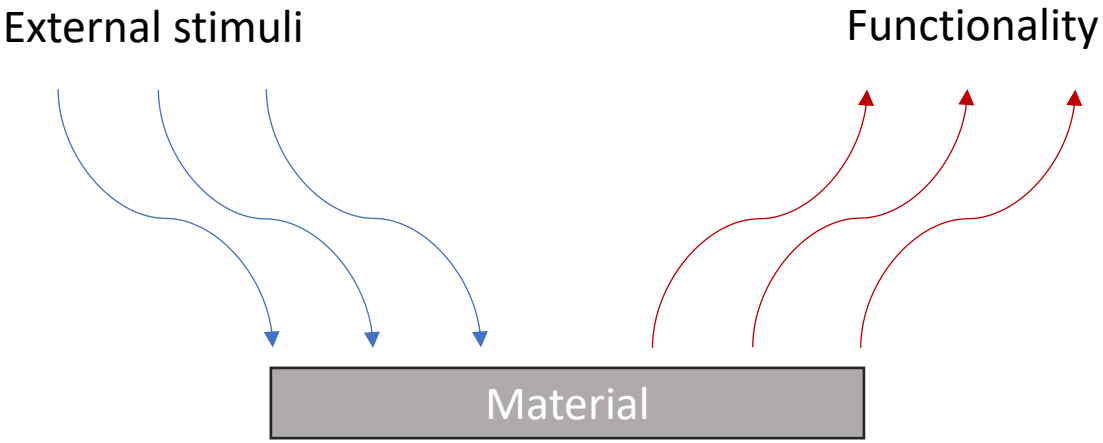
Responsive Functional Materials

Assist.-Prof. Dr. Heidi A. Schwartz

Photoactive Hybrid Materials

Universität Innsbruck



https://www.uibk.ac.at/en/aatc/ag-schwartz/

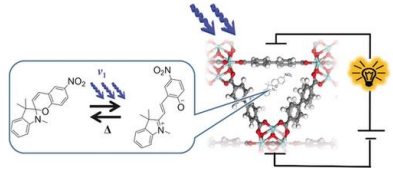
heidi.schwartz@uibk.ac.at

L01.063

Outline for today´s lecture

1. Organizational Points

2. Learning objectives



- Fundamentals and functional materials in everyday life I
- Next time: fundamentals and functional materials in everyday life II

Organizational Points

1. Lecture takes place every Tuesday from 8-10 a.m. (L01.220) and Wednesday (only in March, little complicated) in L03.121 until 29th of April

2. Powerpoint presentation is available on OLAT after every single lecture

3. Examination on during easter holiday and 29th April?

What you will learn the next weeks

1. Introduction into Material Sciences I
2. Introduction into Material Sciences II
3. Analyzation Tools I
4. Analyzation Tools II
5. Porous Materials I
6. **Invited Speaker: Artem Mikhailov (Nancy)**
7. Porous Materials II
8. Responsive Materials
9. Photochromism and Luminescence
10. Hybrid Materials

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Historical Aspects

Materials are intensively used in our culture:

- Transport
- Housing
- Clothes
- Communication
- Food production, …

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The development and change of societies are always closely linked to the ability to produce and change materials in order to satisfy their needs.

Civilizations were named after predominant material:

Stone age · Bronze age · Iron age



Historical Aspects

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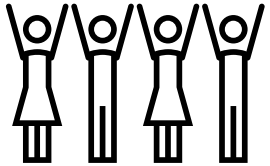
Nowadays - Realization

Structure in strong relation to properties!

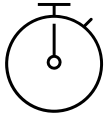
Adjustment of structure – development of numerous materials!

Group-/Tandem-Work 

Which materials do you know from everyday life?

What are their properties?

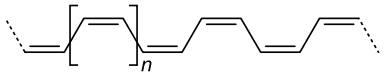
What are they used for?

 15 min

A functional material could be defined as being prepared from a “target-motivated” approach

Ceramics

Polymers



Metals

Composites

Glasses

[Functional Material - an overview | ScienceDirect Topics](#) (3rd March, 2023)

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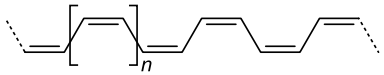

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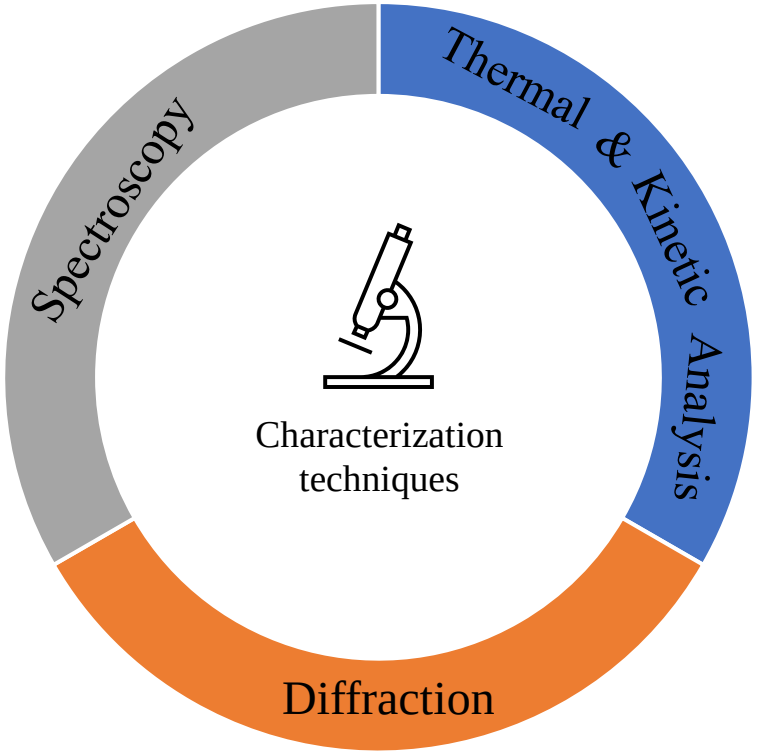

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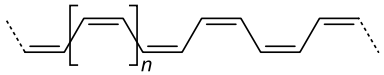

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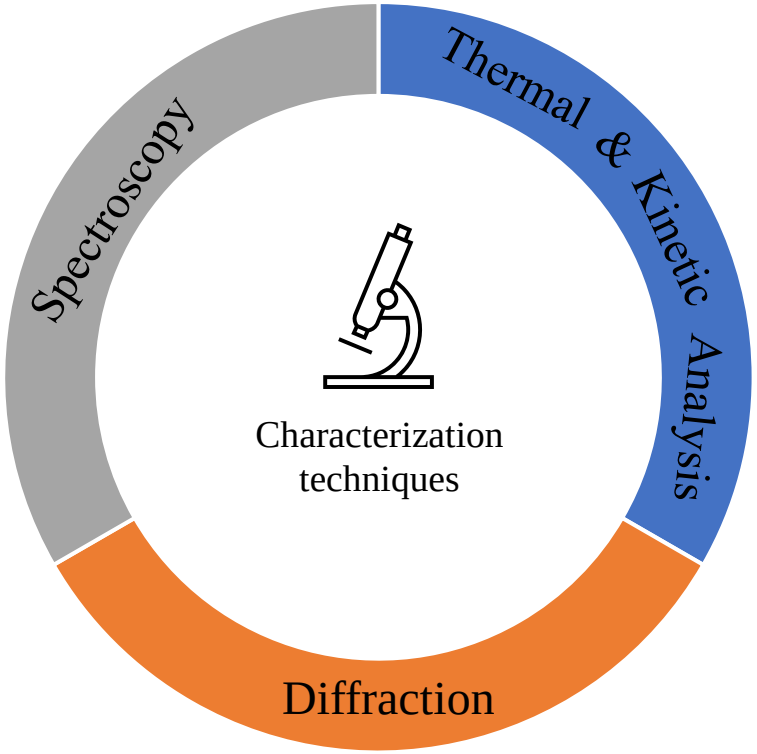
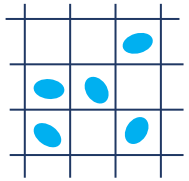


Innovative Materials



Biomaterials

Nanomaterials

Semiconductors

…

Porous materials

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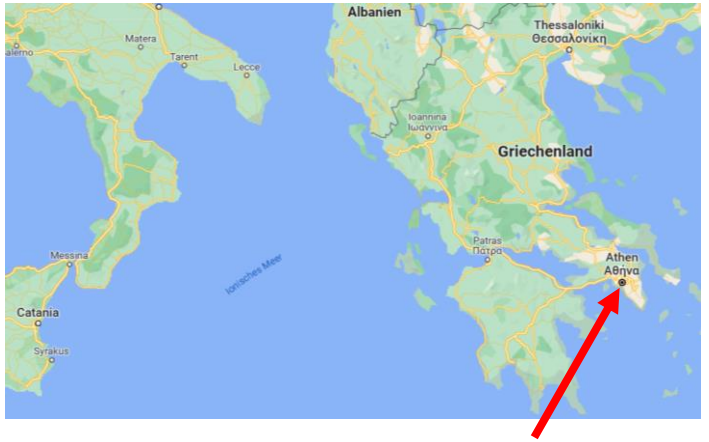
Ceramics – one of the oldest functional material

Venus from Dolní Věstonice
30.000 years old.



Origin in Kerameikos, a district in Athens.

Petr Novák, Wikipedia, https://commons.wikimedia.org/w/index.php?curid=2673615 (3rd March, 2023)

Ceramics – one of the oldest functional material

"Ceramic" is the technical term for a variety of inorganic non-metallic materials. They are almost non-soluble in water, and at least of 30% crystallinity.

