Ceramic Materials

Chapter 5: Glass

F. Filser & L.J. Gauckler
ETH-Zürich, Departement Materials
frank.filser@mat.ethz.ch

SS 2007
Persons in Charge of this Lecture

• I. Akartuna,
  HCI G 538, phone 36842, ilke.akartuna@mat.ethz.ch
F. Krauss
  HCI G 538, phone 3 68 34, franziska.krauss@mat.ethz.ch

• Dr. F. Filser,
  HCI G 529, phone 26435, frank.filser@mat.ethz.ch

• Prof. Dr. L.J. Gauckler
  HCI G 535, phone 25646, ludwig.gauckler@mat.ethz.ch

• Dipl.-Ing. J. Kübler
  EMPA Dübendorf, phone 044 823 4223, jakob.kuebler@empa.ch
Materials Science I: Ceramics

Introduction on ceramic materials, technology, applications

Crystal structures of ceramic materials

Potential well of bonding and physical properties & Examples of Structural ceramic materials

Examples of structural ceramic materials
Overview & schedule

Mar 19, 07  term start
Mar 20, 07  Glass and Glass-Ceramics (FF)
Mar 27, 07  Toughness (JK)
Apr 03, 07  Strength & Weibull statistics (JK)
Apr 10, 07  Sub-critical crack growth, SPT-Diagrams (JK)
Apr 17, 07  Proof-testing, creep, thermal properties (JK)
Apr 24, 07  polymer part (Prof. D. Schlüter)
Jun 22, 07  term finish
Learning Targets

• Definition of glass as a “frozen” liquid
• Viscosity – temperature – behavior
• Structure of Glass, Network
• Network formers, network modifiers, and Zwischenoxide
• Optical properties (refraction, dispersion, transmission)
• Chemical resistance and corrosion
• Fabrication of glass
• Glass ceramics, nucleation rate und crystal growth rate
Glasses are frozen liquids.
- They don’t possess a (distinct) melting temperature but a glass transition temperature.
- The glass transition temperature and the density of a glass depend on the cooling rate.
- We don’t observe an energy of formation during the solidification of a glass melt.
- In glass state the disorder of the melt is preserved.
History:

W. H. Bragg and W. Lawrence Bragg

W.H. Bragg (father) and William Lawrence Bragg (son) developed a simple relation for scattering angles, now call Bragg’s law.

\[
d = \frac{n \cdot \lambda}{2 \cdot \sin \theta}
\]
Another View of Bragg's Law

\[ n\lambda = 2d \sin \theta \]
Laue - Powder X-ray Diffraction
Bragg diffraction of glassy and crystalline material (PbF₂)
Laue-Diagram for a Single Crystal
Zachariasen’s Network-Hypothesis

- regular $\text{SiO}_4$ - network ($\text{SiO}_2$ - quartz, left) and of a
- irregular network (glass, right)

2-dimensionel visualization of a
[SiO$_4$] - Network

[SiO$_4$] - network with network modifiers Na and Ca
Glass

Short range order = Tetrahedron

Si$^{4+}$

O$^{2-}$

[SiO$_4$]$^{4-}$

Tetrahedron

z.B. Na$^+$, K$^+$

Ceramics: Glass, Chap 5
## Network Former

<table>
<thead>
<tr>
<th></th>
<th>Effect on Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>α ↓ → thermocycling ↑</td>
</tr>
<tr>
<td></td>
<td>T₉ ↑ → η ↑</td>
</tr>
<tr>
<td></td>
<td>mech. strength ↑</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>α ↑ → thermocycling ↓</td>
</tr>
<tr>
<td></td>
<td>T₉ ↓ → η ↓</td>
</tr>
<tr>
<td></td>
<td>acid resistance</td>
</tr>
<tr>
<td></td>
<td>mech. strength ↓</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>UV transparency ↑</td>
</tr>
<tr>
<td></td>
<td>IR transparency ↓</td>
</tr>
<tr>
<td></td>
<td>chem. resistance ↓</td>
</tr>
</tbody>
</table>

Network former and their influence on the glass’ properties.
Network Modifier

<table>
<thead>
<tr>
<th>Material</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O</td>
<td>( \eta \downarrow \downarrow )</td>
</tr>
<tr>
<td>Na₂O</td>
<td>( \eta \downarrow )</td>
</tr>
<tr>
<td>K₂O</td>
<td>Glass becomes „longer“*a</td>
</tr>
<tr>
<td>CaO</td>
<td>chem. resistance ( \uparrow )</td>
</tr>
</tbody>
</table>

