Formation of solids from solutions and melts
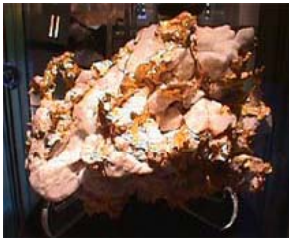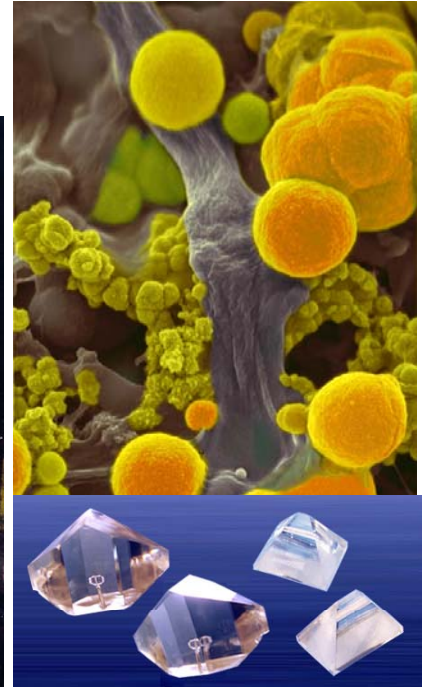
Solids from a liquid phase.
1. The liquid has the same composition as the solid. Formed from the melt without any chemical transformation. Crystallization and glass formation
2. Crystallization and precipitation from a solution

Crystallization processes in biological systems
Solvothermal synthesis
Sol-Gel

Glass

Natural glass

Volcanic, e.g. Obsidian

Lightning, Fulgurites

Meteorite impact

Glass

Prepared by cooling from a liquid state without crystallization

A glass is an amorphous solid without long range order or periodicity in the atomic arrangement

Glass transformation range

Glass temperature, T$_g$:

Depends on heating/cooling rate, and experimental method. No agreed standardized conditions.
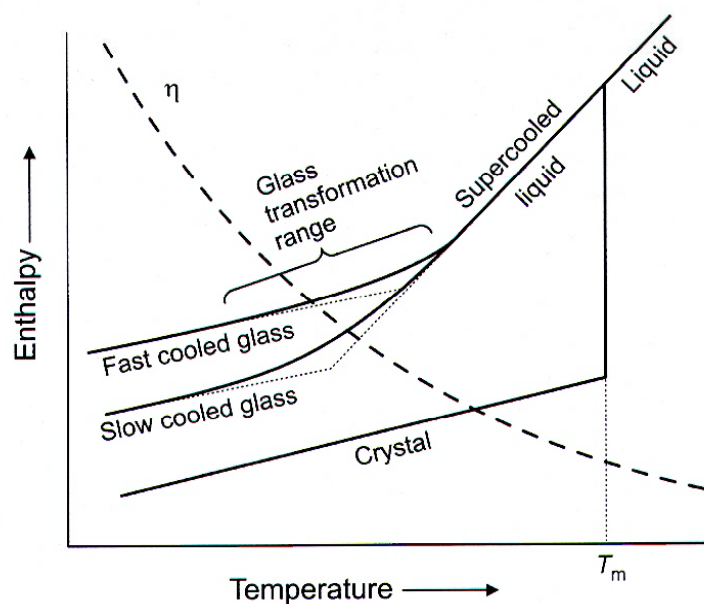

Figure 4-1. Effect of temperature on the enthalpy of a glass-forming melt. η is the viscosity of the melt.

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Glass vs. crystalline
Structural theory of glass formation