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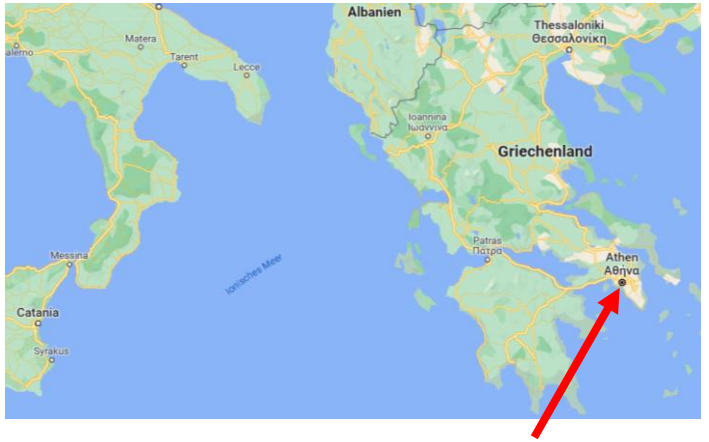

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Synthesis procedure

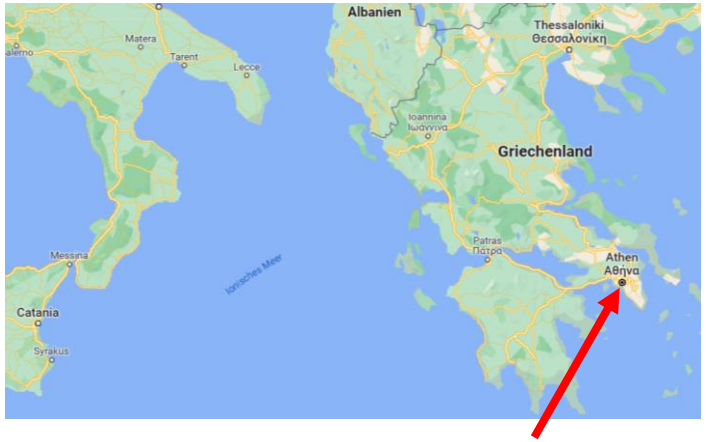
Raw materials formed at RT

Green body.

e.g.,
Silicates
Oxides
SiC
BN
B_4C

WC
Si_3N_4
AlN
$MoSi_2$

Sintering, mostly
> 800 °C



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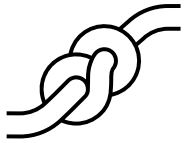
Töpfern Frankfurt ✓ Töpferkurse bei STEINER Pottery & Poetry (steiner-pottery.de) (4th March, 2023)

Bonding situation  and properties

Large range of possible structures/compositions
- Almost all elements
- Almost all type of bonds (mainly covalent & ionic)
- All levels of crystallinity

→

Classification
- Oxides: alumina, zirconia, ceria, …
- Non-oxides: carbides, silicides, borides, nitrides
- Composites

Ceramic – Wikipedia (18th February, 2025)

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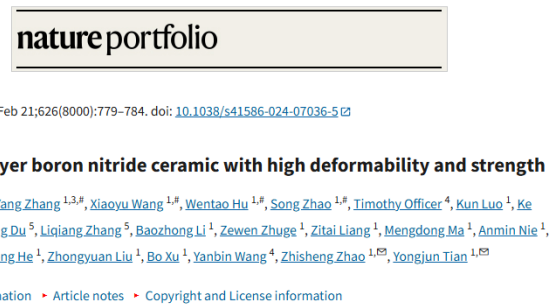
Mechanical properties
- Poor toughness due to bond type
- Pores as stress concentrators

Ceramic matrix composites


nature portfolio

Nature. 2024 Feb 21;626(8000):779–784. doi: 10.1038/s41586-024-07036-5

Twisted-layer boron nitride ceramic with high deformability and strength

Yingju Wu [1,2,#], Yang Zhang [1,3,#], Xiaoyu Wang [1,#], Wentao Hu [1,#], Song Zhao [1,#], Timothy Officer [4], Kun Luo [1], Ke Tong [1], Congcong Du [5], Liqiang Zhang [5], Baozhong Li [1], Zewen Zhuge [1], Zitai Liang [1], Mengdong Ma [1], Anmin Nie [1], Dongli Yu [1], Julong He [1], Zhongyuan Liu [1], Bo Xu [1], Yanbin Wang [4], Zhisheng Zhao [1,✉], Yongjun Tian [1,✉]

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Ceramic matrix composites

Electrical properties
- Semiconductors
- Superconductors
- Ferroelectricity & supersets
- Positive thermal coefficient


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Ceramic matrix composites

Electrical properties
- Semiconductors
- Superconductors
- Ferroelectricity & supersets
- Positive thermal coefficient

Optical properties
- Transmission of light in vis and IR range
- GE manufactured translucent alumina


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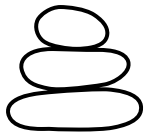
White Board

Technical ceramics

For the resulting properties of ceramic materials, not only the raw materials, but even more the synthesis processes are of outmost importance.

Grain size



Starting materials

+

Firing process

Firing atmospheres

Firing temperatures

Matthias Glätzle, WC cubics

Technische Keramik – Wikipedia (4th March, 2023)

Beschusshemmende Weste – Wikipedia (4th March, 2023)

Porzellahnzahn: Zahnersatz aus hochwertigem Material | Gelencsér Dental Magazin (zahnarzt-ungarn-heviz.de) (4th March, 2023)

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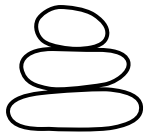

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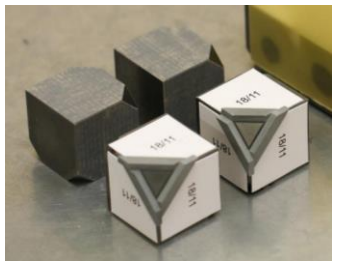
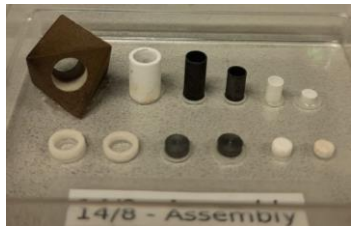


WC.

ZrO_2.



BN.

Oxidic ceramics.

$Ca_5(PO_4)_3(OH)$.

Siliconized carbon fibre.

Matthias Glätzle, WC cubics

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White Board

Ceramics have several advantages over metals for practical applications, including low density, high compressive strength (hardness) and resistance to corrosion. However, they have a fatal weakness when used as engineering materials — they fracture after undergoing a very small deformation.

The first bulk ceramic that deforms like a metal at room temperature (18th February, 2025)
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Metals – old but gold

First gold found in Spain, 40.000 B.C..

Metalle – Wikipedia (4th March, 2023)
CARRS Sterling Silver Cutlery from Lincoln House (4th March, 2023)
History of Gold | Gold Eagle (gold-eagle.com) (4th March, 2023)
Nitinol – Wikipedia (4th March, 2023)
Iron | 7439-89-6 (chemicalbook.com) (4th March, 2023)

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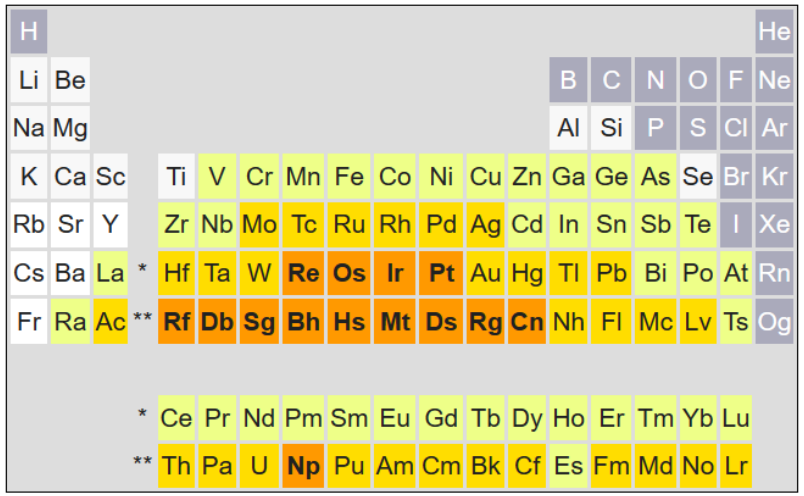

Metallic elements of the periodic table.

Sterling silver, an alloy.

Nitinol, an intermetallic phase.

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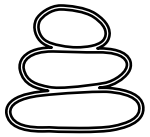


Ore

Metallurgy

White Board

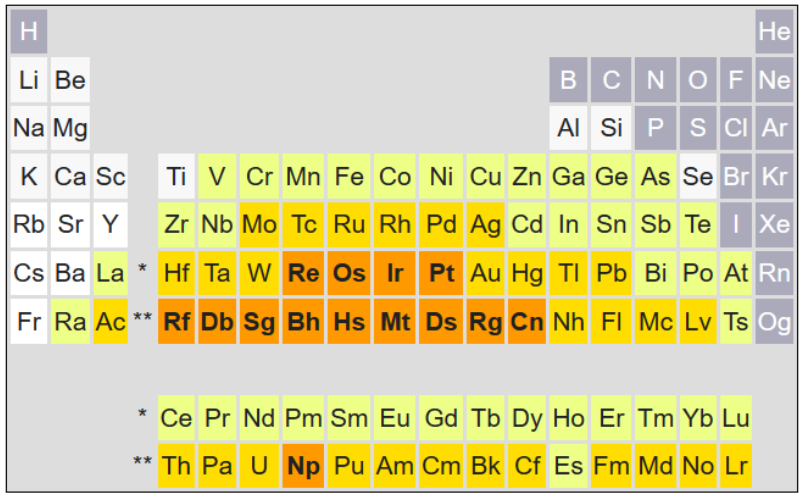
Process of metal mining and purification

1. Mining
2. Further processing

- Roasting
- Extraction with water
- Electrolytic/-thermic and carbothermic processes

Pure iron.

Sterling silver, an alloy.



