

Low frequency Raman scattering and low temperature heat capacity of permanently densified B₂O₃ glasses

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Sample densification was obtained by loading B₂O₃ glasses (dry v-B₂O₃ having H₂O content of 210 ppm) in a multi-anvil high temperature/high pressure apparatus for the synthesis at 5 and 6 GPa. They were kept under those pressures at room temperature for about 2-4 hrs and then the pressure was slowly released. Densified glasses were characterized by X-ray diffraction which revealed no sign of crystallization. The densities have been measured at room temperature: 1829 kg/m³ (v-B₂O₃), 1949 kg/m³ (5-GPa glass) and 1967 kg/m³ (6-GPa glass). The Debye sound velocity $V_D \left(\frac{3}{V_D^3} = \frac{1}{V_l^3} + \frac{2}{V_t^3} \right)$ and the elastic Debye temperature Θ_D have been determined by the

values of longitudinal (V_l) and shear (V_t) sound velocities measured at room temperature: $V_l=3261$ m/s, $V_t=1786$ m/s, $V_D=1992$ m/s, $\Theta_D=254.8$ K (v-B₂O₃); $V_l=3690$ m/s, $V_t=2013$ m/s, $V_D=2245$, $\Theta_D=293.4$ K (5-GPa glass); $V_l=3760$ m/s, $V_t=2042$ m/s, $V_D=2278$ m/s, $\Theta_D=298.6$ K (6-GPa glass).

Inelastic light scattering spectra of normal and permanently densified B₂O₃ glasses were investigated over the frequency range between 7 and 1800 cm⁻¹. Increasing densification gives rise to a decrease of the intensity of the strong band at 808 cm⁻¹, ascribed to breathing vibration of boroxol rings. Below 100 cm⁻¹, the Raman spectra are dominated by the Boson peak which also decreases the intensity with densification and shifts its position from about 26 cm⁻¹ (v-B₂O₃), through 28 cm⁻¹ (1-GPa glass), up to 31 cm⁻¹ (5-GPa and 6-GPa glasses). This increase results to be smaller than that expected from the hardening of the elastic continuum: the elastic moduli increase up to about a factor 1.4 compared to those of normal glass. Increasing atomic packing of the glassy network also leads to a progressive decrease of the excess specific heat capacity C_p observed in v-B₂O₃ between 1 and 20 K (having the shape of a broad peak when reported as $C_p(T)/T^3$). These observations imply that densification drives the system toward a structure having a more efficient packing of molecular units, causing substantial variations of the medium-range order.