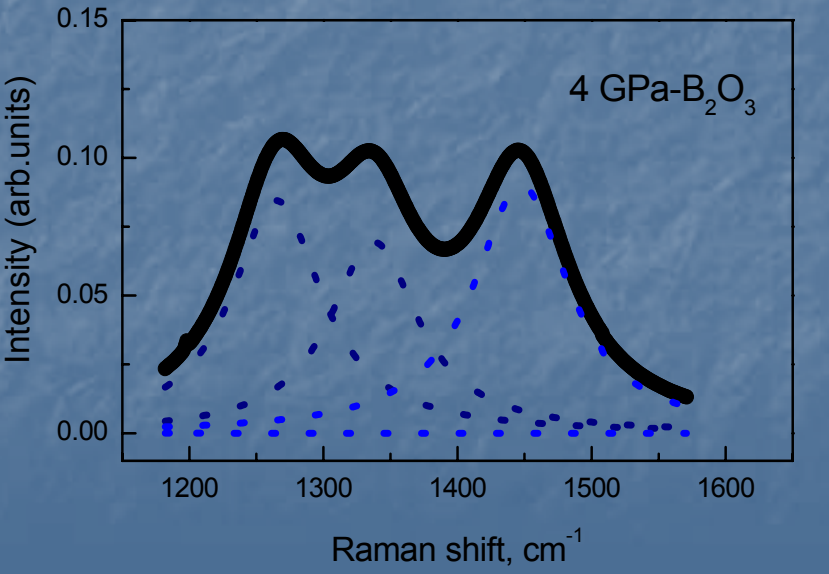
g(ω) must be directly determined by INS.

In analogy with the observations in many crystalline borates, the peak at 770 cm^{-1} is assigned to a vibration of a boroxol ring with one or two BO_4 tetrahedra.


Normal v-B2O3 W
2 GPa-B2O3 W
Intensity (arb. units)
Raman shift, cm-1


4 GPa-B2O3
IVV
Intensity (arb.units)
Raman shift, cm-1


Normal v-B2O3 W
2 GPa-B2O3 W
Intensity (arb. units)
Raman shift, cm-1


4 GPa-B2O3
Intensity (arb.units)
Raman shift, cm-1

Multi-component analysis of the bands at 770 and 808 cm^{-1}, and in the region between 1200-1600 cm^{-1}: Integrated Raman intensities

B_2O_3 Glasses	ρ ($g\ cm^{-3}$)	808	770	1210	1260	1325	1475
Normal	1.826	1545.3		3.53	87.2	157.3	96.8
2 GPa	2.05	1349		2	120	117.2	158.7
4 GPa	2.38	64.3	38.1	0.006	10.9	88.4	12.2

CONCLUSIONS

Increasing "Hot" densification of B_2O_3 up to pressures of 4 GPa gives rise to:

(i) A decrease of the fraction of boroxol ring species

(ii) The formation of tetra-coordinated boron

(iii) A relevant shift of the BP from 26 cm^{-1} up to 74 cm^{-1}