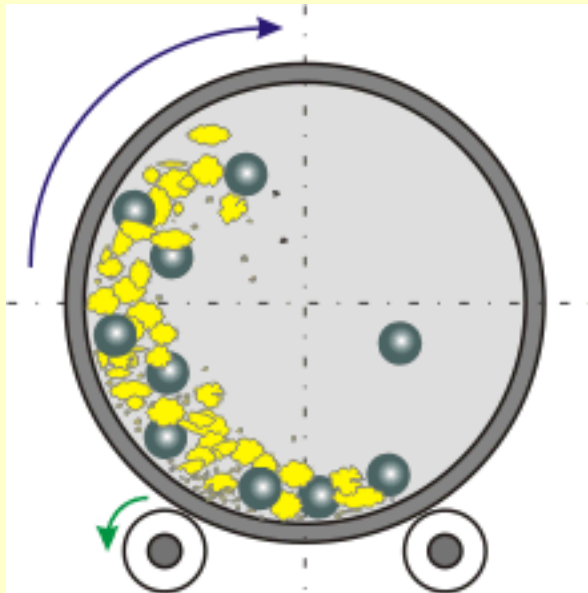


Mechanochemical Synthesis

Reaction Setup



Powder mixing



High-energy ball-milling for several hours

Ball-to-powder ratio (20:1)

Vial (250 ml) and balls (d = 10-20 mm)

WC, stainless steel, zirconia

250 rotations per minute

Controlled atmosphere



Mechanochemical Synthesis

Particles repeatedly subjected to deformation, cold welding, and fracture, homogenization on an atomic scale

On impact, high energy concentrated in a small spot, stress 200 MPa, duration of microseconds

Fragmentation, atomically clean surface exposed

Balance between fragmentation and coalescence

Grain size ~10 nm

Amorphization, product nucleation and crystallization

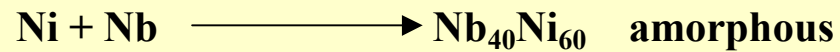
Mechanochemical Synthesis

→ Phase Transitions (to denser structures)

Oxide	Before	V, Å ³	After	V, Å ³
GeO ₂	quartz	40.3	rutile	27.6
TiO ₂	anatase	34.1	rutile	31.2
ZrO ₂	baddaleyite	35.2	fluorite	32.8

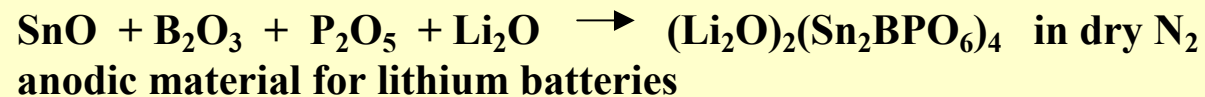
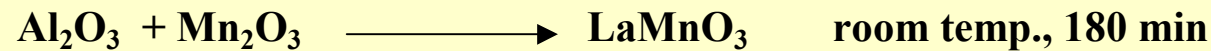
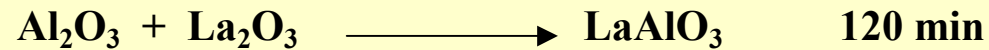
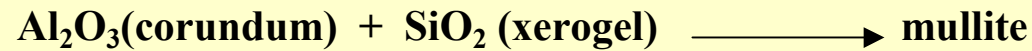
V = volume per formula unit

→ Mechanical Alloying

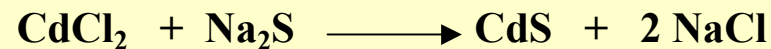
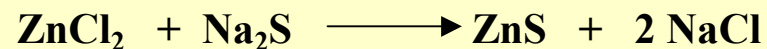
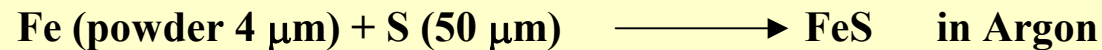