*a. Glasses are termed “long” or “short” glasses according to their Viscosity-Temperature-Function.*
## Zwischenoxide

<table>
<thead>
<tr>
<th>Compound</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>Glass becomes “longer“</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Glass becomes “longer“</td>
</tr>
<tr>
<td></td>
<td>mech. strength ↑</td>
</tr>
<tr>
<td></td>
<td>chem. resistance ↑</td>
</tr>
<tr>
<td>PbO</td>
<td>$T_g$ ↓</td>
</tr>
<tr>
<td></td>
<td>$n$ ↑</td>
</tr>
<tr>
<td></td>
<td>electrical resistance ↑</td>
</tr>
<tr>
<td></td>
<td>Absorption of x-rays (40-80 weight-%)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>$n$ ↑</td>
</tr>
<tr>
<td></td>
<td>resistance against acids ↑</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>chem. resistance ↑</td>
</tr>
<tr>
<td></td>
<td>tarnish for enamels</td>
</tr>
<tr>
<td>ZnO</td>
<td>hardness ↑</td>
</tr>
<tr>
<td>CdO</td>
<td>absorption of thermal neutrons (30-60 weight-%)</td>
</tr>
</tbody>
</table>
## Typical Glass Compositions I

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure vitreous silica</td>
<td>&gt;99.9 weight-% SiO$_2$</td>
<td>$\alpha = 0.5 \cdot 10^{-6}$ K$^{-1}$</td>
</tr>
<tr>
<td>(quartz glass)</td>
<td>impurities in the ppm-range</td>
<td></td>
</tr>
<tr>
<td>Vycor Glass</td>
<td>96 weight-% SiO$_2$, 3 weight-% B$_2$O$_3$, rest alkali, impurities in the ppm-range</td>
<td>$\alpha = 0.8 \cdot 10^{-6}$ K$^{-1}$</td>
</tr>
<tr>
<td>Commercial window glass</td>
<td>SiO$_2$ 72,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ 1.5, MgO 3.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaO 8.5, Na$_2$O 14.5 (weight-%)</td>
<td></td>
</tr>
<tr>
<td>chem. laboratory glass</td>
<td>SiO$_2$ 72, B$_2$O$_3$ 10</td>
<td></td>
</tr>
<tr>
<td>(aluminium-borosilicate glass)</td>
<td>Al$_2$O$_3$ 3,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CaO 1, MgO 1, Na$_2$O 5 (weight-%)</td>
<td></td>
</tr>
</tbody>
</table>
### Typical Glass Compositions II

<table>
<thead>
<tr>
<th>Glass Type</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical glass (heavy flint glass)</td>
<td>SiO$_2$ 28,</td>
</tr>
<tr>
<td></td>
<td>PbO 70,</td>
</tr>
<tr>
<td></td>
<td>Na$_2$O 1, K$_2$O 1 (weight-%)</td>
</tr>
<tr>
<td>Glass for X-ray protection</td>
<td>SiO$_2$ 29,</td>
</tr>
<tr>
<td></td>
<td>PbO 62,</td>
</tr>
<tr>
<td></td>
<td>BaO 9 (weight%)</td>
</tr>
<tr>
<td>X-ray transparent glass</td>
<td>B$_2$O$_3$ 83,</td>
</tr>
<tr>
<td></td>
<td>BeO 2,</td>
</tr>
<tr>
<td></td>
<td>Li$_2$O 15 (weight%)</td>
</tr>
<tr>
<td>„hydrofluoric acid“ resisting glass</td>
<td>P$_2$O$_5$ 72,</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$ 18,</td>
</tr>
<tr>
<td></td>
<td>ZnO 10 (weight%)</td>
</tr>
</tbody>
</table>
Glass softens steadily but doesn’t melt (at a distinct temperature)!
The viscosity of glass is a steady curve which spans 16 to 18 orders of magnitude.
“Melt“ exists for temperature higher than Tg (= infexion point of its viscosity curve), „solid“ exists for a temp. lower than Tg.
VFT-equation describes the viscosity for temperatures higher than Tg.

\[ \log \eta = A + \frac{B}{T - T_0} \]

Vogel-Fulcher-Tamman Equation

\[ \eta = 10^{13} \text{ dPa} \cdot \text{s} \]
“long” Glass – “short” Glass

$\eta$-T-function of Dow-Corning’s glasses ("long" glass, "short" glass)
Elongation of Glass I

\[ \alpha_{th} = \frac{1}{l_0} \cdot \frac{\Delta l}{\Delta T} \]

Dilatometry for the determination of \( T_g \) and \( \alpha \) of a glass.
Cooling Rate

Influence of the cooling rate on the formation of glass.