Silicates easily form glasses.
The ability of forming three dimensional networks is important
Highly ionic materials do not form network structures
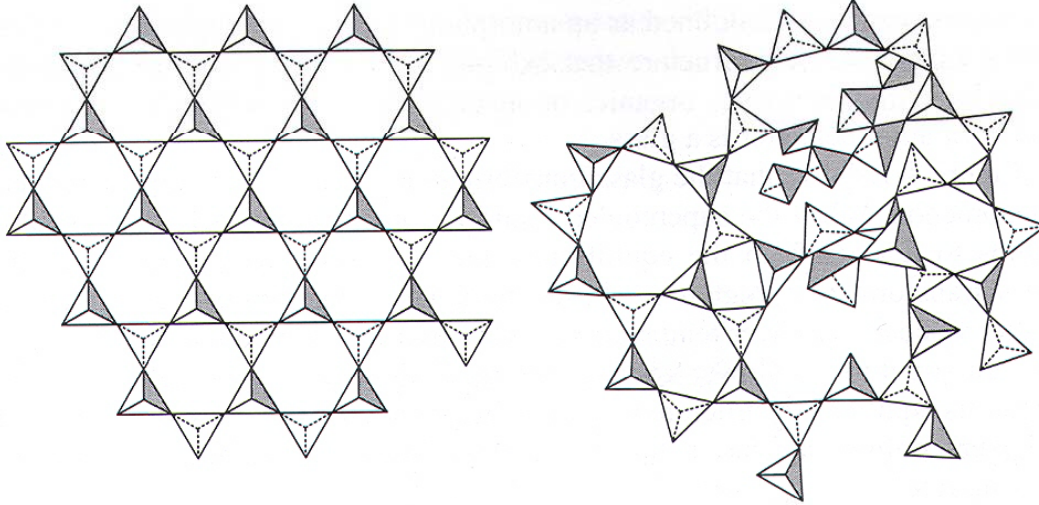Vitreous (glass-like) networks are isotropic

Figure 4-2. Schematic structure of crystalline (left) and amorphous silica (right). In the crystalline forms of silica the $[SiO_4]$ tetrahedra (the silicon atoms are located in the center of the tetrahedra, and the oxygen atoms at the vertices) are regularly arranged. There is no long-range order in the amorphous form.

Zachariasens rules

1. **An oxygen atom is linked to, at most, two other atoms**
2. **The coordination polyhedra, formed by oxygen around the other atoms, share corners and not edges or faces**
3. **The coordination number of the other atom is small**
4. **The polyhedra link up to form three-dimensional networks. At least three corners of the polyhedra must be shared.**
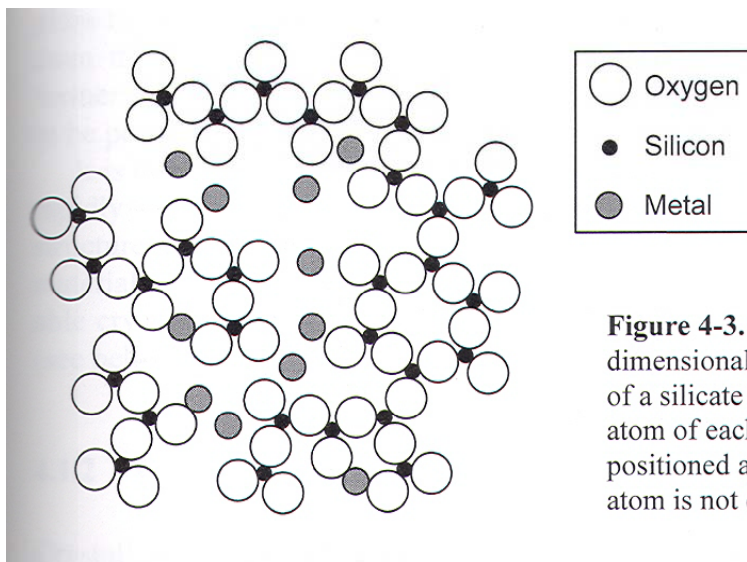

○ Oxygen
● Silicon
◉ Metal

Figure 4-3. Schematic two-dimensional drawing of the structure of a silicate glass. The fourth oxygen atom of each $[SiO_4]$ tetrahedron positioned above or below the silicon atom is not drawn for clarity.

Borate glasses

Many different building blocks

Silicate + metal oxide: non-bridging oxygen atoms.

Borate + metal: convert planar [BO$_3$] to tetrahedral [BO$_4$]

Modification of Zachariasen:

A *high percentage* of network cations must share three anions with other network cations by corner sharing.