Mechanochemical Synthesis

→ Preparation of mixed oxides

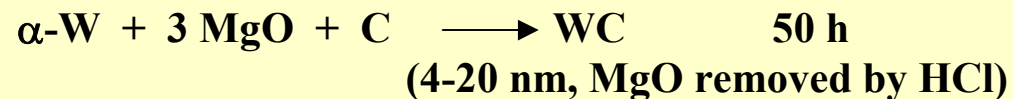
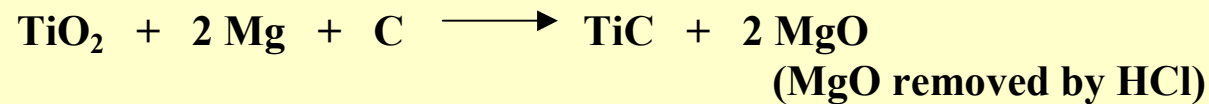
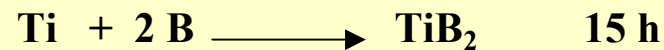
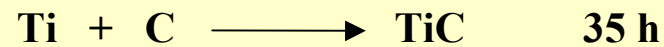
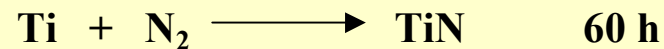
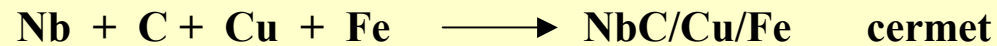
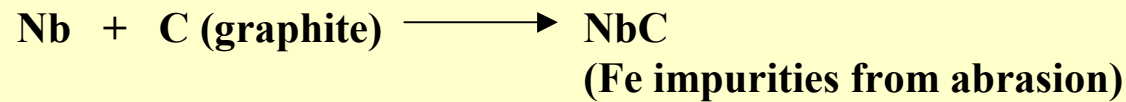


→ Preparation of chalcogenides



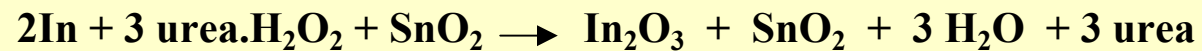
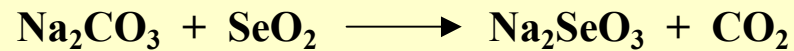
Mechanochemical Synthesis

→ Preparation of carbides, borides, nitrides, silicides

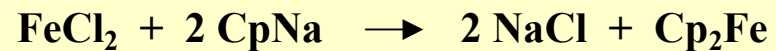


Mechanochemical Synthesis

→ Reactive milling



heating to 473 K for 4h to remove organics and calcination at 573-673 K in oxygen gives ITO

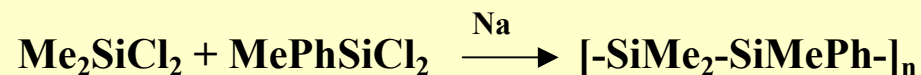
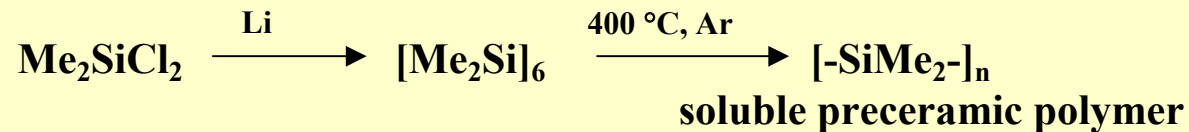