- $T_g$ and density of a glass depend on the cooling rate.
- A low cooling rate (i.e. slow cooling) leads to higher density than a high cooling rate.
Elongation of Glass II

Contraction and elongation curves of a glass. 0: equilibrium curve; 1: normal cooling; 2: slow cooling; 3: fast cooling; 3’: normal heating
Density as function of the alkali amount

Density of binary alkalisilicate glasses
Density as a function of the network former and its amount

Density variation of a binary alkalisilicate glass in function of the replacement of SiO$_2$ by other oxides in the same weight amount.
Reduction of the strength caused by flows

Strength of glass and its reasons

Flaws in glass structure

- Micro flaws in the surface
- Macro flaws in the surface

Theoretical strength

- Strength of glass fibers
- Strength of brand new acid polished glass
- Strength of normal glass ware
- Strength of damaged glass ware
Stress profiles for the a) thermal and the b) chemical method of pre-stressing.
Chemical Resistance of Glasses

- hydrofluoric acid HF attack (corrosion)
- diluted aqueous acids attack
- base attack
- combined water and acid / base attack
Chemical Resistance of Glass against Hydrofluoric Acid HF

$$\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$$

- Hydrofluoric acid breaks up the SiO$_2$ structures of silicate based glasses.
- Easy soluble silicon hexafluorid SiF$_6$ (hexafluoro silcia) is formed during the reaction.
Chemical resistance of glass against aqueous acids

Attack by aqueous acids: ion exchange reaction

\[-\text{Si-O-Na}^+ + \text{H}^+ \rightarrow -\text{Si-OH} + \text{Na}^+\]

- Gel – layer at the surface which is proton saturated
- This gel layer serves as a diffusion barrier.
- The thicker this gel-layer the more difficult for ions (Na\(^+\), H\(^+\)) to diffuse through this layer. -> Passivation!


Bases attack directly in a detrimental way the network of the glass in contrast to acids. Bases destroy the network.

- The SiO$_2$ molecules are dissolved and remain in the solution as poly-silicates.

- No protection layer is formed in this type of corrosion process

- BUT always a new surface forms which is continuously attacked by the hydroxide-ions of the solution.
Chemical resistance of glass against water and combined acid / base exposure

- Pure water at pH 7-9 corrodes glass because of free protons ($H_3O^+$) by auto protolysis.

- The glass corrodes by leach-out of alkaline cat ions.

- The alkaline cat ions increase the pH of the water by formation of hydroxyl ions ($OH^-$).

- The hydroxyl ion start to solubilise the glass network and/or the gel layer.

- Thus, hydroxyl ions are consumed, and the proton concentration in the solution increases and the cycle starts over.
Time dependence of glass corrosion

• **Type I:**
  - A surface layer is formed which acts as a protection layer (adsorption protection layer).
  - Vitreous silica in neutral salt solution accounts for this type.

• **Type II:**
  - A protection layer is formed by leaching out of alkalines. The glass network remains stable.
  - Attack of acids at silicate glasses accounts for this type.

• **Type III:**
  - Leaching and reaction at the surface form two protection layers of different composition.
  - The glass network remains stable.
Time dependence of glass corrosion

• Type IV:
  • Leaching and wear (material removal) take place at the same time.
  • A new leached out layer is formed at the surface which will be continuously shifted more and more inside the bulk glass by the wear of the glass network (i.e. material removal).
  • Alkalisilicate glasses in water account for this type.

