LN–7 IDLE MIND SOLUTIONS

1. The formation of a crystalline (ordered) phase upon cooling to below the melting point of a given system requires the relocation of atoms or molecules from their random, disordered position in the liquid phase to specific positions dictated by the characteristics of the “unit cell” system. This ordering process on atomic dimensions is normally accomplished by “diffusion” which requires mobility of species in the liquid state.

   The formation of an ordered (crystalline) state is impeded (1) if the mobility of the species in the liquid state is very limited, such as is the case during the formation of three–dimensional covalent networks of oxides (SiO_2, Al_2O_3, B_2O_3, P_2O_5, and others) or (2) if the unit cell involved is complex or, for example, demands the formation of ring structures in given lattice positions (S, Se, Te). Alternately, the formation of a crystalline phase can also be prevented if the atomic or molecular unit cell structure in two or multi–component systems demands specific components (elements) in specific unit cell locations and if, upon rapid cooling (quenching), the species involved “prematurely” lose their kinetic energy and thus their mobility. All disordered solids formed are in principle unstable and tend to assume, at largely varying rates, ordered configuration.

2.

SiO_2	Glass forming matrix
Na_2O	Matrix (network) modifier which decreases the number of Si–O–Si bonds and thus reduces the softening temperature from approximately 1800^{o}C (for pure SiO_2) to about 900^{o}C.
CaO	Network modifier which decreases the high H_2O solubility of soda glass through the formation of Ca–O–Si– which has decreased solubility in water. [Instead of pure $CaCO_3$ ($CaCO_3 \rightarrow CaO + CO_2$), it is also customary to use the mineral “dolomite”, which is a mixed carbonate ($CaCO_3$–$MgCO_3$), with a Ca/Mg ratio of about 2:1. Mg–O–Si– is also significantly less water soluble than Na–O–Si–.
Al_2O_3	Matrix former which decreases the softening temperature but does not accelerate devitrification (crystallization); an additive to soda–lime glass (ordinary window glass), which decreases the devitrification tendency introduced by soda.

3. Tempering consists of heating glass to just below its softening temperature and subsequently quenching it with a jet of cold air or oil so as to achieve a “frozen” outer layer while the core of the glass is still in a hot, “expanded” state. Upon subsequent slow cooling, the inside attempts to contract but is largely prevented from doing so because of the solidified outer shell. As a consequence, the outer portion of the glass is under compression while the core remains under tension.

   Tempering has two consequences on the mechanical properties of glass: (1) The heat treatment decreases the density of surface flaws (fissures) which are primarily responsible for the low tensile strength of glass – the tensile strength increases. (2) The high surface compression markedly increases the glass strength; under tensile load fracture takes place only after elimination of the compressive stresses (approximately 10^5 kPa) and the establishment of tensile stresses in excess of 10^4 kPa.

4. (a) Thermal shock resistance is inversely proportional to the thermal expansion coefficient of the glass. With the introduction of Na_2O into the SiO_2 matrix (window glass), the irregular matrix voids become blocked by the Na^+ ions and internal accommodation of bond length increases with temperature, possible in quartz glass (low thermal expansion coefficient) is no longer possible – the thermal expansion coefficient increases – the thermal shock resistance decreases.

   (b) By incorporating B_2O_3 (instead of Na_2O) into the SiO_2 matrix, the Si–O–Si bond density can be decreased with a resulting noticeable lowering of the working temperature; however, the irregular voids now remain empty: the thermal expansion coefficient changes only insignificantly; the thermal shock resistance is retained.

5. “Glassy” substances can readily be differentiated from crystalline substances through their inability to diffract X–rays in the Ångstrom wavelength range.

6. Without knowing any details about the particular semiconductor glasses and devices tested, it is reasonable to assume that the inherent instability of all glasses may be detrimental to their use for just about any type of devices. It must also be considered that a frequent requirement of semiconductor devices is high–speed operation. High–speed operation requires high charge carrier mobility. It is reasonable to conclude that crystalline matrices, such as silicon, germanium and the like, provide a higher charge carrier (electrons and holes) mobility than do amorphous disordered matrices.

7. The mechanical strength of glass can be increased by pre–stressing the glass. This is done by heating it to just below the melting temperature and then chilling it. The exterior of the glass cools and contracts immediately, but the interior stays plastic. When the interior finally cools, it draws the exterior together as it shrinks, generating compressive stresses in the outer layers of the glass. These stresses counteract any applied tensile stresses, so the glass will not fracture until after the tensile stresses “are condensed” and excessive tensile stresses have been established.

8. The thermal shock resistance of Pyrex makes it extremely valuable in the kitchen. It is a borosilicate glass with B_2O_3 as an additive to the SiO_2. B_2O_3 is a network former, but it has one less oxidation state than silicon, so it tends to shorten the chains. The voids in the center of the structure, which allow for internal accommodation of expansion and contraction due to temperature changes, are left vacant. (The glass has a small thermal expansion coefficient.)

9. Adding soda (Na_2O) will decrease the density of the three–dimensional bonding network and lower the working temperature of the glass. The addition of soda to glass also causes it to absorb ultra–violet radiation, to become water soluble, and to lose its thermal shock resistance. The water solubility can be reduced by adding “lime”, and the thermal shock resistance can in part be restored by reducing Na_2O addition in favor of B_2O_3 addition.