Polymer Pyrolysis

**Preparation of:
powders, monoliths, fibers, films, impregnation (PIP)**

Example: SiC fibers

☺ **polymer synthesis**

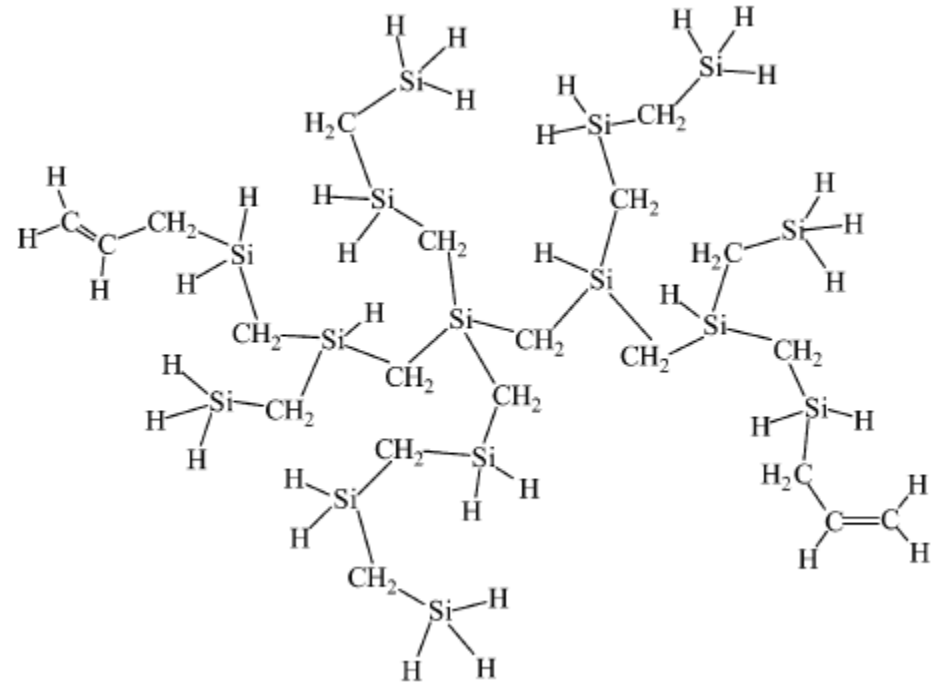
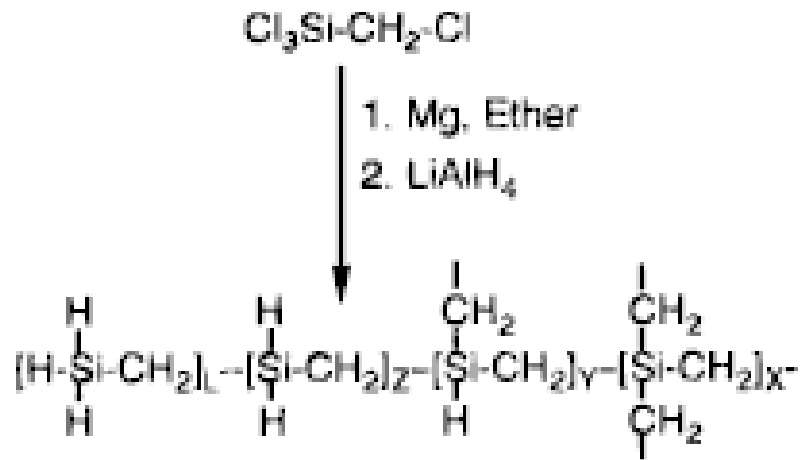
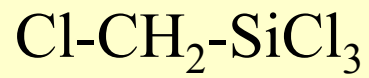