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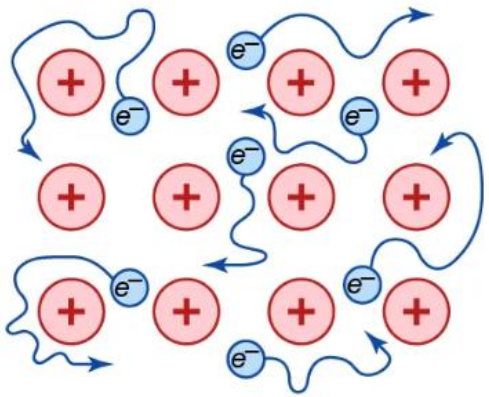
Bonding situation

Electron-sea model
Positively charged atomic bodies surrounded by freely mobile negatively charged valence electrons.



Charles E. Mortimer, Ulrich Müller, Chemie – das Basiswissen der Chemie, Thieme Verlag
Metallic bond | Properties, Examples, & Explanation | Britannica (17th February, 2025)
Valence band - Energy Education (17th February, 2025)

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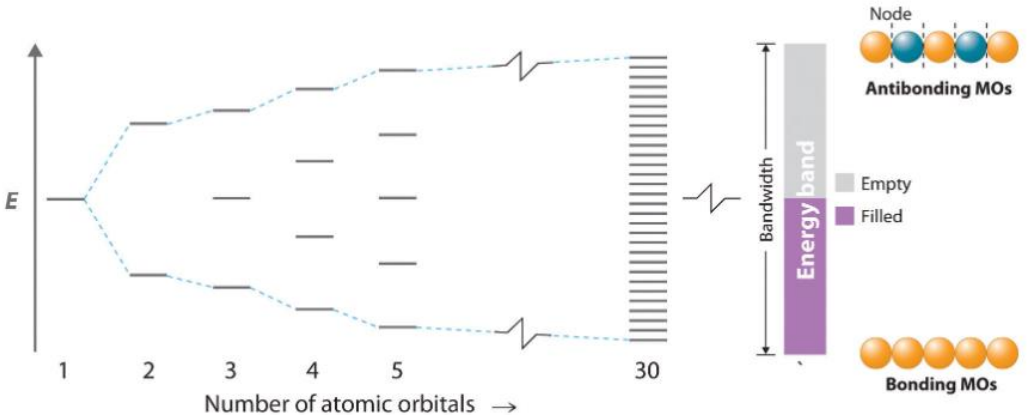
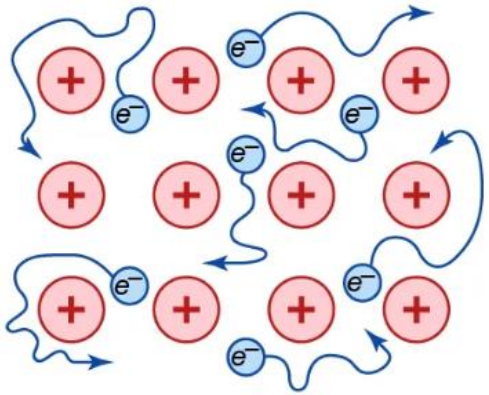
Band theory
Set of molecular orbitals is generated that extends throughout the solid: formation of bands with delocalized electrons.





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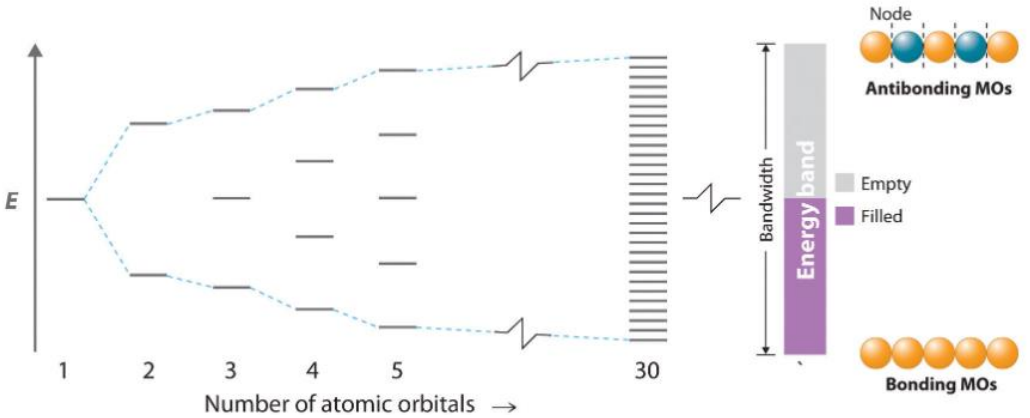

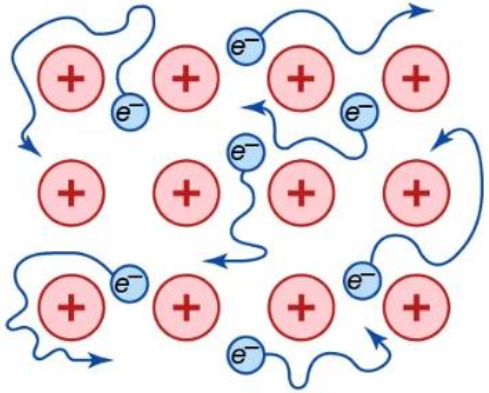

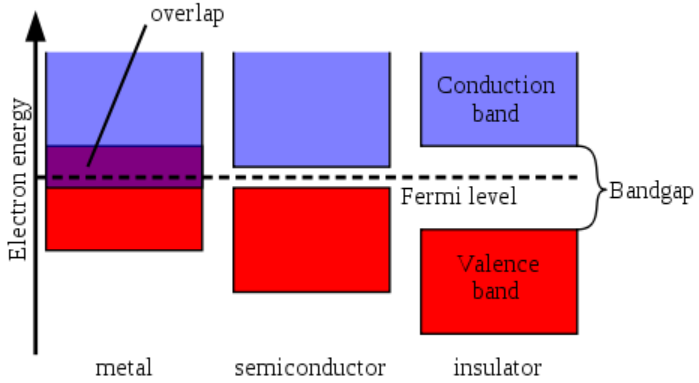

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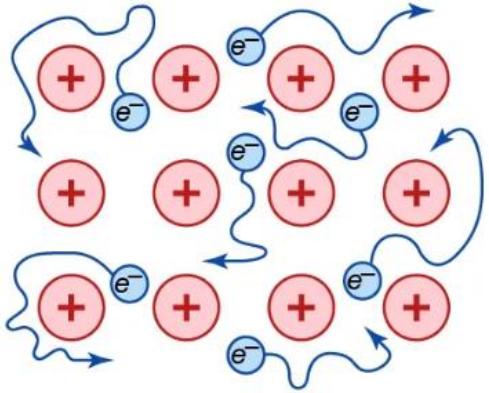
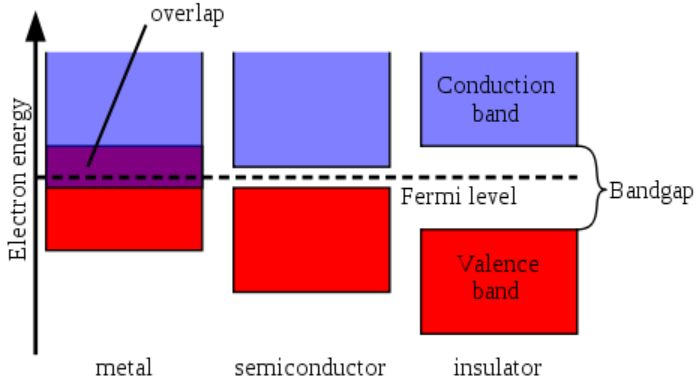
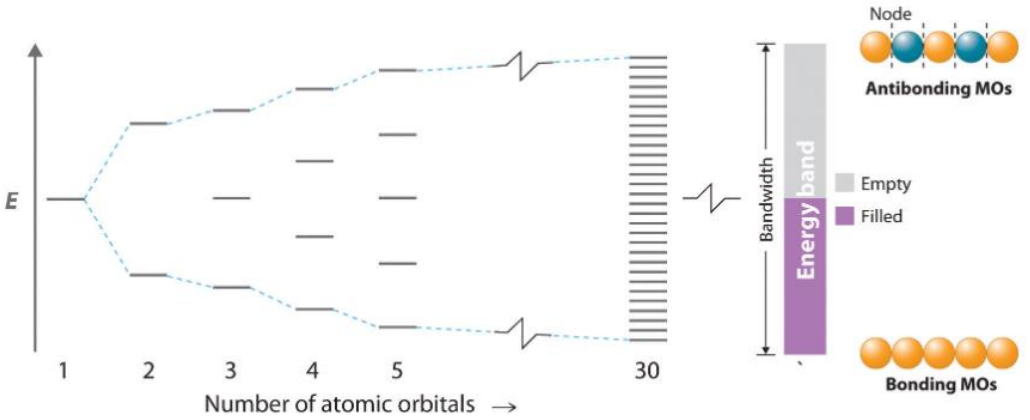


Band theory
Set of molecular orbitals is generated that extends throughout the solid: formation of bands with delocalized electrons.





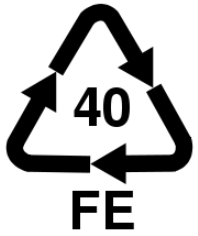
Resulting properties
- Lustrous
- Malleable
- Ductile
- Good conductors of electricity and heat

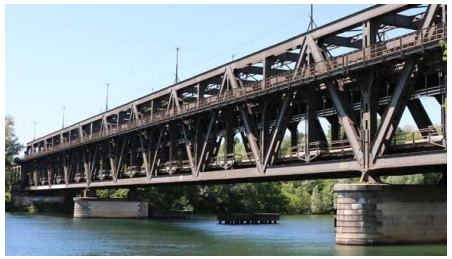
Charles E. Mortimer, Ulrich Müller, Chemie – das Basiswissen der Chemie, Thieme Verlag
Metallic bond | Properties, Examples, & Explanation | Britannica (17th February, 2025)
Valence band - Energy Education (17th February, 2025)

Technical applications

Pure metals (*e.g.*, copper) used for wires because of their high electric conductivity.
In further applications, metals are applied as alloys or intermetallic phases.

Steel, an iron alloy.





Indium and gallium.

Tungsten wire.

Aluminum.