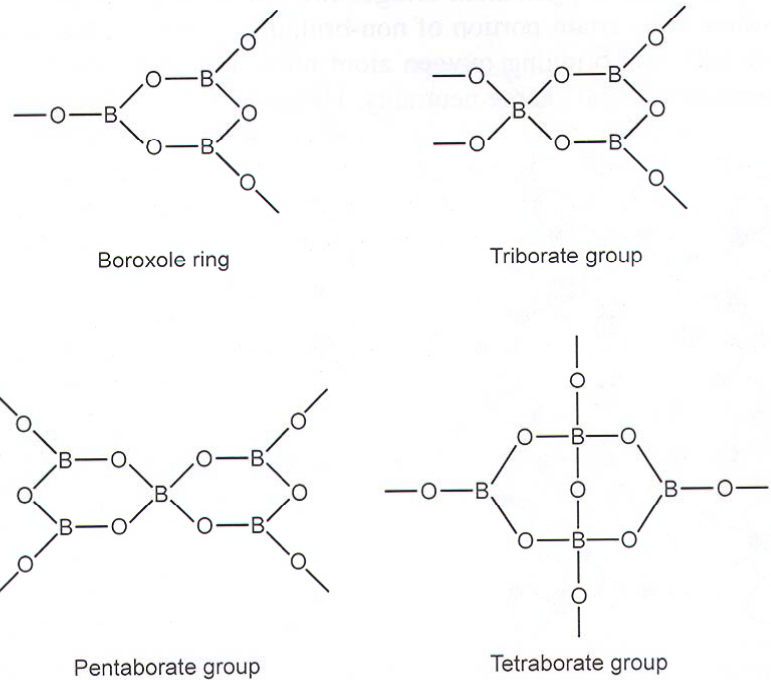> **Virtually any material will form a glass if cooled fast enough…**

Boroxole ring   Triborate group

Pentaborate group   Tetraborate group

Figure 4-4. Structural elements of borate glasses.

Leads to: **Kinetics theory of glass formation**

Crystallization versus glass formation

Crystallization: Nucleation and growth (Homogeneous/heterogeneous nucleation)
Absence of nuclei or no growth → glass formation
Many components facilitate glass formation

Homogeneous nucleation: Nucleation rate I

$$I \propto e^{\left[\frac{-(\Delta G_N + \Delta G_D)}{kT}\right]}$$

ΔG_N is the free energy change for formation of the nucleus. (thermodynamic barrier to nucleation

ΔG_D is the kinetic barrier for diffusion across the liquid-nucleus surface.

Spherical nuclei:

Volume energy term	Surface energy term

$$\Delta G_N = 4/3\pi r^3 \Delta G_V + 4\pi\, r^2\gamma$$

γ is the crystal-melt interfacial energy,
ΔG_V is the change in volume free energy per unit volume (ΔG_V is negative)

Nucleation

Critical radius: the size where ΔG begins to decrease → growth is favoured
(r^* is positive because ΔG_V is negative)
At temperatures just below T_M the volume free energy, ΔG_V, is small, resulting in a large critical radius → low probability of reaching r*
Decreasing temperature results in smaller critical radius, i.e. larger survival probability of nuclei (However, viscosity also increases…)
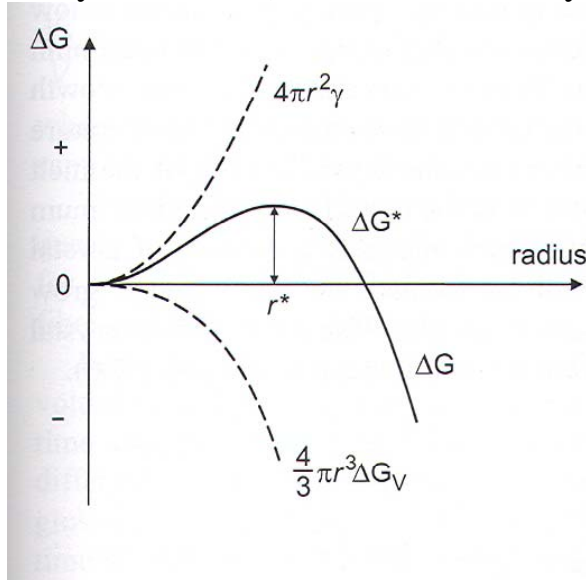
$$r^* = \frac{-2\gamma}{\Delta G_V}$$

Figure 4-5. Changes in the thermodynamic barrier (ΔG_N) upon formation of a crystalline nucleus.

Heterogeneous nucleation when the free surface energy for a solid-solid interface between an existing surface and the crystal is low

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Crystal growth

Crystals grow at any temperature below T_M, as long as a nucleus or crystal is present
Growth rates are determined by thermodynamics and viscosity

Both nucleation and growth will show a maximum growth rate due to viscosity effects

How large a fraction of a glass may be crystallized, while still considering it a glass?