☺ **melt spinning or drawing from solution gives continuous polymer fiber**

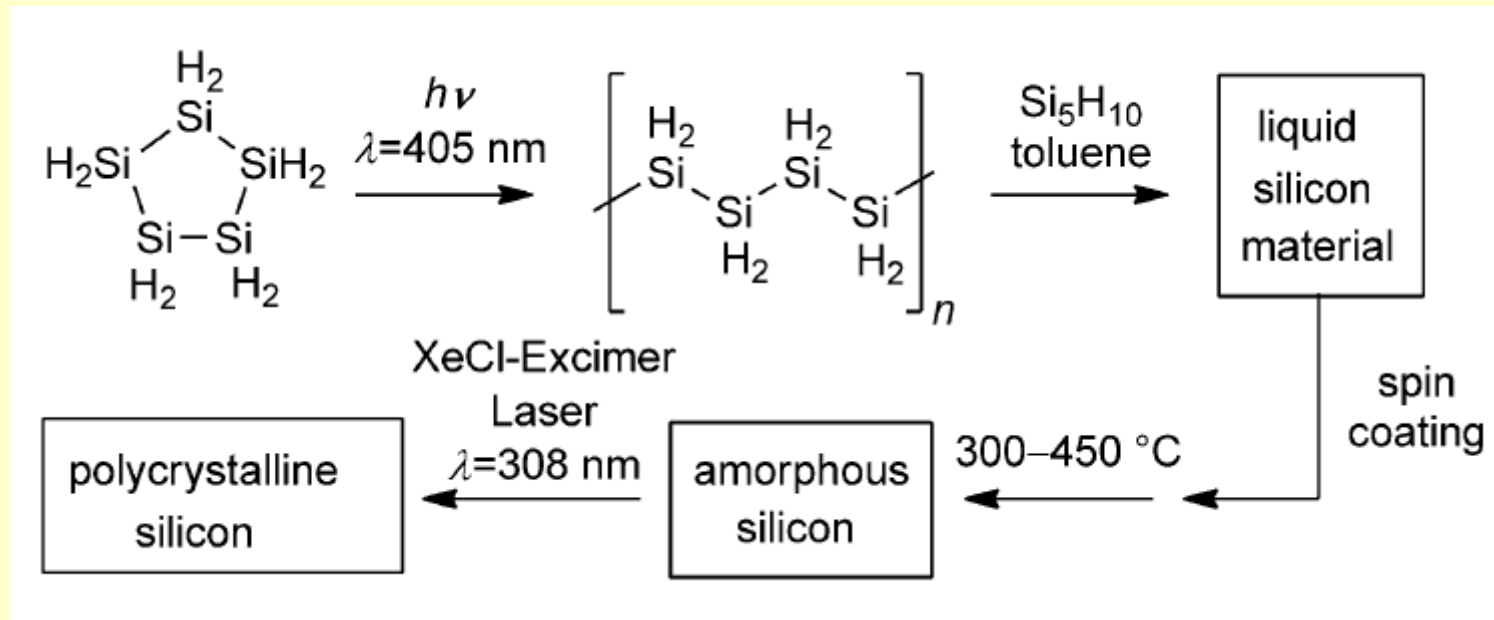
☺ **curing in O₂, heat to 400 - 500 °C, thermoset, crosslinking to prevent melting**

☺ **pyrolysis at 1000 - 1500 °C to polycrystalline β-SiC fiber**

Polymer Pyrolysis

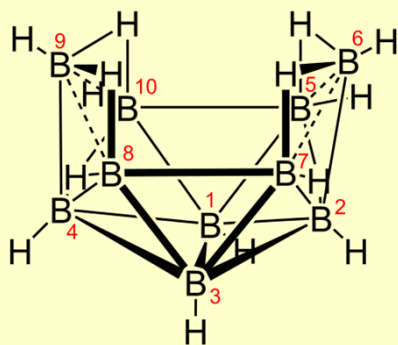


Polymer Pyrolysis

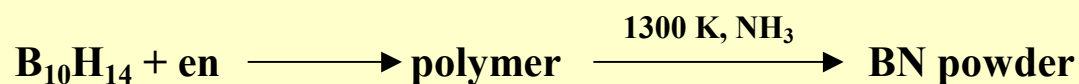


Nature **440**, 783-786 (6 April 2006) doi:10.1038/nature04613

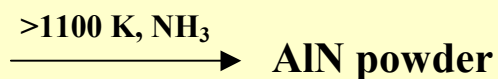
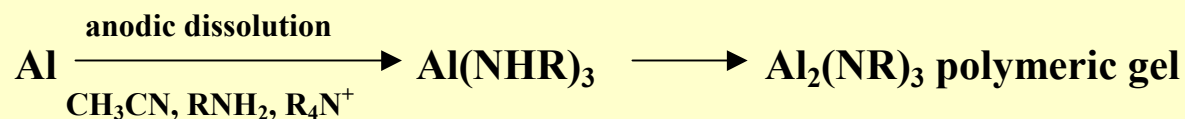
Polymer Pyrolysis