• Type V:
  • Constant wear of the glass network and material removal.
  • No leaching layer is formed!
  • Hydofluoric acid and strong base attack at silicate glasses account for this type.
Time dependence of glass corrosion

**Case 1:** For the types I, II and III corrosion stops after formation of a protection layer (passivation), i.e. the corrosion front $c$ moves on with a decreasing speed.

$$\frac{dc}{dt} \propto te^{-at}$$

**Case 2:** For type IV corrosion involves two competing reactions:

1. the diffusion: $c \propto \sqrt{t}$
2. the dissolution: $c \propto t$

**Case 3:** For type V reaction or corrosion rate has a constant value:

$$\frac{dc}{dt} = a$$

**Case 4:** progressive corrosion takes place when we have the solution deficiency on the glass surface. Then, the corrosion reaction changes the pH-value of the solution which leads to a “stronger” corrosion at a higher rate. The wear or corrosion rate increases with reaction time:

$$\frac{dc}{dt} = at$$
Reaction progress for the corrosion of glasses

Reaction rates for the different cases.
Transmission of a light beam through glass

Way of a light beam transmitting a interface of two media (air, glass)
Influence of Alkaline content on the refractive index $n_D$

Variation to the refractive index as a function of the alkaline content of binary alkalisilicate glasses.
Influence of the network former on the refractive index

Variation of the refractive index $n_D$ of a Na$_2$O - SiO$_2$ - glass (20-80 weight%) if SiO$_2$ (network former) is substituted according to weight by other network former (Al$_2$O$_3$, B$_2$O$_3$) or elements.
## Fraunhofer Lines

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>h</td>
<td>g</td>
<td>F′</td>
<td>F</td>
<td>e</td>
<td>d</td>
<td>C′</td>
<td>C</td>
</tr>
<tr>
<td>Hg purple</td>
<td>Hg blue</td>
<td>Cd blue</td>
<td>H blue</td>
<td>Hg green</td>
<td>He yellow</td>
<td>Cd red</td>
<td>H red</td>
</tr>
<tr>
<td>404.66</td>
<td>435.84</td>
<td>479.99</td>
<td>486.13</td>
<td>546.07</td>
<td>587.56</td>
<td>643.85</td>
<td>656.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### What is Dispersion?

The dependence of the refractive index from the light-wavelength.

#### Dispersion splits white light in its colours !!!!
That effect is fatal for optical applications of glass!!!

<table>
<thead>
<tr>
<th>h</th>
<th>g</th>
<th>F'</th>
<th>F</th>
<th>e</th>
<th>d</th>
<th>C'</th>
<th>C</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg purple</td>
<td>Hg blue</td>
<td>Cd blue</td>
<td>H blue</td>
<td>Hg green</td>
<td>He yellow</td>
<td>Cd red</td>
<td>H red</td>
<td>He red</td>
</tr>
<tr>
<td>404.6 4</td>
<td>435.8 9</td>
<td>479.9 9</td>
<td>486.1 3</td>
<td>546.0 7</td>
<td>587.56</td>
<td>643.85</td>
<td>656.2 7</td>
<td>706.5 2</td>
</tr>
</tbody>
</table>

![Dispersion diagram showing a prism splitting white light into its colors](dispersion_diagram.png)
What is Dispersion?
The dependence of the refractive index from the light-wavelength.

<table>
<thead>
<tr>
<th></th>
<th>h</th>
<th>g</th>
<th>F'</th>
<th>F</th>
<th>e</th>
<th>d</th>
<th>C'</th>
<th>C</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg purple</td>
<td>Hg blue</td>
<td>Cd blue</td>
<td>H blue</td>
<td>Hg green</td>
<td>He yellow</td>
<td>Cd red</td>
<td>H red</td>
<td>He red</td>
<td></td>
</tr>
<tr>
<td>404.66</td>
<td>435.84</td>
<td>479.99</td>
<td>486.13</td>
<td>546.07</td>
<td>587.56</td>
<td>643.85</td>
<td>656.27</td>
<td>706.52</td>
<td></td>
</tr>
</tbody>
</table>

\[ \vartheta_{rel} = \frac{n_F - n_C}{n_D - 1} \]

\[ \nu = \frac{n_d - 1}{n_F - n_C} \]
Dispersion und Refractive index

\[ v = \frac{n_d - 1}{n_F - n_C} \]

n\textsubscript{D}-v-Diagram of optical glasses

Flint glasses

Crown glasses
Dispersion and Refractive Index

\[ v = \frac{n_d - 1}{n_F - n_C} \]

Material Science II

Ceramics: Glass, Chap 5

Dispersion and Refractive Index

Diagram of optical glasses

Refractive index \( n_d \) (\( \lambda = 587.6 \text{ nm} \))