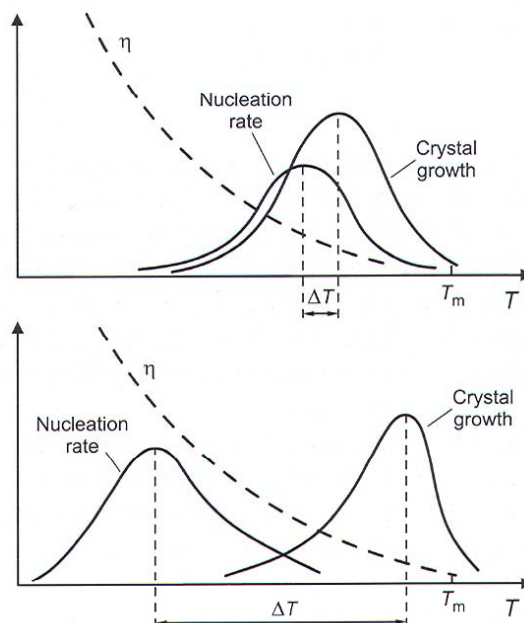Depends on application. Typical value ca. 1 ppm

Figure 4-6. The diagrams show the different relation between nucleation rate and crystal growth in a crystallizing system (upper diagram) and glass-forming system (lower diagram). η is the viscosity of the melt.

Glass ceramics

Crystallization in glass is most often avoided.
However, a group of materials, the glass ceramics, obtain their properties
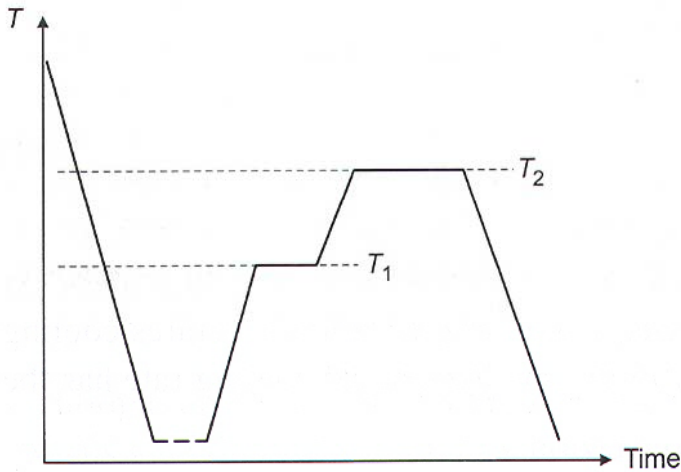**from crystal formation in a glass matrix (this is not sintering)**

Figure 4-8.
Temperature profile
during the production
of glass ceramics.

Macor®

*Macor® machinable glass ceramic withstands high
temperature while providing tight tolerance capability.*
Special Features
 1.Excellent physical properties
  2.High dielectric strength
  3.Electrical resistivity
  4.Non-porous and non-shrinking
  5.Machined into complicated shapes and precision
parts using ordinary metal working tools
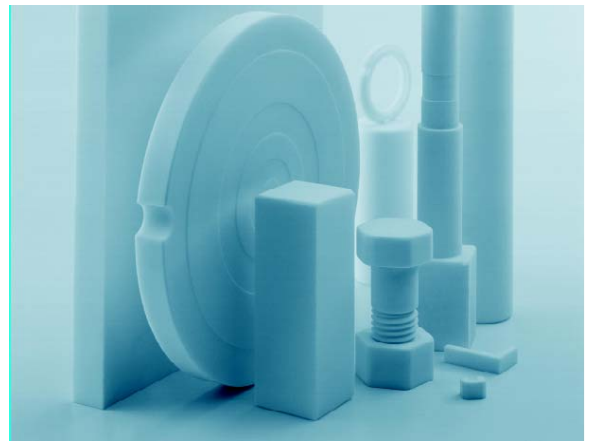
Properties	SI/Metric
Temperature Limit	1000° C
Dielectric Constant,1Khz at 25° C	6.03
Dielectric Strength. AC or DC (at .01" thickness, 25° C)	40KV/mm
DC Volume Resistivity at 25° C	>10^{16} ohm-cm
Thermal Conductivity at 25° C	1.46 W/m° C
Coefficient of Expansion 25-300° C	93 x 10^{-7}/° C
Density, g/cm³	2.52
Modulus of Elasticity at 25° C	64 GPa
Porosity	0

Silicon - SiO_2 46%
Magnesium - MgO   17%
Aluminum - Al_2O_3 16%
Potassium - K_2O 10%
Boron - B_2O_3 7%
Fluorine -   F   4%