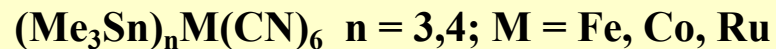
BN



AlN



Thermolysis of Organometallic Coordination Polymers



thermolysis in Ar or H₂ gives intermetallics FeSn₂, CoSn₂, Ru₃Sn₇

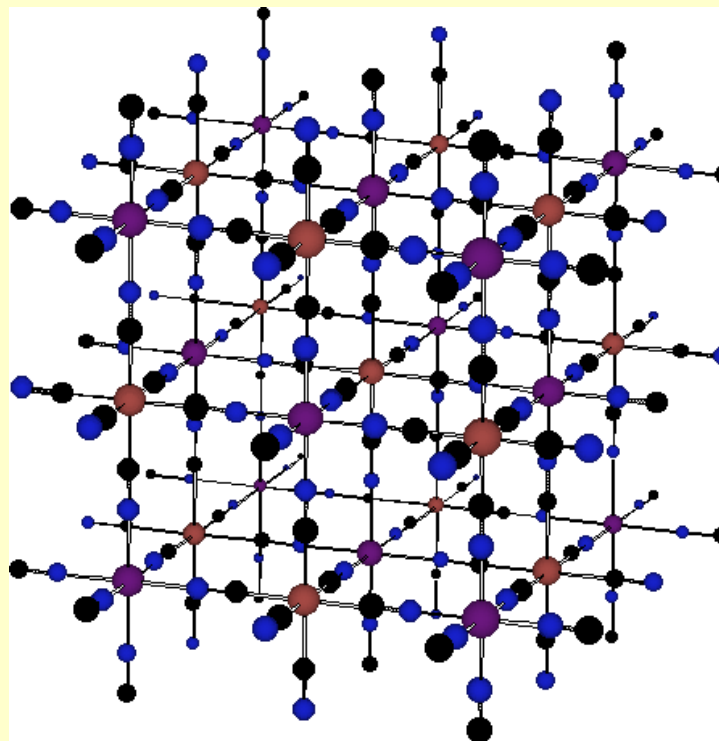
thermolysis in air gives oxides Fe₂O₃/SnO₂, Co₂SnO₄, RuO₂

Thermolysis of Organometallic Coordination Polymers

$(\text{Me}_3\text{Sn})_n\text{M}(\text{CN})_6$ $n = 3,4$; $\text{M} = \text{Fe}, \text{Co}, \text{Ru}$

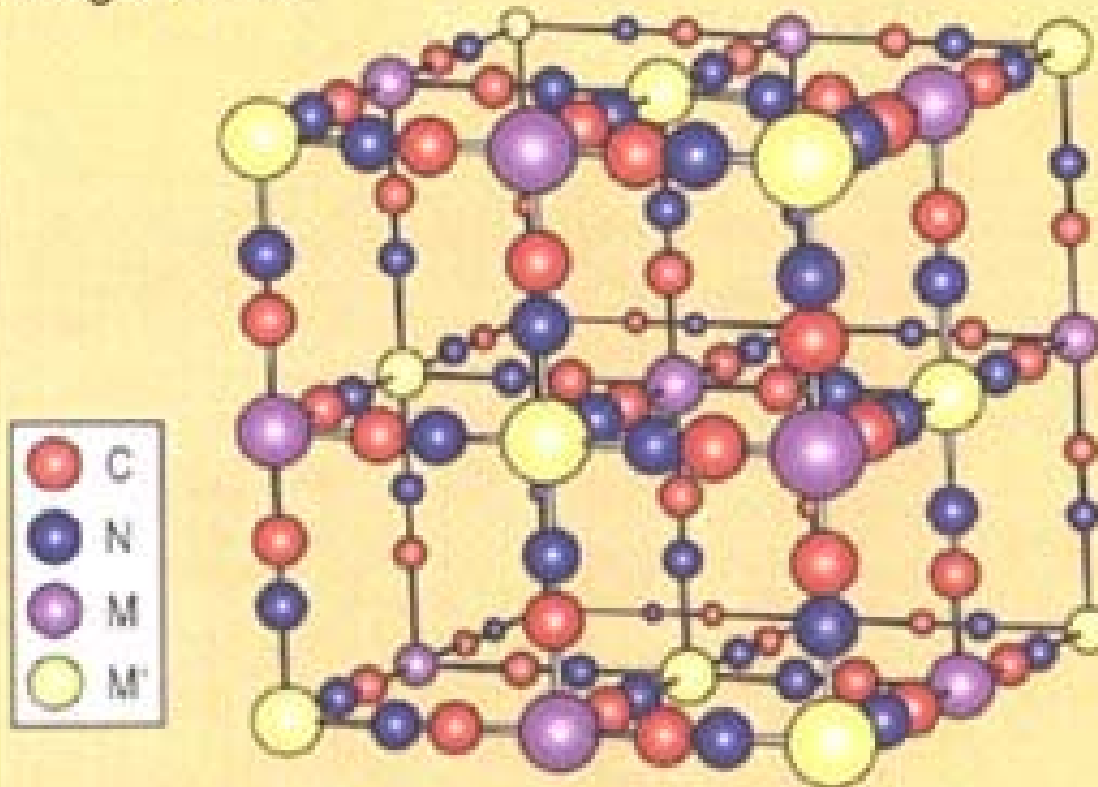
thermolysis in Ar or H_2 gives intermetallics
 $\text{FeSn}_2, \text{CoSn}_2, \text{Ru}_3\text{Sn}_7$