Abbe number \( V \)
Chromatic Aberration

Chromatic aberration in case of a bi-convex and bi-concave lens.
Achromatic Lens

Correction of the chromatic aberration by combining two suitable lenses.
Transmissions spectrum of a commercial float glass (thickness 1mm)
UV rim of glasses of various composition
1: SiO$_2$-Glass very pure, 2: SiO$_2$-Glass normal,
3: Na$_2$O - 3 SiO$_2$ Glass very pure,
4: Na$_2$O-3 SiO$_2$-Glass, normal
Transmission spectrum of Glasses I

Transmission spectra of coloured glasses.
Transmission spectrum of Glasses II

Transmission spectra of colored glasses.
## Colorizing Ions and their Effect I

<table>
<thead>
<tr>
<th>Valency</th>
<th>Coordination</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(III)</td>
<td>6</td>
<td>purple</td>
</tr>
<tr>
<td>V(III)</td>
<td>6</td>
<td>green</td>
</tr>
<tr>
<td>V(V)</td>
<td>4</td>
<td>colorless</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>6</td>
<td>green</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>6</td>
<td>yellow</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>6</td>
<td>colorless</td>
</tr>
<tr>
<td>Mn(III)</td>
<td>6</td>
<td>purple</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>6</td>
<td>blue</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>6</td>
<td>yellow</td>
</tr>
</tbody>
</table>
Colorizing Ions and their Effect II

<table>
<thead>
<tr>
<th>Valency</th>
<th>Coordination</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(II)</td>
<td>4</td>
<td>blue</td>
</tr>
<tr>
<td>Co(II)</td>
<td>6</td>
<td>pink</td>
</tr>
<tr>
<td>Co(III)</td>
<td>4</td>
<td>green</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>4</td>
<td>blue</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>6</td>
<td>yellow</td>
</tr>
<tr>
<td>Cu(I)</td>
<td>?</td>
<td>colorless</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>6</td>
<td>blue</td>
</tr>
</tbody>
</table>
Float Glass Process

Pilkington Float Glass Process

http://www.glasswebsite.com
The Float Glass Process
Float Glass process

N₂ / H₂ mix injection

Furnace

Float Bath (Tin Bath)

Molten Glass

Glass Sheet
**Float Glass Process**

**Batch Charger**

![Batch Charger Image]

**Furnace**

![Furnace Image]

**Raw Materials**

![Raw Materials Image]

**Tin Bath (Float Furnace)**

![Tin Bath Image]

**Annealing Lehr**

![Annealing Lehr Image]

**Cutting System**

![Cutting System Image]
### Composition of commercial float glass

<table>
<thead>
<tr>
<th>Material</th>
<th>Glass Composition</th>
<th>Reason for Adding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand (SiO₂)</td>
<td>72.6</td>
<td>-</td>
</tr>
<tr>
<td>Soda Ash (Na₂CO₃)</td>
<td>13.0</td>
<td>Easier melting</td>
</tr>
<tr>
<td>Limestone (CaCO₃)</td>
<td>8.4</td>
<td>Durability</td>
</tr>
<tr>
<td>Dolomite(CaMg(CO)₂)</td>
<td>4.0</td>
<td>Working &amp; weathering properties</td>
</tr>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>Others</td>
<td>1.0</td>
<td>-</td>
</tr>
</tbody>
</table>
Composition Float Glass

Composition of float glass:
- Sand
- Aluminium oxide
- Iron oxide
- Silica
- Soda ash/saltcake
- Sodium oxide
- Limestone
- Calcium oxide
- Dolomite
- Magnesium oxide
- Calcium oxide

http://www.pilkington.com
Chemistry of Glass

Important glassmaking chemistry: the basic reactions

$$\text{Na}_2\text{CO}_3 + \text{SiO}_2 \xrightarrow{1,500^\circ\text{C}} \text{Na}_2\text{SiO}_3 + \text{CO}_2$$

$$\text{Na}_2\text{SiO}_3 + x\text{SiO}_2 \xrightarrow{\text{Digestion}} (\text{Na}_2\text{O})(\text{SiO}_2)^{(x+1)}$$
Glass-Ceramics

• Structure

• Nucleation and crystal growth

• Fabrication

• Examples

  • next: mechanical properties of ceramics (J. Kübler, EMPA)
Glass-Ceramics

- “Glass-ceramic” refers to materials which are fabricated from glass melts by a process of controlled crystallisation.