Stahlbrücke von Sesto Calende am Lago Maggiore (4th March, 2023)
Stahlrohr verzinkt 42,4 mm | Rohr-verbinder.de (4th March, 2023)
Physik-Nobelpreis: Erfindung der blauen LED führte zu 17,7-Milliarden-Dollar-Markt - LED/Lighting - Elektroniknet (4th March, 2023)
Iron | 7439-89-6 (chemicalbook.com) (4th March, 2023)
Warum Flugzeuge weiß sind - [GEO] (4th March, 2023)

Alloys – better together

Combination of chemical elements, possessing the characteristic properties of a metal. The production of alloys is of great importance, as it is one of the main processes used to modify the properties of pure metallic elements.

Alloy – Wikipedia (17th February, 2025)
Brown, LeMay et al., Chemie – Studieren kompakt, 14th edition, Pearson Studium, **2018**.
Infographic: 20 Common Metal Alloys and What They're Made Of (17th February, 2025)

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- Substitutional solid solution alloy
- Interstitial solid solution alloy
- Heterogeneous alloys
- Intermetallic compounds

Homogeneous mixtures

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Homogeneous mixtures, components are regularly and randomly distributed
→ Solid solutions

If r_A(metal A) and r_A(metal b) are within 15% deviation

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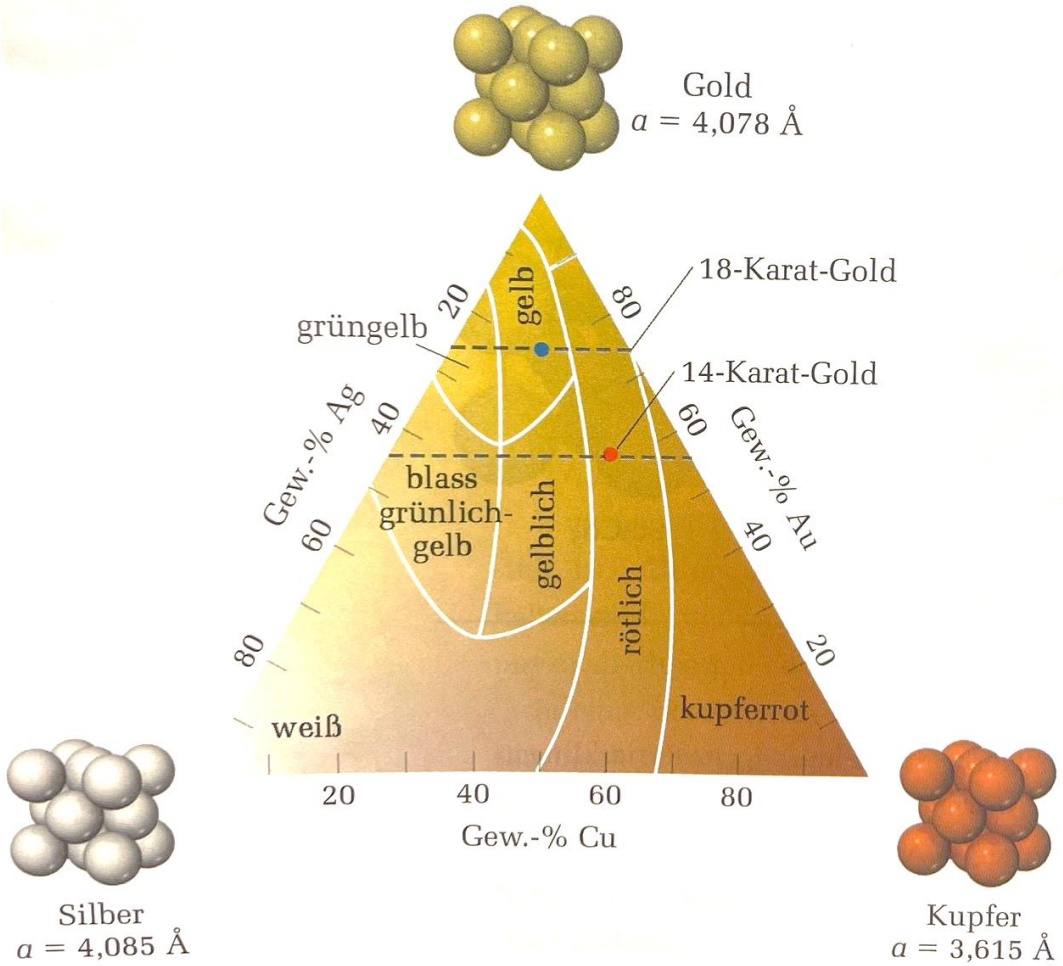

Pure gold too soft – better as alloy!

- Pure gold: 24 Karat
- Ag, Cu and Au: fcc structure and almost same radii
- Same amount Ag and Cu: 18 Karat gold
- Copper-rich alloy: 14 Karat (roségold)
- Silver-rich alloy: white-gold (Karat depending on amount of Ag)

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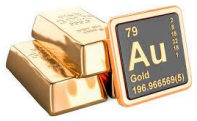

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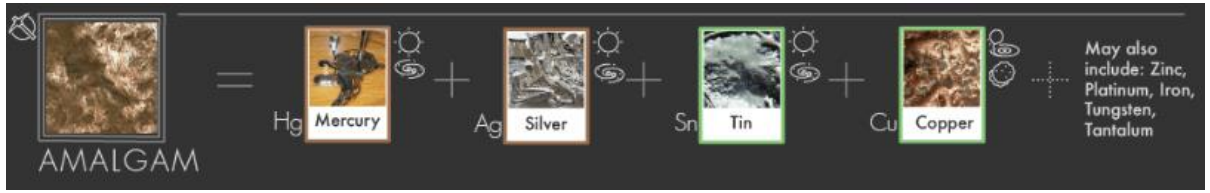

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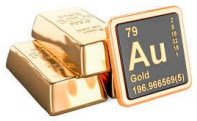

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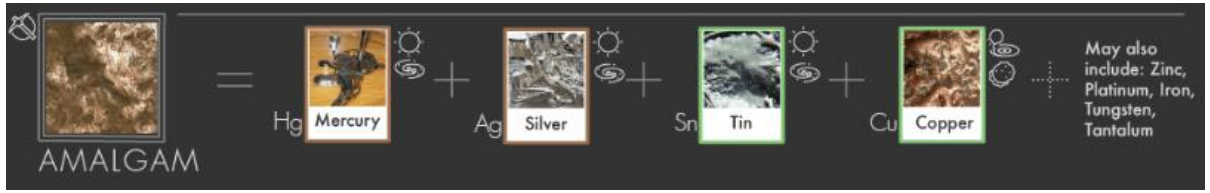
Steel



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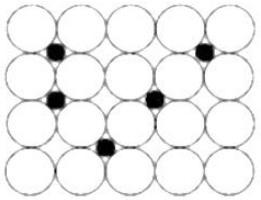

[Werkzeugstahl & Edelstahl bei Stauber GmbH im Online Shop - Stauber Stahl Online-Shop!](#) (17th February, 2025)
Brown, LeMay et al., Chemie – Studieren kompakt, 14th edition, Pearson Studium, **2018**.

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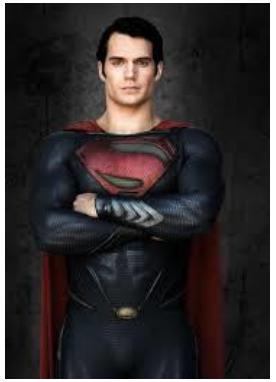

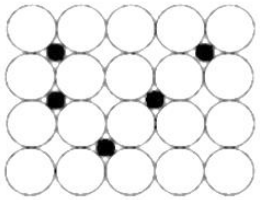

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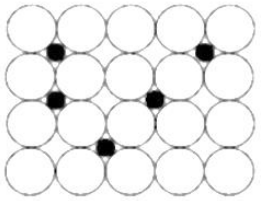

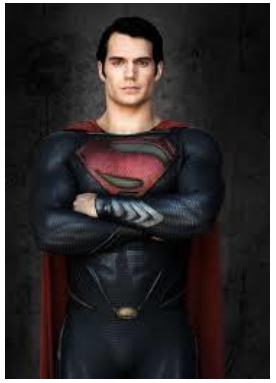

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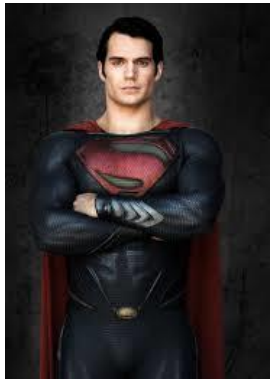

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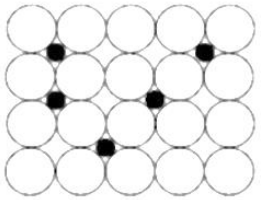

aluminum	Increases desoxygenation and ferrit stabilization
boron	Increases yield strength, strength, brittleness and heat resistance
chromium	Increases cooling rate, wear resistance, heat resistance, tensile strength, hardness
cobalt	Increases strength, heat resistance
molybdenum	Increases hardenability, tensile strength, weldability, ductility, heat resistance
nickel	Increases tensile strength, hardness, strength, yield strength, ferrite stabilization

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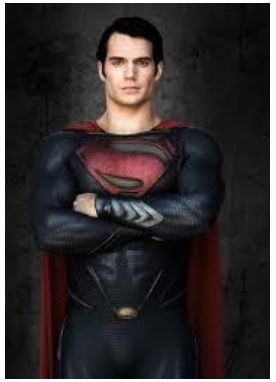

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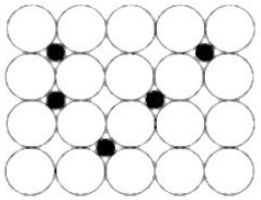

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White Board

Intermetallic compounds

Intermetallic compounds are solid phases with ≥ 2 (semi-) metallic elements possessing an ordered structure with a well-defined stoichiometry.

→ Structure results in higher strength and higher melting points compared to single components → very interesting for high temperature applications!