thermolysis in air gives oxides
 $\text{Fe}_2\text{O}_3/\text{SnO}_2, \text{Co}_2\text{SnO}_4, \text{RuO}_2$



Prussian Blue structure

An idealised structure of Prussian Blue with $M \leftarrow C=N \rightarrow M'$ linkages in 3-D



When $M = \text{Cr}$, $M' = \text{Ni}$ material is a ferromagnet, $T_c = 90\text{K}$
When $M = \text{V}$, $M' = \text{Mn}$ material is a ferrimagnet, $T_c = 125\text{K}$
When $M = \text{Cr}$, $M' = \text{V}$ material is a ferrimagnet, $T_c = 315\text{K}$

Microwave-Assisted Synthesis

Microwave radiation = electromagnetic radiation **Microwaves:**

$\lambda = 1 \text{ mm to } 1\text{m}$, $\nu = 0.3 \text{ to } 300 \text{ GHz}$

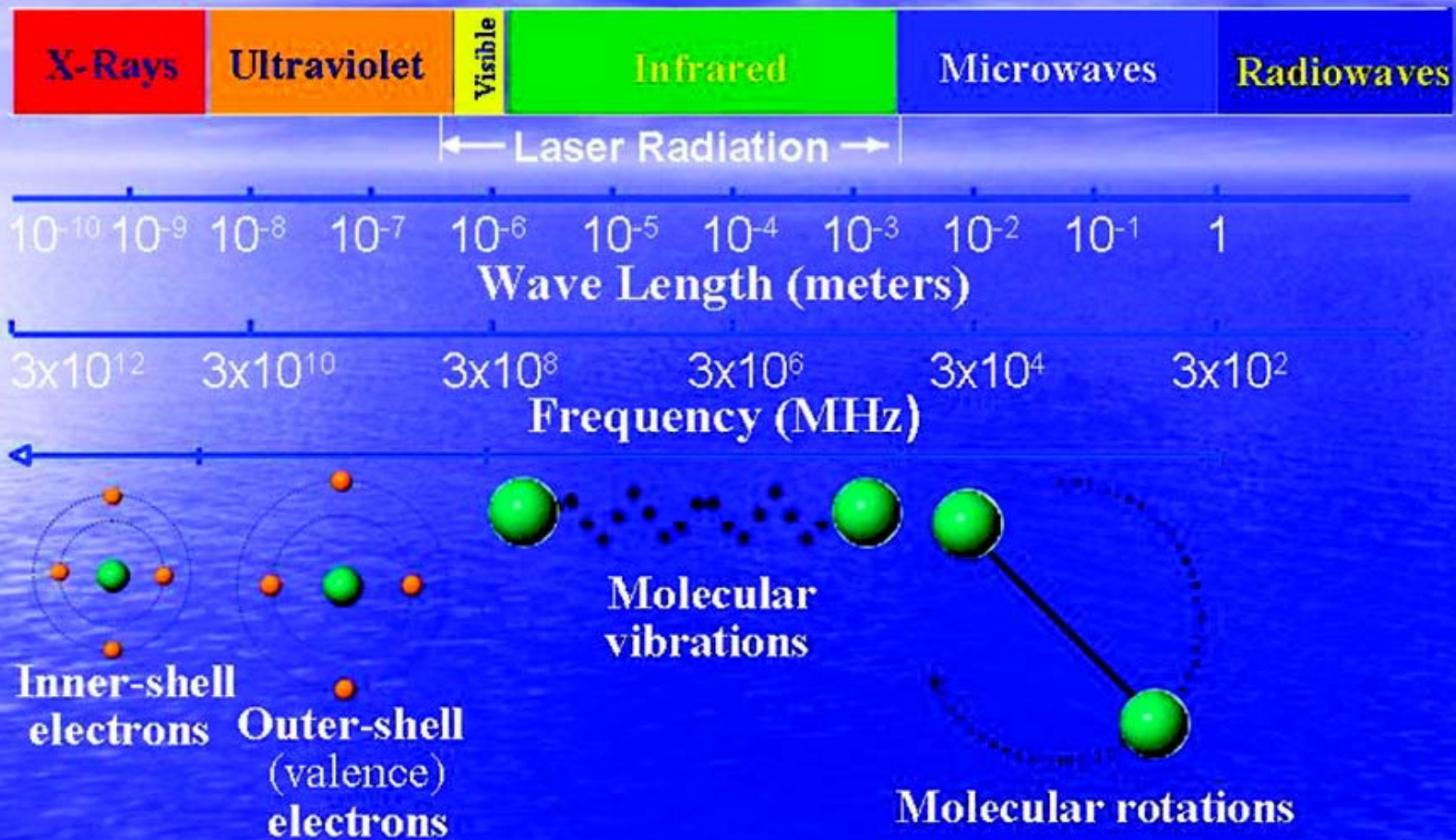
Microwave ovens 2.45 GHz, $\lambda = 12.24 \text{ cm}$