- Glass-ceramics is a partially crystalline material which is fabricated by an incomplete crystallisation (“Ceraming“) of suitable glasses.

- Brands: Ceran, Zerodur, Robax, Neoceram, Macor
Glass-Ceramics

- Glass
- Short-range order
- Grain with grain boundary
- \( \text{SiO}_4 \text{ tetrahedron} \)

\( \text{Si}^{4+} \)\( \text{O}^2- \)

\( \text{O}^2- \)
Nucleation energy and radius of the nucleus

Glass (amorph) to Crystal Energy \( \propto r^3 \)
Surface Energy = \( r^2 \)

Dependence of the nucleation energy from its nucleus' radius
**Critical Nucleus Radius**

\[
\Delta G = \frac{4\pi}{3} r^3 \Delta G_v + 4\pi r^2 \sigma
\]

\(-\) Derivative must be zero for \(r^*\)

\[
\Delta G^* = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta G_v)^2} = \frac{4}{3} \pi r^{*^2} \sigma
\]

\[
r^* (T) \sim \frac{1}{(T_s - T)}
\]

\[
\Delta G^* (T) \sim \frac{1}{(T_s - T)^2}
\]
**Nuclei Formation Rate (Nucleation Rate)**

\[
\nu_{KB} = \nu N_v \exp\left( -\frac{(E + \Delta G^*)}{kT} \right)
\]
Crystal Growth Rate (KG)

\[ N'' = N \cdot \nu \cdot \exp\left(-\frac{\Delta G + E}{kT}\right) \]

\[ N' = N \cdot \nu \cdot \exp\left(-\frac{E}{kT}\right) \]

Crystal Growth Rate

\[ \nu_{KG} = \frac{(N' - N'')}{N} \cdot a_0 = a_0 \cdot \nu \cdot \left[ \exp\left(-\frac{E}{kT}\right) \right] \cdot \left[ 1 - \exp\left(-\frac{\Delta G}{kT}\right) \right] \]
Temperature Dependence of $\nu_{KB}$ and $\nu_{KG}$

$T_E$: Freezing Temperature  $T_S$: Melting Temperature
Temperature-Time (T-t)-Curve for the Fabrication of a typical Glass-Ceramics
# Examples for Glass-Ceramic-Systems

<table>
<thead>
<tr>
<th>System</th>
<th>Crystalline Phase</th>
<th>TEC $10^{-7}$ K</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$O-Al$_2$O$_3$- n SiO$_2$, n= 4-6</td>
<td>H- Quartz mixed crystal</td>
<td>0 - 0.7</td>
<td>cooktop, fireproof cookware fire protection glass, reflecting telescope, gyroscope</td>
</tr>
<tr>
<td>Li$_2$O - Al$_2$O$_3$ - n SiO$_2$, n= 4-10</td>
<td>β-Spodume</td>
<td>1.5 - 2</td>
<td>fireproof cookware, heat exchanger</td>
</tr>
<tr>
<td>Na$_2$O - Al$_2$O$_3$ - 2 SiO$_2$</td>
<td>Nepheline</td>
<td>11</td>
<td>plates</td>
</tr>
<tr>
<td>2 MgO- 2 Al$_2$O$_3$ – 5 SiO$_2$</td>
<td>Cordierite</td>
<td>1.5 - 3</td>
<td>car exhaust filter, substrates for microelectronics, composite materials</td>
</tr>
<tr>
<td>Li$_2$O- 2 SiO$_2$</td>
<td>Lithium-disilicate</td>
<td>12</td>
<td>fabrication of microstructures</td>
</tr>
<tr>
<td>(Na,K) Mg$_3$AlSi$<em>3$O$</em>{10}$F$_2$</td>
<td>Phlogopite</td>
<td>8 - 12</td>
<td>bioceramics (dental implants, bone substitutes)</td>
</tr>
</tbody>
</table>
Properties of Glass-Ceramics

- thermal expansion: -20 to $200 \cdot 10^{-7} \text{ K}^{-1}$
- strength: 60 – 600 MPa
- optical property: transparency – opaque
- chemical resistance: water soluble – inert
- electrical property: semi-conducting – isolating
- mech. machinability: brittle – machinable
Fabrication of Ceran cooktop panels (Schott)

