(a) A melt of magnesium borate glass with the composition 20% MgO – 80% B₂O₃ is cooled at a rate of \( r_1 \). The glass transition temperature, \( T_g \), is measured to be \( T_1 \). In order to raise the value of \( T_g \) to \( T_2 > T_1 \) while keeping the cooling rate equal to \( r_1 \), how should the MgO content of the glass be changed? Explain with reference to atomic structure.

Decrease the MgO concentration to less than 20%. The addition of MgO to B₂O₃ modifies the melt by promoting chain scission of the borate network. The resulting decrease in viscosity of the melt confers greater mobility than would be the case at comparable undercooling at a lower MgO content and therefore reduces the excess volume of the solidified glass. We know from the relationship between volume and temperature that the value of \( T_g \) is given by the break in the \( V \) vs. \( T \) trace, and furthermore that \( T_g \) tracks with \( V^{xs} \). To raise \( T_g \) is tantamount to raising \( V^{xs} \) which then argues for changing the composition of the melt in a way that raises its viscosity, i.e., decreasing the amount of modifier.

(b) On a plot of molar volume, \( V_m \), versus temperature, \( T \), sketch cooling curves for a borate melt that solidifies to form (1) crystalline B₂O₃; and (2) amorphous B₂O₃. Indicate which material was cooled more quickly. No calculation necessary. Label the melting point of (1) and the glass transition temperature of (2). Indicate the excess molar volume, \( V^{xs} \), and describe why it is a measure of atomic disorder.

The glassy solid was cooled more quickly.
For a given compound, the crystal represents the tightest packing of atoms in order to establish the highest number of bonds and thereby achieve maximum decrease in energy. In the liquid state, the interatomic spacing is large in comparison to that of the solid state. Glass formation is the result of the inability of the atoms to reach the proper positions they would occupy in the crystal lattice owing to inadequate time to do assume said positions during cooling. In effect, the system is quenched en route from the loose packing of the melt to the tight packing of the crystal. The molar volume compares, on the basis of a constant mass of material (1 mole!) the degree to which the atomic packing of the solid reaches that of the crystal. The greater the deviation from this tight packing, the greater the deviation from crystallinity, and hence the greater the degree of disorder.