**power up to 1 kW, pulses, magnetron, microwaveguide,
microwave cavity**

**All kitchen microwave ovens and all microwave
reactors for chemical synthesis operate at a frequency of 2.45
GHz to avoid interference with telecommunication and cellular
phone frequencies.**



Microwaves in the Synthesis of Nanomaterials



Microwave-Assisted Synthesis

**The energy of the microwave photon in this frequency region is too low (10^{-5} eV) to break chemical bonds
lower than the energy of Brownian motion at 298 K**

Microwaves cannot induce chemical reactions

Microwave-enhanced chemistry

**the heating of materials by “microwave dielectric heating” effects =
the ability of a material (solvent or reagent) to absorb microwave
energy and convert it into heat**

Microwave-Assisted Synthesis

Dielectric heating

electric dipole reorientation in the applied alternating field

**the dipoles or ions aligning in the applied electric field
applied field oscillates, the dipole or ion field attempts to realign
itself with the alternating electric field
energy is lost in the form of heat through molecular friction and
dielectric loss**

**if the dipole does not have enough time to realign, or reorients too
quickly with the applied field, no heating occurs**

Microwave-Assisted Synthesis

Resistive heating

polarization current, a reorientation phase lag

Joule heating

ionic current, ionic conduction, ions drift in the applied field

Electronic transport

metal powders, semimetallic and semiconducting materials

Rotational excitation: weak bonds (interlayer bonds in graphite and other layer materials)

Eddy currents: metal powders, alternating magnetic fields

Microwave absorption = f (frequency, temperature)

Thermal runaway = increased dielectric loss at higher T

Dielectric Properties

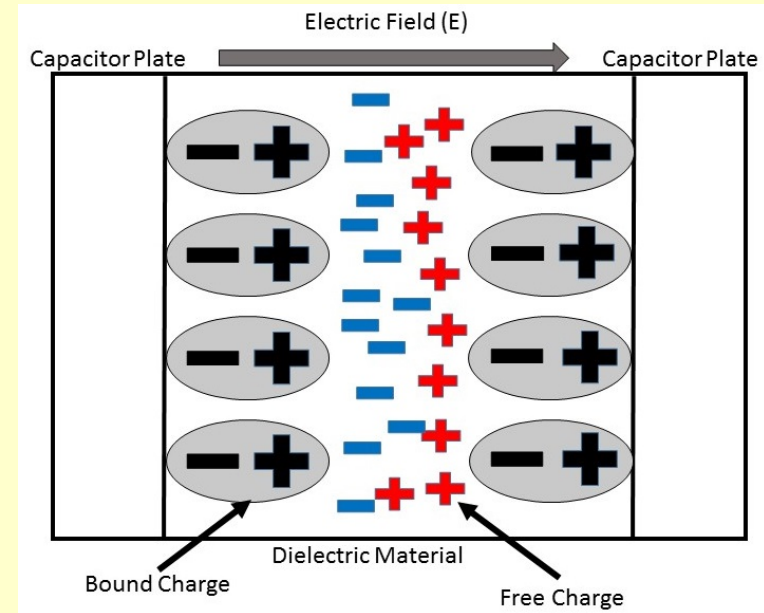
Dipolar polarization, P

$$P = \epsilon_0(\epsilon_r - 1)E$$

E = external electric field of strength E , potential (V)