1st step

Production of glass

- Raw materials
- Melting tank
- Annealing furnace
- Cutting and inspection
- In-process storage

Mixture → Liquid glass → Glass ribbon → Annealing → Glass panels

2nd step

Manufacture of Ceran cooktop panels

- Cutting
- Edge processing
- Decoration
- Ceramization
- Distribution

Customer dimensions → Tolerances → Cooking zone and surface decoration → Glass ceramic → Ceran cooktop panels

Ceramics: Glass, Chap 5
Advantages of glass-ceramics over ordinary ceramics

Advantages:

• forming is as simple as in case of glass

• transparent pre-forms

• good reproducibility of the materials properties

• free of pores

• mono-size crystals

• economic fabrication process

Disadvantages:

• limited to certain crystalline phases
Summarizing: Glass & Glass Ceramics

- Glass can be regarded as frozen melt (liquid)
  - which solidified without crystallisation
  - which has a short range order but no long-range order.

- The glass structure can be described using Zachariasen’s network model.

- Glass solidifies at the glass transition temperature $T_g$,
  - for $T > T_g$ glass is a (liquid) melt,
  - for $T < T_g$ glass is a solid.

- The viscosity as a function of temperature is a smooth (steady) curve spanning a range of 16 to 18 orders of magnitude.

- Glass-ceramics is fabricated from glass by using controlled crystallisation process, and it has special properties.
Ersatz
### Overview on the composition of important glass types

<table>
<thead>
<tr>
<th>Glass type</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>MgO</th>
<th>CaO</th>
<th>B₂O₃</th>
<th>PbO</th>
<th>TiO₂</th>
<th>F</th>
<th>As</th>
<th>Se</th>
<th>Ge</th>
<th>Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>quartz glass</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Kalk-Natron-glass</td>
<td>72</td>
<td>2</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(ordinary glass)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>float glass</td>
<td>72</td>
<td>1,5</td>
<td>13,5</td>
<td>-</td>
<td>3,5</td>
<td>8,5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>lead crystal glass</td>
<td>60</td>
<td>8</td>
<td>2,5</td>
<td>12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>17,5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Laboratory glass</td>
<td>80</td>
<td>3</td>
<td>4</td>
<td>0,5</td>
<td>-</td>
<td>-</td>
<td>12,5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E-glass</td>
<td>54</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>4,5</td>
<td>17,5</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>enamel</td>
<td>40</td>
<td>1,5</td>
<td>9</td>
<td>6</td>
<td>1</td>
<td>-</td>
<td>10</td>
<td>4</td>
<td>15</td>
<td>13</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>chalcogenide glass 1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12</td>
<td>55</td>
<td>33</td>
<td>-</td>
</tr>
<tr>
<td>chalcogenide glass 2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>13</td>
<td>32</td>
<td>30</td>
<td>25</td>
</tr>
</tbody>
</table>

All amounts in weight -%.

http://de.wikipedia.org/wiki/Glas#Einstellung_der_Glaseigenschaften
The basic idea of the float glass process

- Molten glass poured onto a bath of clean molten tin, will spread out in the same way that oil will spread out if poured onto a bath of water.
- Gravity and surface tension will result in the top and bottom surfaces of the glass becoming approximately flat and parallel.
The basic idea of the float glass process

The equilibrium thickness \( T \)

\[
T^2 = \left( S_g + S_{gt} + S_t \right) \cdot \frac{2\rho_t}{\rho_g (\rho_t - \rho_g)}
\]

where \( S_g \), \( S_{gt} \), and \( S_t \) are the values of surface tension at the three interfaces.

For standard soda-lime-silica glass under a protective atmosphere and on clean tin the equilibrium thickness is approximately 7 mm.
The Production Process

Raw Material Silos

Weighing & Mixing

Melting
- Heaters

Float Area
- Molten Glass
- Molten Tin

Annealing Lehr
- Molten glass (1050°C)

Glass Ribbon at 600°C
- Edge rolls

Inspection
- Glass is slowly cooled in lehr to prevent build up of stress
- Glass is automatically inspected to detect flaws

Cutting & Storage
- Glass is automatically cut to size

Materials are weighed and mixed
- Mix is melted in furnace
- Molten glass is floated on top of a bath of molten tin and starts to cool slowly