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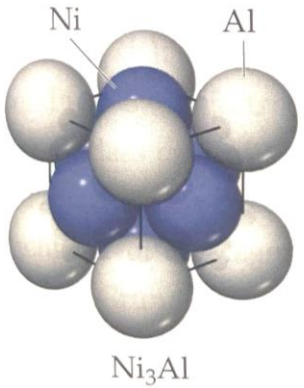

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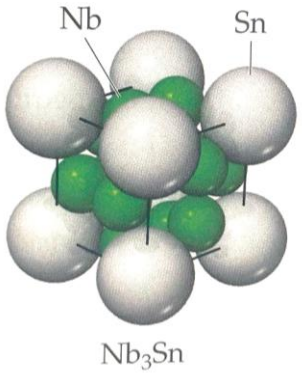
Strength at high temperatures and low density
Jet engines



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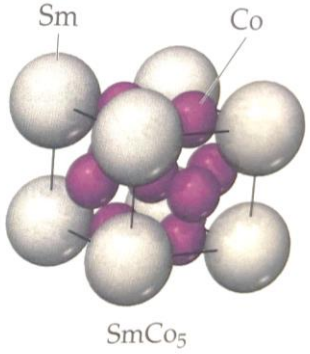
Superconductor at < 18 K
MRI and NMR



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Permanent magnet in light
Headsets or loudspeakers

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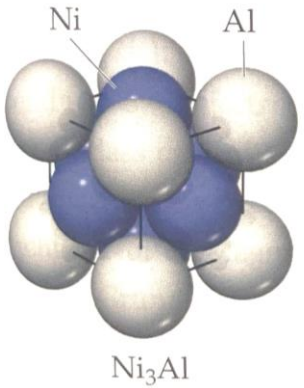
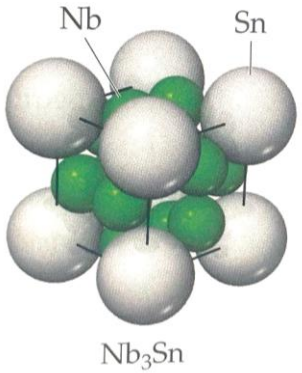


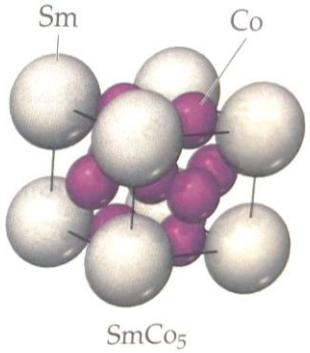
Ni_3Al

→ Strength at high temperatures and low density **Jet engines**



Nb_3Sn

→ Superconductor at < 18 K **MRI and NMR**



$SmCo_5$

→ Permanent magnet in light **Headsets or loudspeakers**

What´s your wish?

Brown, LeMay et al., Chemie – Studieren kompakt, 14th edition, Pearson Studium, **2018**.

Pyrochlore magnets – no thermal expansion

Eiffel tower: 15 cm higher in summer than in winter!

Local chemical heterogeneity enabled superior zero thermal expansion in nonstoichiometric pyrochlore magnets | National Science Review | Oxford Academic (17th February, 2025)
Ein Metall ohne Wärmeausdehnung - Legierung aus vier Metallen bleibt selbst bei 400 Grad Temperaturunterschied fast unverändert - scinexx.de (18th. February, 2025)

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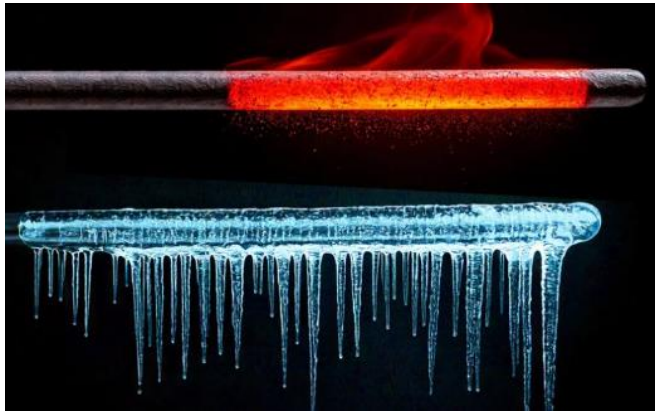

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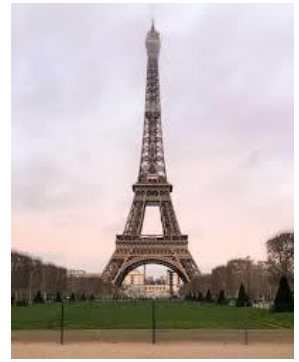

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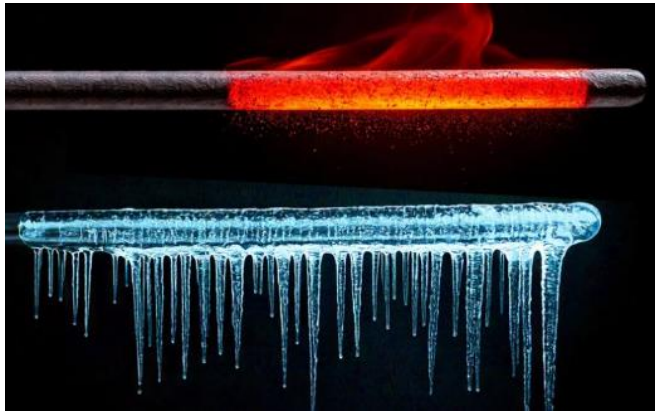

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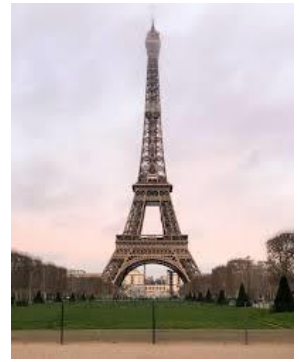

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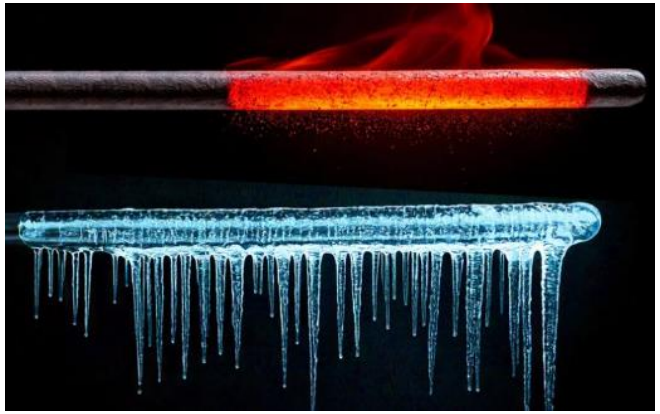

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Reason: additional magnetic effect
Thermal expansion vs. decreasing magnetic repulsion

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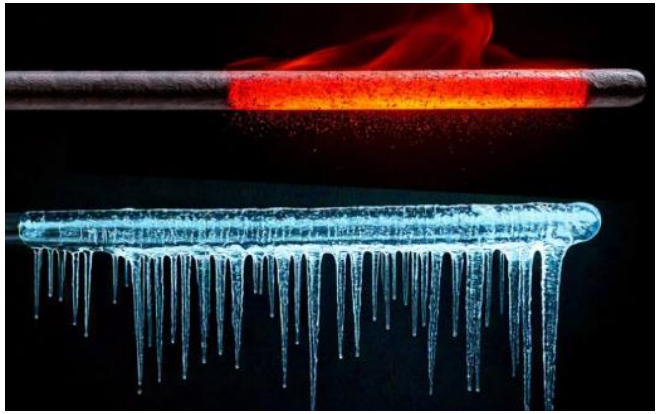

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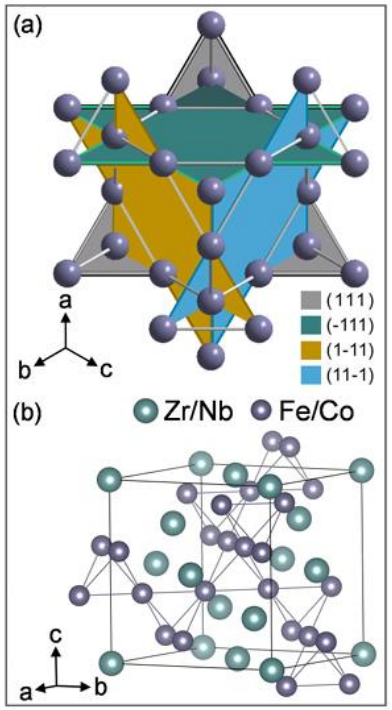

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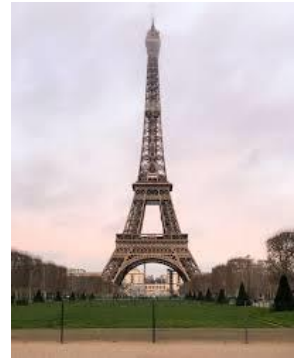
Reason for almost ZTE
- Heterogeneous lattice structure, not ideally cubic
- Parts within structure react thermally and magnetically differently

Thermal treatment: partial contraction and repulsion with net-balance zero



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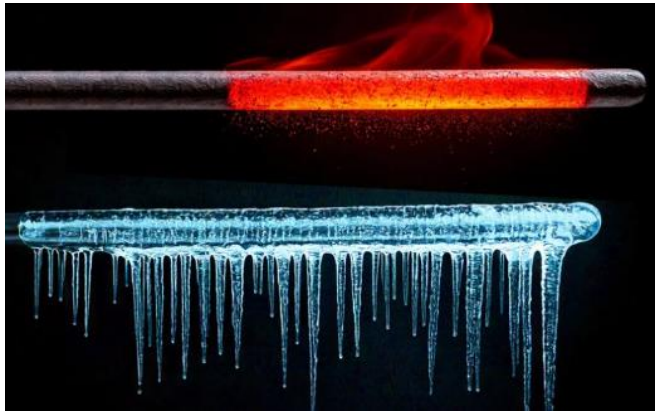

