Glass (Amorphous Solids)

Glass can be widely defined as an amorphous solid. An amorphous solid can be considered to have a random arrangement of atoms, such as observed in a gas, but more realistically can considered to only lack long-range order such as those found in crystalline solids.[1]

Historically the most common and familiar form of glass is clear (optically transparent) silica glass which is composed largely of silicon dioxide (SiO$_2$). The definition of glass does not restrict either the composition or the optical properties of the material, implying a wide variety of different materials that are considered glass. In fact, theoretically, any crystalline solid that can be brought to a liquid state, can be forced into an amorphous solid state through rapid solidification via extraordinary cooling rates.[1] This is easily observable by recognizing that quartz, a very common crystalline solid, has the same composition as silica glass (SiO$_2$) but was cooled slowly enough to form long-range order. Non-silica glasses, in particular metallic glasses, can obtain unique electric, optical, or thermal properties from their crystalline counterparts through glassification. Non-metallic glasses can obtain similarly unique properties by adjusting elemental compositions and introducing dopants.

Optical Properties of Glasses

For centuries silica glass has been desirable for its optical properties since silica glass is transparent in the visible spectrum. Although there are crystalline materials that are similarly transparent (quartz), they have several properties which make them undesirable as optical media in many cases; though each grain may be transparent, grain boundaries reflect and/or scatter light in poly crystalline materials; unless cut along specific planes, the faces of crystals are forced to conform to a rigid geometric order which may also scatter light.[2] Silica glass is not restricted by these constraints and has properties making it even more desirable both in terms of clarity and malleability; being unrestricted by a defined internal structure, the surface of glass is molecularly smooth, bound only by surface tension, even along curved faces.
This is particularly important since most optical instruments (microscopes, telescopes, and eyeglasses) require smooth curved surfaces.

Silica glass isn't the only amorphous solid that fits the profile for optical functions. Acrylic glass, poly(methyl methacrylate), is a polymer, fitting the description of glass by being an amorphous solid. Acrylic glass has a very similar refractive index to silica glass (~1.5) and is physically lighter, softer, and more shatter-resistant than glass.\footnote{3} Polycarbonates is another class of optically transparent polymers. It has even more desirable physical properties than acrylic glass in terms of strength and impact resistance.

The optical properties of silica glass, in particular the index of refraction, can be modified by doping the glass. Doping the glass with low density materials such as boron can lower the index of refraction. Similarly, doping the material with higher density dopants, such as oxides of lead, titanium, barium or zirconium, can drastically increase the index of refraction. Glasses made or doped with germanium or phosphates are vitally important in the field of Fiber Optics.

The optical application of glasses isn't limited to the visible spectrum; infrared (IR) filters are important components of IR photography, spectroscopy, and data storage. Infrared glass filters are often made of chalcogenide glass, composed of two non-oxygen group 16 elements (sulfur, selenium, tellurium) and one group 14 element (silicon, tin, lead) or group 15 element (phosphorus, arsenic, antimony, bismuth) in its most simple form. Often the size of the atoms allow for leniency to create more complex amorphous chalcogenide glasses involving several different elements in compositions that only roughly match the two to one ratio of silica. These materials transmit only in the IR or near IR range, appearing black or faintly blue, while still having similar malleability of silica glass. Example IR filter chalcogenide glasses include As$_{40}$Se$_{60}$, Ge$_{10}$As$_{40}$Se$_{50}$, and Ge$_{30}$As$_{13}$Se$_{32}$Te$_{25}$\footnote{11}.

## Electrical Properties of Glasses

Pure silica glass is a well-known insulator, having a resistivity on the order of $10^{14}$ ohm m.\footnote{7} Glass is especially desirable in the field of semiconductors for its insulating properties; in device fabrication, glass is deposited between metals or semiconductors as very thin insulators. Doped glass, such as phosphosilicate (phosphorus doped) or borophosphosilicate (boron and phosphorus doped) are often used instead of pure silica glass for their lower melting temperatures and increased planarization (forming smooth flat surfaces). The addition of fluorine, a highly electronegative element, into the glass can lower the polarizability and thus the dielectric constant of the glass, making it more desirable for integrated circuits. The addition of large ions, such as lead (II) oxide, can reduce the mobility of other ions significantly increasing the resistivity of the material. It's possible to give silica glass a level of electrical conductivity by dissolving small alkali metal ions into the glass, which have high mobility's at increasing temperatures.\footnote{10}