Macor®

Microstructure of MACOR MGC 5000X magnification.
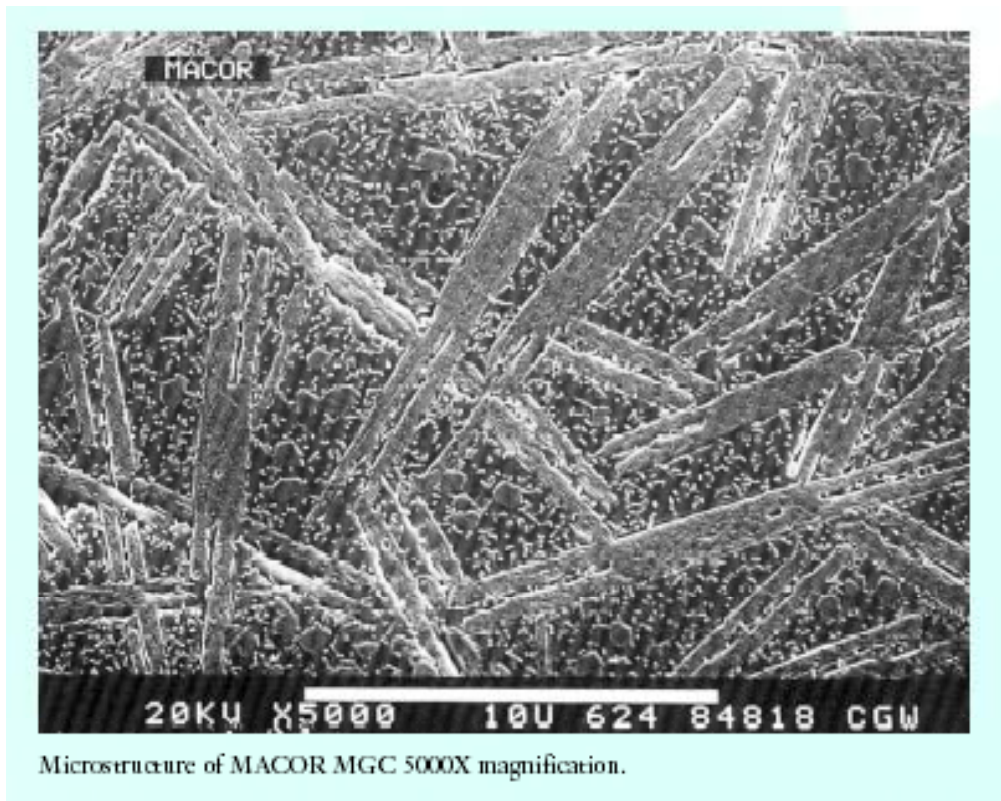
Randomly oriented mica flakes in the microstructure of MACOR MGC
are the key to its machinability.

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Glass formation

Raw materials

•**Glass formers**
•**Network modifiers**
•**Colorants**
•**Fining agents**

Raw materials
↓
Batching and mixing
↓
Batch melting
↓
Fining
↓
Homogenization
↓
Product
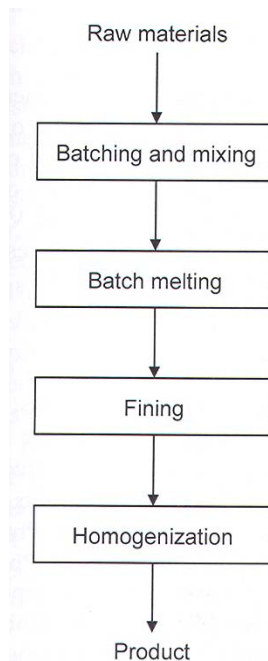
Figure 4-9. Steps in the fabrication of glass.