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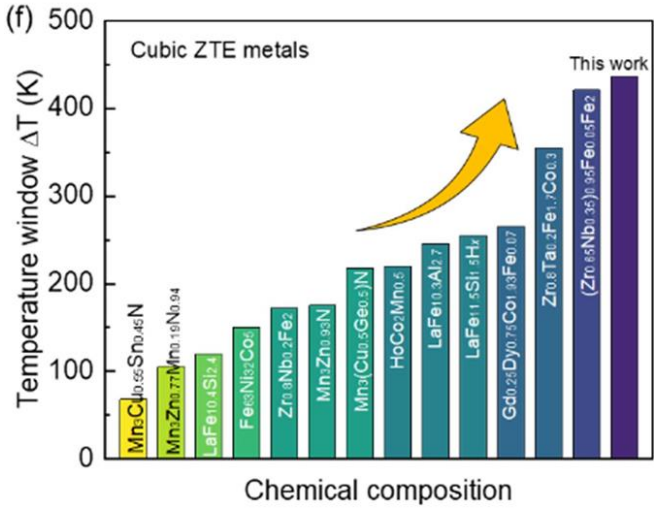

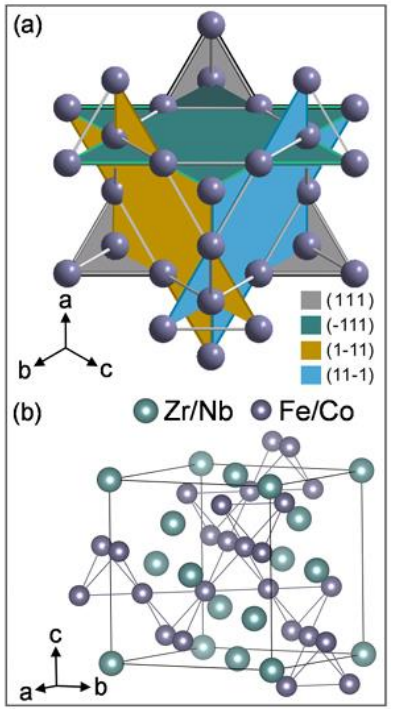

History
1896 alloy *Invar* (65% Fe, 35% Ni) shows small TE
Reason: additional magnetic effect
Thermal expansion vs. decreasing magnetic repulsion

Reason for almost ZTE
- Heterogeneous lattice structure, not ideally cubic
- Parts within structure react thermally and magnetically differently

Thermal treatment: partial contraction and repulsion with net-balance zero

Eiffel tower: 15 cm higher in summer than in winter!

Note
Pyrochlor: $Ca_2Nb_2O_7$ with ideal cubic structure, natural mineral

Local chemical heterogeneity enabled superior zero thermal expansion in nonstoichiometric pyrochlore magnets | National Science Review | Oxford Academic (17th February, 2025)
Ein Metall ohne Wärmeausdehnung - Legierung aus vier Metallen bleibt selbst bei 400 Grad Temperaturunterschied fast unverändert - scinexx.de (18th. February, 2025)

Excursion: Amorphous metals - Metallic glasses

Usually alloy containing atoms with significant different sizes (>12%) – low free volume!
Higher viscosity in molten state, which prevents atoms to form an ordered lattice.
In contrast to “normal” metals, they are non-crystalline and have a glass-like structure.
They are electrically conductive and lustrous!

Amorphous metal – Wikipedia (18th February, 2025)
Liquid metal golf clubs - bulk metallic glass golf clubs – BMG (19th February, 2025)
Metallic Glasses | RHP (19th February, 2025)

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Formation
Extremely rapid cooling
Mechanical alloying
Ion irradiation
…

Properties
Low shrinkage when cooling
Wear resistance
Less corrosion due to missing grain boundaries
Great hardness
Best magnetic soft materials, …

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Scalpels, maybe implants

Difficult shapes

Mobile phones, USB sticks

Solar wind collectors (Genesis probe)

Armor-piercing kinetic energy penetrators, aviation

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LIQUID METAL GOLF CLUBS

Unusual springiness and a soft feel, how about liquid metal golf clubs?

25/02/2020

One of the first commercial applications of the **Liquid metal** was in the golf field, in order to produce **golf clubs** heads.
Bulk Metallic Glass has several outstanding attributes, such as: high strength-to-weight ratios, high hardness, good forming and shaping qualities, unusual magnetism and, above all, BMG is extremely elastic.

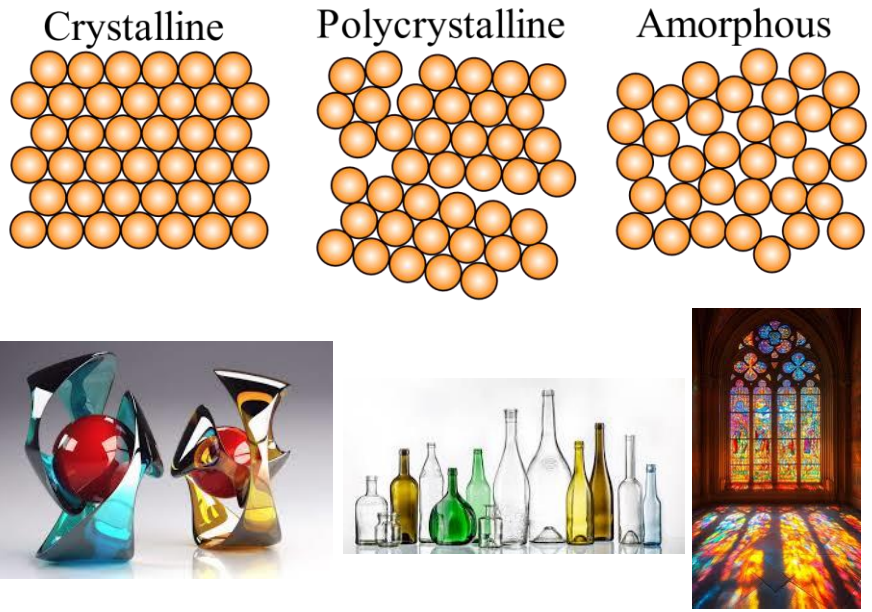
The incomparable mechanical properties of **BMG** can increase the coefficient of restitution at the impact between a golf club and a ball. And, moreover, in addition to all the other characteristics we've already mentioned, liquid metal provides a softer, more solid feel for better control when a golfer strikes the ball.

Amorphous metal – Wikipedia (18th February, 2025)
Liquid metal golf clubs - bulk metallic glass golf clubs – BMG (19th February, 2025)
Metallic Glasses | RHP (19th February, 2025)

Glasses

Standard definition glass

- A glass is a non-crystalline solid formed by rapid melt quenching
- It is an amorphous solid and can be understood as a supercooled liquid
- Glasses are arbitrarily shapeable



Why is Glass Transparent? | MATSE 81: Materials In Today's World (19th February, 2024)

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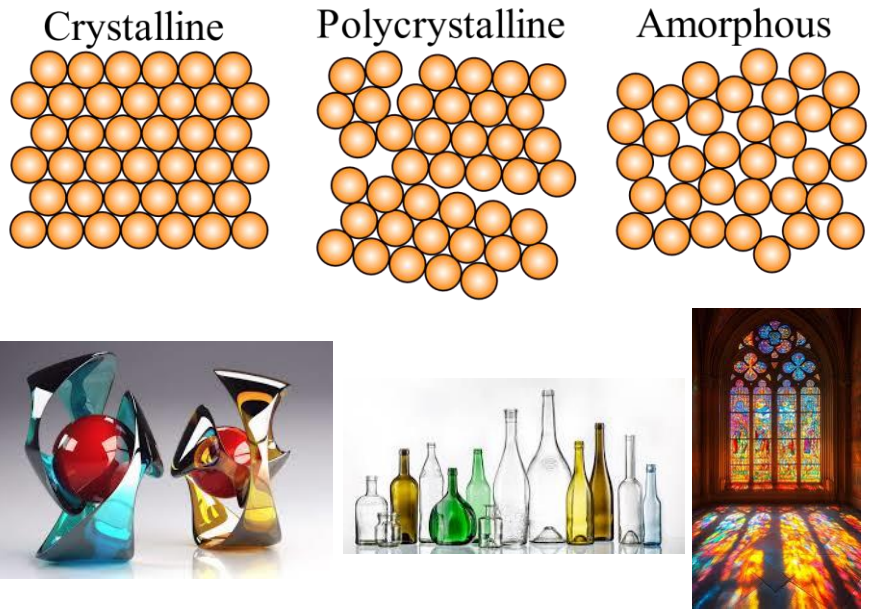
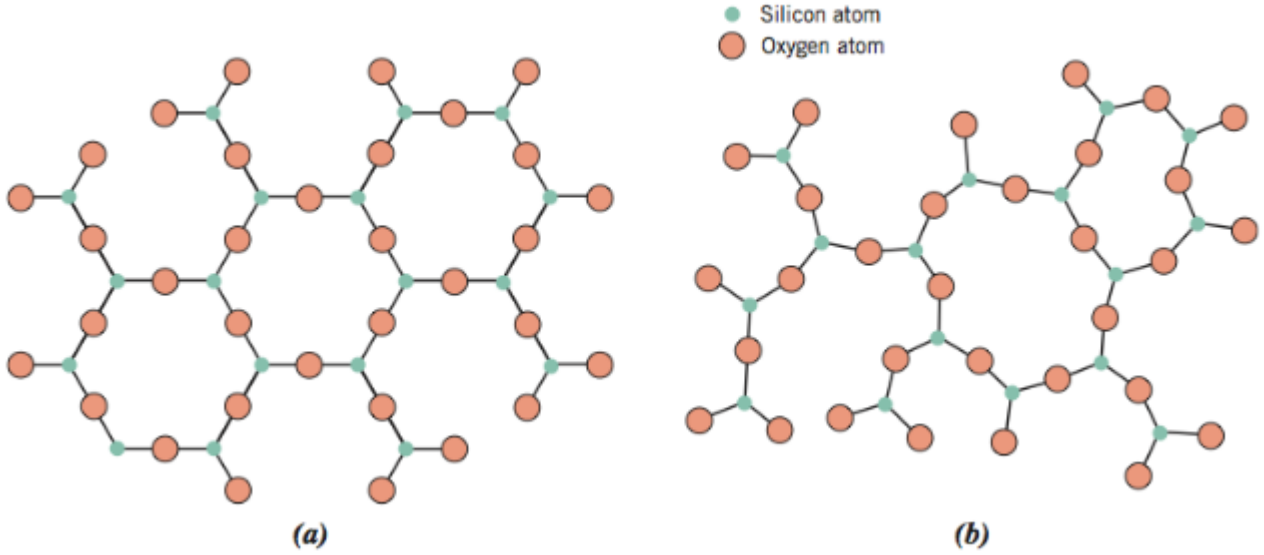