Though having a higher conductivity that silica glasses, metallic glasses have significantly lower electrical conductivity than their crystalline counterparts, on the same order as the metals' liquid counterpart, as a result of the molecular disorder.\footnote{8} Of particular interest is the electrical properties of amorphous metals at low temperatures ($\sim$2-40K); within this range the resistivity of the material increases linearly, unlike the non-linear behavior of crystalline metals, theoretically due to the lack of phonon scattering (organized lattice vibrations).\footnote{9}
Thermal Properties of Glasses

Silica glass is commonly considered to be very susceptible to thermal shock and breaks or cracks easily when suddenly changing temperatures. This is true for the cheapest and most common form of glass which is soda-lime-silica glass, which contains roughly 30% sodium oxide ($\text{Na}_2\text{O}$), lime ($\text{CaO}$), magnesia ($\text{MgO}$) and alumina ($\text{Al}_2\text{O}_3$). Soda-lime has a coefficient of thermal expansion of 93.5E-7 cm/cm.°C, which describes the relative increase in size per degree Celsius change in temperature. Pure or nearly pure (~96%) silica glass has a small coefficient of thermal expansion of 7.5E-7 cm/cm.°C due to the homogeneity of the solid. Silica glass also has a significantly higher melting temperature, combined with the purity requirements, this makes it more expensive to produce. Borosilicate glass (~13% $\text{B}_2\text{O}_3$) is a very common form of glass used in cookware for its thermal shock resistance, having a coefficient of 35E-7 cm/cm.°C.[13] Unlike pure silica glass, borosilicate glass is cheaper to produce, having a lower melting temperature and having less stringent purity requirements. Corning has developed glasses with ultra-low thermal expansion coefficients with values on the order of 10⁻⁹ cm/cm.°C.[14]

In terms of thermal conduction, solid silica glasses have a mild specific heat of ~0.84 J/g.K which is only a fifth that of water and only twice that of copper. This makes silica glasses ill-suited for thermal insulation in many cases. Glass does play a huge role in thermal insulation in the form of fiber glass and glass wool. Glass wool involves the production of very thin strands on soda-lime glass to form a low density packing material. Glass wool can achieve higher specific heats than either glass or water on the order of 7 J/g.K.[15]

Methods of Achieving Glasses

Creating some glass requires massive cooling rates, on the order of $10^5$ K/s. These cooling rates can be achieved by a variety of methods including:

- Fast Quenching: Quickly submerging a material in a liquid of a significantly lower temperature (generally oil or water) to solidify a material before long range ordering can occur.
- Splat/Roller Quenching: A sample melt is pressed by or rolled through internally cooled (water or liquid nitrogen) rollers or anvils causing near instantaneous cooling and solidification.[6]
• Melt Spinning: An internally cooled wheel (water or liquid nitrogen) is rotated and a thin stream of liquid is dripped onto the wheel causing it to rapidly solidify.[4]

• Sputtering: Atoms are ejected due to bombardment of high energy particles on the surface, causing the ejected particles to be deposited on nearby surfaces. Used to create thin-films of amorphous solids.

• Aerodynamic Levitation: The levitation of a sample by streams of gas. Can be used on a melt to prevent nucleation as it cools thus resulting in glassy materials.[5]

Questions

1. Why are glasses more desirable in optics than their crystalline counterparts?
2. How could changing the index of refraction of glass be beneficial?
3. What is a 'phonon' and why would these not have the same electron-scattering effects in metallic glass?

Answers

1. Why are glasses more desirable in optics than their polycrystalline counterparts?
   ◦ Glasses, due to their amorphous nature, lack the light-scattering grain boundaries present in crystals. Similarly, the amorphous nature of glass allows for molecularly smooth curved surfaces, unrestricted by lattice ordering constraints.

2. How could changing the index of refraction of glass be beneficial?
   ◦ (Variety of correct answers) Glasses used in fiber optics require low refractive indices in order to maintain the total internal reflection condition within the core for long distances.

3. What is a 'phonon' and why would these not have the same electron-scattering effects in metallic glass?
   ◦ A 'phonon' is a collective organized vibration or excitation of atoms in a periodic lattice. A glass, by definition, lacks an organized lattice or crystal structure and thus any phonon formation would be unlikely and small, unable to scatter electrons reliably.

Additional Links

• Fiber Optics
• Optical Computing
• Resistivity
• Dielectric Polarization
• Snell's Law

References

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