Table 4-1. Composition of some typical glasses

Window glass	72 % SiO_2, 1.5 % Al_2O_3, 3.5 % MgO, 8.5 % CaO, 14.5 % Na_2O
Laboratory glass	80 % SiO_2, 10 % B_2O_3, 3 % Al_2O_3, 1 % MgO, 1 % CaO, 5 % Na_2O
Fluoride fiber glass	53 % ZrF_4, 20 % BaF_2, 20 % NaF, 2 % LaF_3, 3 % AlF_3, 2 % LnF_3

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Metallic glasses

Au$_3$Sn (1960)

Gas pressure

Melt

Orifice

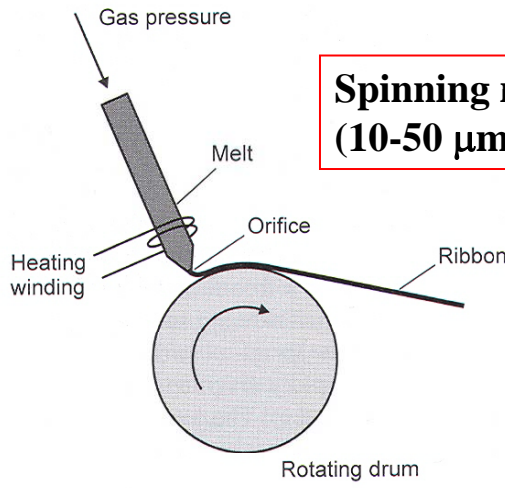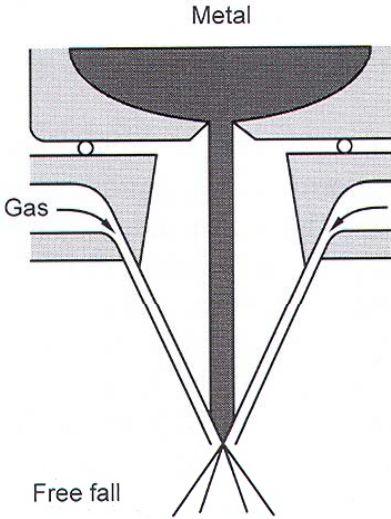Heating winding

Ribbon

Rotating drum

Figure 4-12. Schematic drawing of chill-block melt-spinning for the formation of glass ribbons.

Metal

Gas

Free fall

Figure 4-11. Principle of spray-atomization by impingement of a high-velocity gas jet on a free-falling melt stream.
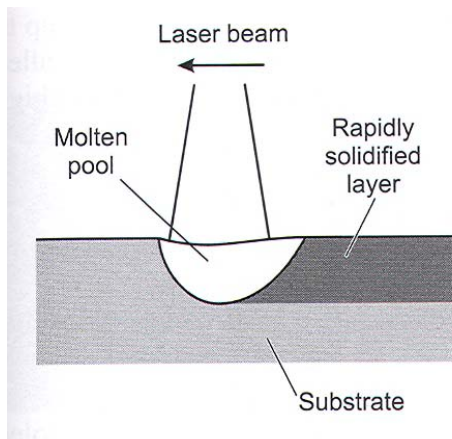
15

Laser beam

Molten pool

Rapidly solidified layer

Substrate

Figure 4-13. Laser surface melting and quenching.

Metal A

Metal B

Alloy
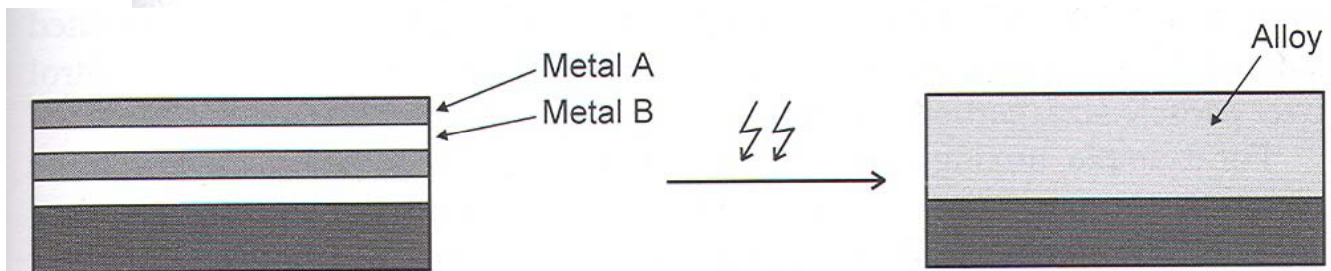
Figure 4-14. Ion-mixing of multilayered films consisting of metal layers A and B.

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Bulk metallic glasses

Contain more than three elements
Significant difference in sizes (>12%)
Negative heat of mixing

Cooling 10^5-10^6K/s

Metglass: Fe-Si-B, Fe-Ni-P-B, …

Liquidmetal® ($Zr_{41.2}Be_{22.5}Ti_{13.8}Cu_{12.5}Ni_{10.0}$)

Bounce.mov