- SiO_2 can also occur as a non-crystalline (amorphous) solid (silica gel or quartz glass)
- Other oxides such as B_2O_3 or GeO_2 can also form glasses
- These materials are called network formers



Crystalline SiO_2

Amorphous SiO_2

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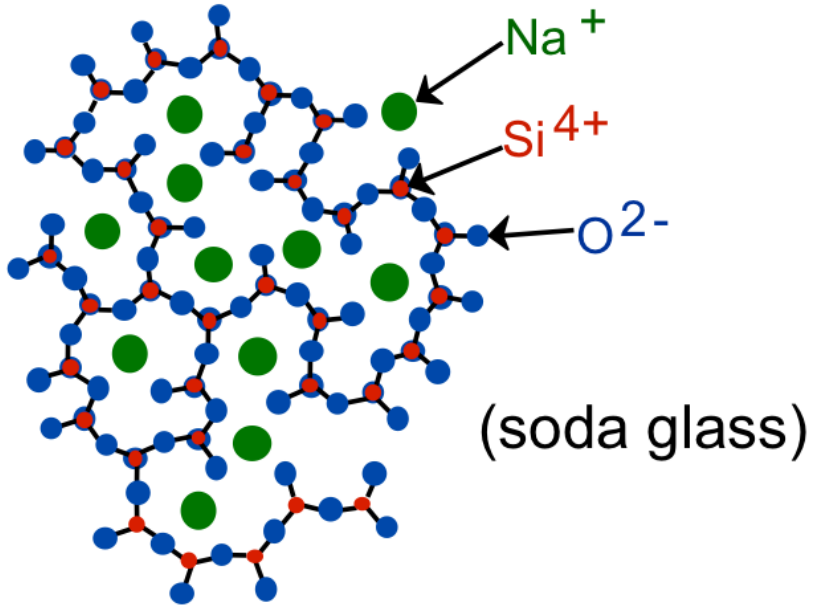
Glasses – more than SiO_2

- The most common glasses are silicate glasses, to which additional oxides such as CaO or Na_2O are added
- The cations are incorporated into the tetrahedral network, thereby altering its properties
  Therefore, these cations are called network modifiers
- Other oxides such as TiO_2 or Al_2O_3 can replace Si in the network and stabilize it (stabilizers)
- Physically, the addition of network modifiers and stabilizers lowers the melting temperature and the viscosity of the glass



Schematic representation of the ion positions within a sodium-silicate glass

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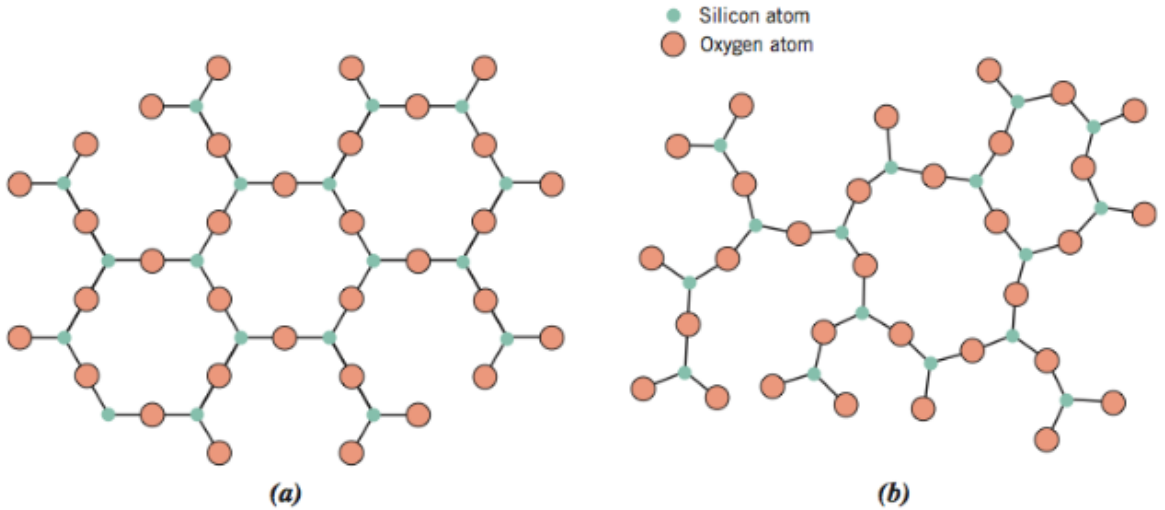
Bonding situation and properties

In its amorphous structure, the band gap of SiO_2 is broken in a way that no electron transition can occur. As a result, glasses are optically transparent.
Further, glass manufacturing is comparably easy.



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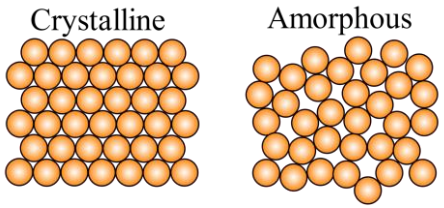
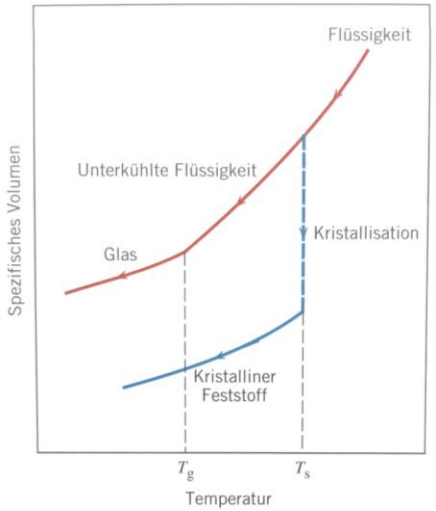
- Glas: V ↓ continuously at T_S





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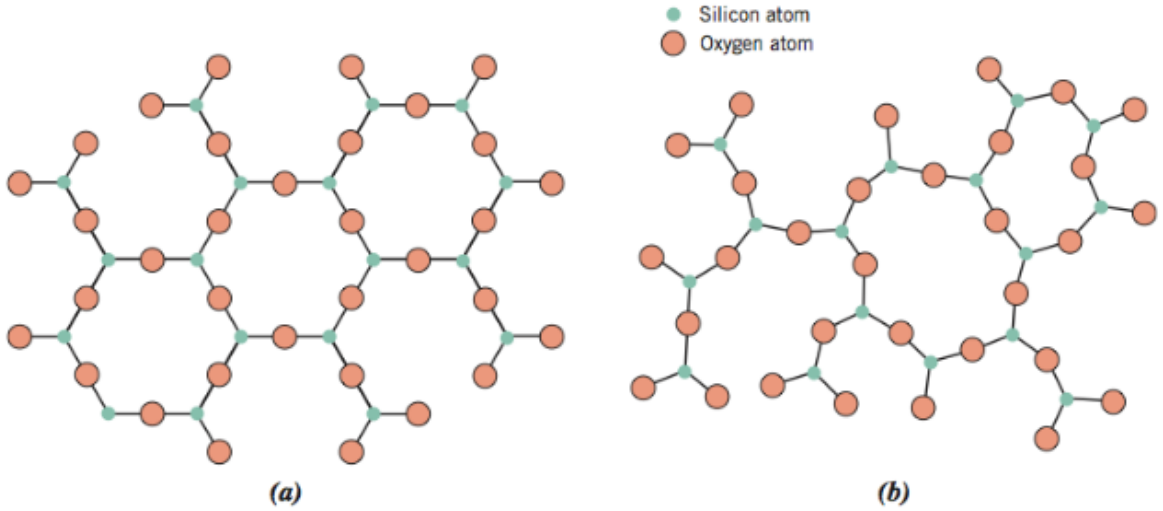

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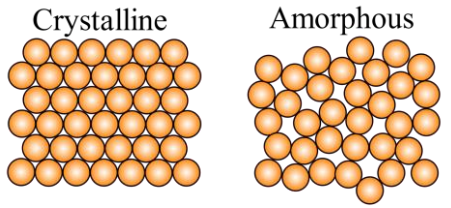

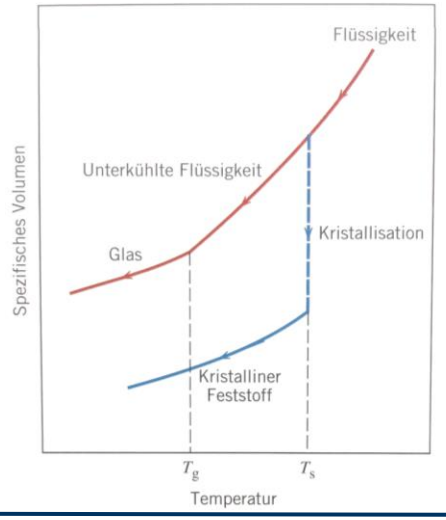

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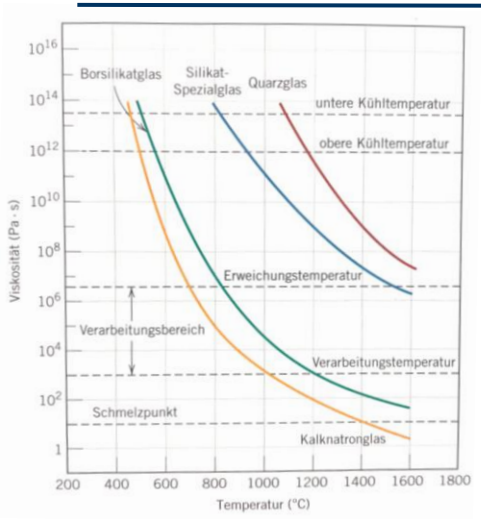

