CERAMICS, GLASS AND REFRACTORIES

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3) Glass Constituents and Properties
CONSTITUENTS OF GLASSES

3 types of oxides

Glass Formers
SiO₂ and B₂O₃

- SiO₂: Fundamental sub-unit: SiO₄⁴⁻ tetrahedra
- B₂O₃: Fundamental Sub-unit: plane triangles BO₃³⁻ ⟜ triangles BO₃³⁻ become BO₄⁴⁻ tetrahedra when we add oxides of alkaline M and alkaline earths. The cations give electroneutrality. The glasses that are made only of B₂O₃ have little durability.
- Normally we add B₂O₃ to SiO₂: borosilicate glasses

Glass modifiers
(Na₂O, K₂O) and (CaO and MgO)

- Are the oxides that break the silicate lattice
- Alkaline (Na₂O, K₂O) alkaline earths (CaO y MgO)
- They are accommodated in interstitials (do not form part of the silicate lattice)
- ↓ viscosity ⇒ facilitates moulding and workability

Intermediates: Al₂O₃
DO NOT form glasses only by themselves.

They are incorporated in the silicate lattice
- Al₂O₃ ⟜ tetrahedra AlO₄⁴⁻ replacing SiO₄⁴⁻
- Charge defects (Al³⁺: Si⁴⁺) compensating with alkaline cations and alkaline earths.

Improve special properties:
- Al₂O₃ ⟜ ↑ strength at high T (aluminosilicate glasses)
- PbO
  - Modifies optical properties
  - ↓ Tᵣ (glass soldering)
  - Radiation protection of ↑ E

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## CONSTITUENTS OF GLASSES

### Substances constituents of glasses

<table>
<thead>
<tr>
<th>ION</th>
<th>M⁺ as a</th>
<th>MODIFIER</th>
<th>COLOUR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr³⁺</td>
<td>6</td>
<td>Blue</td>
<td></td>
</tr>
<tr>
<td>Cr⁶⁺</td>
<td>6</td>
<td>Green</td>
<td></td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>8</td>
<td>Blue – green</td>
<td></td>
</tr>
<tr>
<td>Cu⁺</td>
<td>6-8</td>
<td>Transparent</td>
<td></td>
</tr>
<tr>
<td>Co²⁺</td>
<td>6-8</td>
<td>Rose</td>
<td></td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>8</td>
<td>Yellow – green</td>
<td></td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>6</td>
<td>Light orange</td>
<td></td>
</tr>
<tr>
<td>Mn³⁺</td>
<td>6-8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>6</td>
<td>Blue-green</td>
<td></td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>6-10</td>
<td>Light yellow</td>
<td></td>
</tr>
<tr>
<td>U⁶⁺</td>
<td>6</td>
<td>Light yellow</td>
<td></td>
</tr>
<tr>
<td>V³⁺</td>
<td>6</td>
<td>Green</td>
<td></td>
</tr>
<tr>
<td>V⁴⁺</td>
<td></td>
<td>Blue</td>
<td></td>
</tr>
</tbody>
</table>
**Type of Glasses and Applications**

- **Soda-lime Glass**
  70% SiO$_2$, 10% CaO, 15%Na$_2$O, 5% MgO / Al$_2$O$_3$:
  Windows, bottles etc.
  Low melting/softening point, easily formed

- **Borosilicate Glass (Pyrex)**
  80% SiO$_2$, 13% B$_2$O$_3$, 4% Na$_2$O, 3% Al$_2$O$_3$:
  Cooking and chemical glassware.
  High temperature strength, low coefficient of thermal expansion (CTE), good thermal shock resistance

- **Glass-Ceramic**
  The term mainly refers to a mix of lithium and aluminosilicates that yields an array of materials with interesting thermomechanical properties.
  60% SiO$_2$, 20% Al$_2$O$_3$, 20% Li$_2$O, + TiO$_2$ (nucleating agent): cooker tops, ceramic composites. Heat treatment causes glass to crystallize to form crystal/amorphous composite with greater creep resistance and very low CTE – hence excellent thermal shock resistance.

**Thermal Tempering of Glass**
Glass can be significantly strengthened by a process referred to as *thermal tempering*, which introduces a state of compressive residual stresses on the surface.

The appropriate thermal process, involves heating the glass body to a temperature above its glass transition temperature, followed by a two-step quenching process
PROPERTIES OF GLASSES

Mechanical Properties

Brittle Materials (\(\uparrow\uparrow\) elastic modulus \(= f\) (composition, macroscopic (surface) imperfections, volume of material and \(T\))
Low modulus of Weibull
Mechanical strength \(\downarrow\) (presence of water/air + humidity)

Electrical Properties

Generally insulators \((\sigma \approx 10^{-10} - 10^{-20} \ \Omega \text{cm}^{-1})\)
\(\sigma\uparrow\uparrow\) with Temperature
\(\sigma\uparrow\uparrow\) with modifier \((= f\) (size and amount of modifier))

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Expansion coeff. ((\text{C}^{-1}))</th>
<th>Thermal Shock failure ((\text{C}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda-lime glass</td>
<td>(10^{-6})</td>
<td>80</td>
</tr>
<tr>
<td>Sodium borosilicate (Pyrex (\text{TM}) type)</td>
<td>(10^{-4})</td>
<td>270</td>
</tr>
<tr>
<td>Fused silica</td>
<td>(10^{-6})</td>
<td>1600</td>
</tr>
<tr>
<td>Lithia-alumina-silicate glass ceramic (Pyroceram (\text{TM}) type)</td>
<td>(10^{-6})</td>
<td>670</td>
</tr>
<tr>
<td>Transparent lithia-alumina-silicate glass ceramic (Visions (\text{TM}) type)</td>
<td>(10^{-6})</td>
<td>1330</td>
</tr>
</tbody>
</table>

Thermal Shock

\(\uparrow\uparrow \alpha = \downarrow R_{\text{thermal shock}}\)

Thermal shock resistance of common glasses and glass ceramics

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**Glass transition temperature** $T_g$: temperature at which a glass-forming liquid transforms from a rubbery, soft plastic state to a rigid, brittle, glassy state

**Glasses:**
Lack of long range order of constituent atoms
Do not have a sharp melting point and do not cleave like crystals
Solid at low temp, soften at intermediate temp and liquid at high temp
Show elasticity up to fracture (like crystal solid)
CRYSTALLINE MATERIALS

CRYSTAL: Highly ordered two or three dimensional network of atoms or ions, the repeat pattern theoretically extend to infinity in all directions.

SINGLE CRYSTAL: Have in theory continuous order throughout the material (can extend to over many cms)

POLYCRYSTALLINE MATERIAL: Consist of a collection of "welded" single crystals (grains)