10. The addition of B_2O_3 to glass increases the thermal shock resistance and lowers the working temperature of the glass. The addition of PbO increases the density and decreases the working temperature of the glass. And Au particles with diameters ranging from 110–170 nm will give the glass a brown color.

working temperature	SiO_2 ~40 w/o Na_2O ~5 w/o
high thermal shock resistance	B_2O_3 ~15 w/o
high density	PbO ~35 w/o
brown color	Au particles (ϕ 110–170 nm) MnO_2

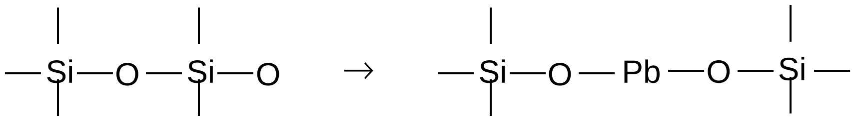
11. The tensile strength of glass can be increased by:
    (a) Tempering – thermal: High temperature anneal followed by a rapid surface temperature decrease – quenching with air jet or oil. This treatment eliminates (most) surface flaws and imparts a compressive surface stress on the material; both render the material stronger under applied tensile stresses.
    (b) Ion Exchange – Chemical Tempering: By immersing the glass in molten KNO_3, K^+ ions replace the smaller Na^+ ions on the surface, resulting in compressive surface stresses.

    In both cases, these compressive stresses must be overcome before the glass will fail in tension.

12. Self-explanatory - I hope you did it!

13. The question is answered by rationalizing Table 1 on LN7–8 and using the density information provided (ρ of soda–lime glass = 2.4 ρ/cm^3).

    Since a working temperature of about 800^{o}C is desired, we need network modifies, but the requirement of high density precludes the use of substantive amounts of Na_2O and CaO + MgO. The proper substitute is PbO which acts as an ionic modifier (located in irregular voids) and as a linear chain former in substitutional position:



$$-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O} \rightarrow -\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\mathrm{Pb}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-$$

Replacing most of the Na_2O present in soda–lime glass with PbO will also improve the water solubility of the glass. The blue color can be obtained through the addition of Cr^{++} ions as CrO.

Suggested Glass:

SiO_2	~55 wt%	Basic network former
Na_2O	~5 wt%	Network modifier to lower T_W
PbO	~35 wt%	To increase glass density and lower T_W
CaO	~5 wt%	To reduce H_2O solubility
CrO		To achieve blue color

14. The opaque appearance in daylight of windows coated with reflective metallic coatings can be attributed to the fact that the reflected light intensity which reaches the eye is, by close to an order of magnitude, higher than the simultaneously observed transmitted (through the window) intensity – thus, the perception of opaqueness. During night the outside light intensity is low and the intensity of the transmitted light (provided a light is turned on inside) dominates to the eye – the window appears transparent.

15. Al will not form a stable glass because atomic scale (re)ordering into an FCC structure requires only atomic jumps of short distance and thus small amounts of activation energy (available to some extent already at low temperatures). Ordering of Se (transition of Se from glassy to crystalline state) is impeded by the complexity of unit species on lattice sites (Se_8 rings) and by inadvertent chain growth (Se_8 – Se_{20}). These result in steadily increasing viscosity (with decreasing temperature) and, thus, in decreasing probability of stabilizing an ordered atomic structure.

16. Pyrex (trade name by Corning) is a glass of the approximate composition:

wt%

SiO_2	B_2O_3	Al_2O_3	Na_2O	CaO
76	14	3	5	2

Its properties are significantly different from those of soda–lime glass because of the replacement of about 75wt% of Na_2O by B_2O_3. This change in composition brings about 2 changes in properties:

(1) The reduction in the covalent bond density is less than that achieved through the addition of Na_2O. As a result, the working temperature (T_W) is noticeably higher than that of Soda–lime glass.

(2) The reduction in the concentration of void blocking cations (Na^+) and (Ca^{++}) increases markedly the thermal shock resistance of the glass and makes it suitable as cookware.

17. (a)

	T_W (^oC)	T_s (^oC)
Silica glass	~1950	1700
Pyrex	~1200	800
S–L glass	~900	700

17. (b) Both T_W and T_s are expected to be highest in Silica–glass where matrix breakdown is strictly thermal. Replacement of some 15w/o of SiO_2 with B_2O_3 results in a lowering of the overall bond density since (B) exercises 3 covalencies while Si exercises 4 covalencies. As a consequence, the working temperature, the temperature at which the viscosity assumes a value of about 10^6 poise, is reduced from ~1900^{o}C to ~1200^{o}C and the softening termperature (T_s) from 1700^{o}C to 800^{o}C. The reduction of both temperatures is even more pronounced when considering the difference between silica glass and Soda–lime glass. It can be attributed to the large ionic content which results in the irreversible rupture of convalencies, and thus, in a further decrease of the viscosity at any given temperature.

18. Annealing: The glass is heated to near the softening temperature (T_S) for an extended period and is subsequently cooled down gradually through the annealing temperature (T_A). Subequent cooling to room temperature may be at a faster rate. Annealing will tend to eliminate residual stresses, but more importantly, will “cure” surface cracks (flaws) which are responsible for the reduced tensile strength of commercial glass.
Tempering: Is just about the reverse of annealing. By rapid cooling (air quenching) from near the softening temperature, the glass surface contracts and is put under a high degree of compressive stress due to the impeded contraction of the glass interior which cools at a slower pace. The compressive stress adds “tensile strength” to the glass.