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- $\mathbf{T_{proc}}$ viscosity 10^3 Pa/s: glass can be formed
- $\mathbf{T_{soft}}$ viscosity ~10^6 Pa/s: glass is not deformed
- $\mathbf{T_{up\text{-}cool}}$ viscosity 10^{12} Pa/s: present tensions can be reduced
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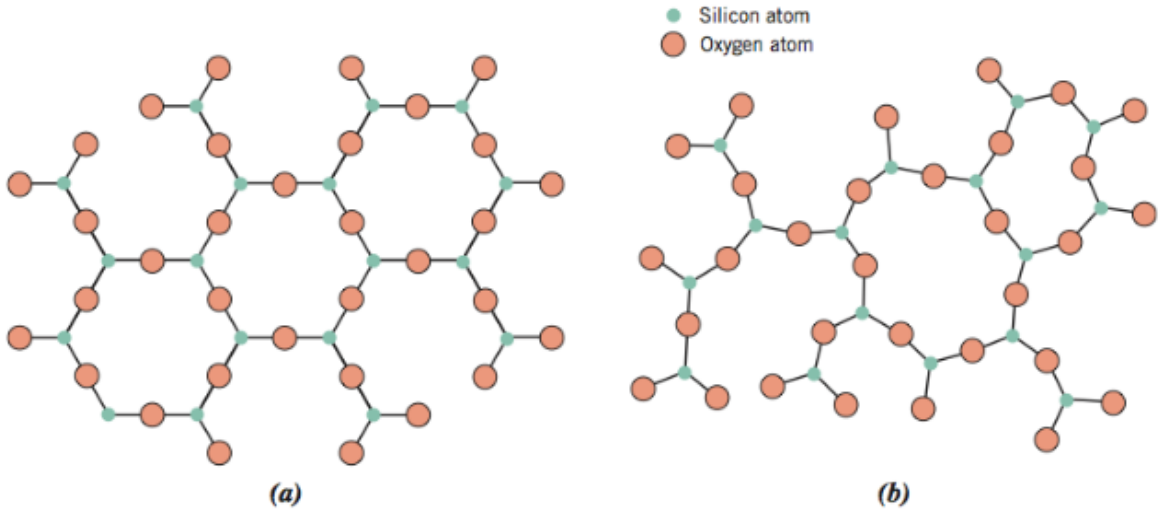

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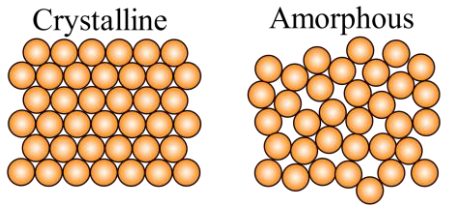

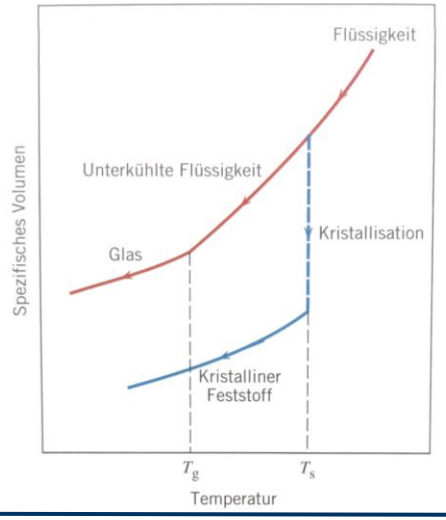

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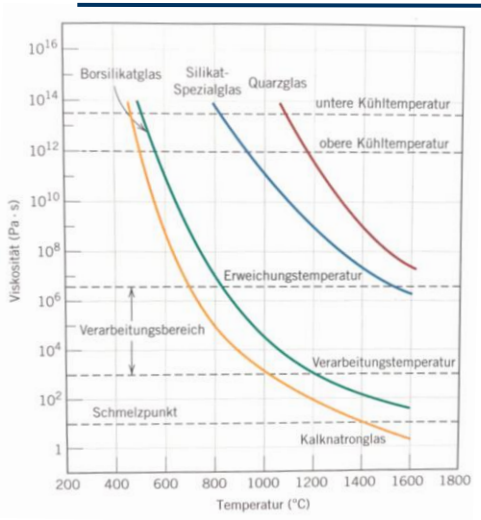

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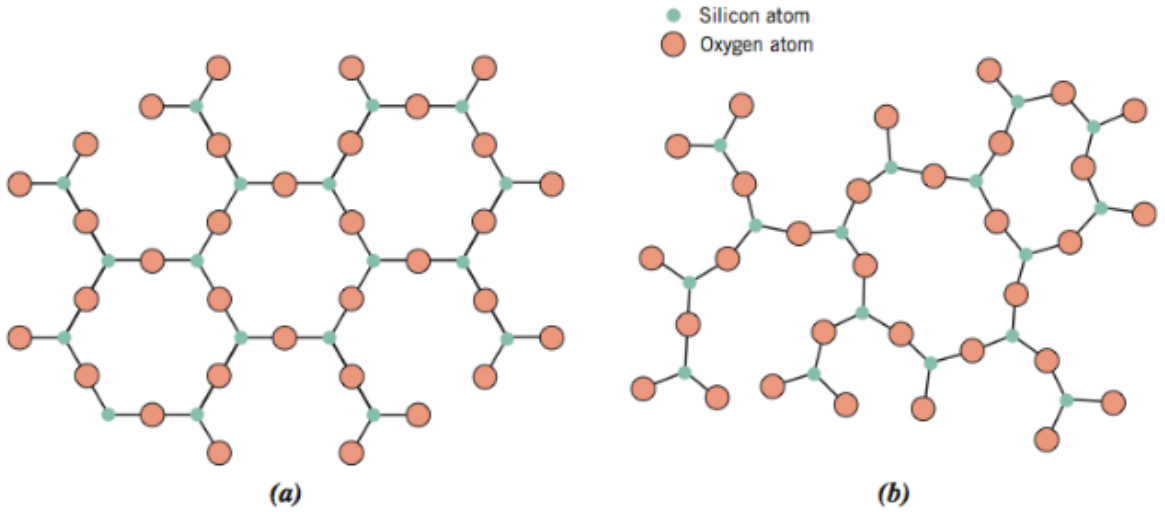

More details in glass chemistry lecture – Gunter Heymann!

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Excursion: Organic glasses

Vesuvius eruption 79 BC
One special victim: Parts of brain and spinal cord remained intact as organic glass.

Herculaneum: Rätsel des gläsernen Gehirns gelöst

Ursache für das einzigartige, verglaste Hirngewebe eines Vulkanopfers identifiziert

28. Februar 2025, Lesezeit: 3 Min.

Teile des Gehirns eines Vulkanopfers von Herculaneum sind bei der Katastrophe verglast – aber wie? © Pier Paolo Petrone

Unique formation of organic glass from a human brain in the Vesuvius eruption of 79 CE | Scientific Reports (3rd March, 2025)
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"The cloud must have dissipated just as quickly so that its remnants could cool down rapidly enough to trigger the vitrification process."

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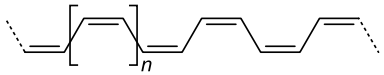
A functional material could be defined as being prepared from a “target-motivated” approach

Ceramics

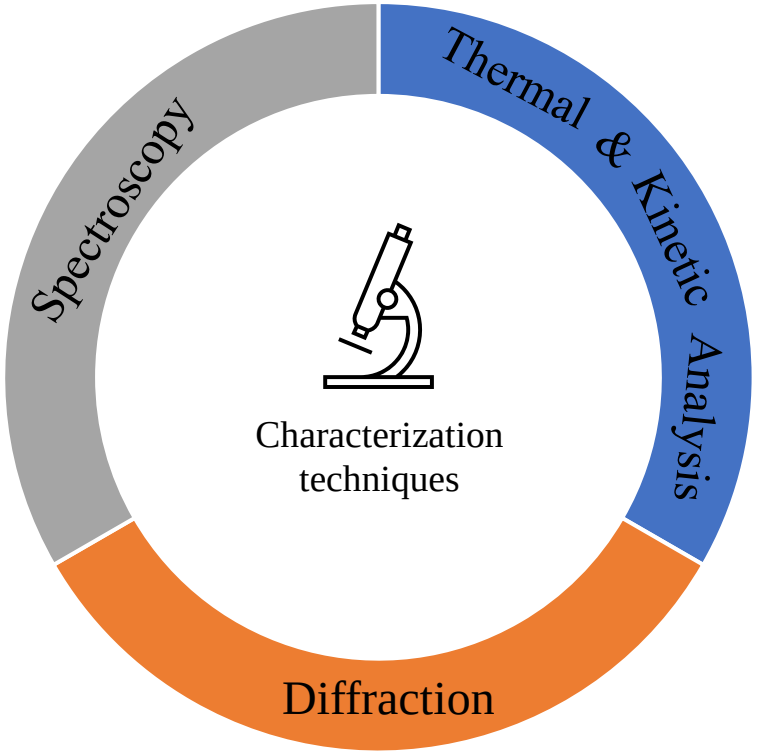
Polymers



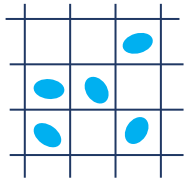
Metals

Composites

Glasses



Innovative Materials



Biomaterials

Nanomaterials

Semiconductors

…

Porous materials

[Functional Material - an overview | ScienceDirect Topics](#) (3rd March, 2023)

universität innsbruck

Questions?