ϵ_0 = permittivity of free space

ϵ_r = relative permittivity of a material



ϵ^* permittivity is a complex quantity: $\epsilon^* = \epsilon_0\epsilon_r$ $\epsilon^* = \epsilon' + i\epsilon''$

ϵ' = time-independent polarizability of a material in the presence of an external electric field

ϵ'' = time-dependent component of the permittivity, quantifies the efficiency with which electromagnetic energy is converted to heat

Dielectric Properties

The ability of a substance to convert electromagnetic energy into heat at a given frequency and temperature

Loss factor $\tan\delta$ $\tan \delta = \varepsilon''/\varepsilon'$

ε'' is the dielectric loss, the efficiency of radiation-to-heat conversion

ε' is the dielectric constant, the ability of molecules to be polarized by the electric field

a high $\tan\delta$ value required for efficient absorption and for rapid heating

Loss factors ($\tan\delta$) of different solvents (2.45 GHz, 20 °C)

Solvent	$\tan\delta$	Solvent	$\tan\delta$
ethylene glycol	1.350	DMF	0.161
ethanol	0.941	1,2-dichloroethane	0.127
DMSO	0.825	water	0.123
2-propanol	0.799	chlorobenzene	0.101
formic acid	0.722	chloroform	0.091
methanol	0.659	acetonitrile	0.062
nitrobenzene	0.589	ethyl acetate	0.059
1-butanol	0.571	acetone	0.054
2-butanol	0.447	tetrahydrofuran	0.047
1,2-dichlorobenzene	0.280	dichloromethane	0.042
NMP	0.275	toluene	0.040
acetic acid	0.174	hexane	0.020

microwave absorbing properties

high $\tan\delta > 0.5$

medium $\tan\delta 0.1-0.5$

low $\tan\delta < 0.1$

Dielectric Heating

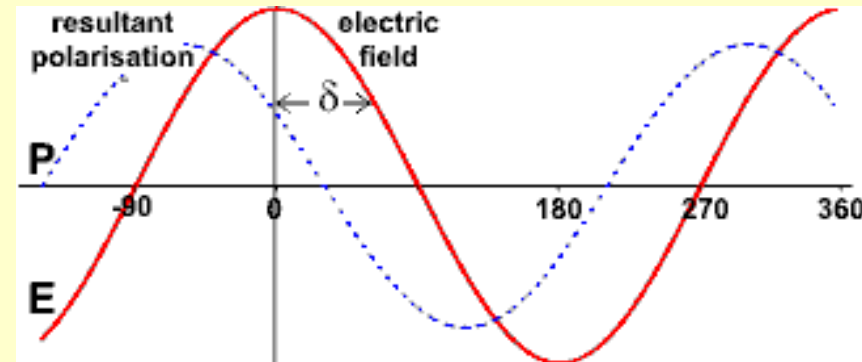
The applied field potential E of electromagnetic radiation

$$E = E_{\max} \cdot \cos(\omega\tau)$$

E_{\max} = the amplitude of the potential (V)

ω = the angular frequency (rad s^{-1})

τ = the time (s)



If the polarization lags behind the field by the phase (δ , radians, phase lag) then the polarization (P , coulombs) varies as

$$P = P_{\max} \cdot \cos(\omega\tau - \delta)$$

P_{\max} is the maximum value of the polarization

Dielectric Heating

The current (I , A) varies as $I = (dP/dt) = -\omega P_{\max} \sin(\omega\tau - \delta)$

The power (P , watts) given out as heat is the average value of (current x potential).

P is zero if there is no lag (*i.e.* if $\delta = 0$), otherwise

$$P = 0.5 P_{\max} E_{\max} \omega \sin(\delta)$$

The penetration depth, D_p , is the distance into the sample at which the electric field is attenuated to $1/e$ of its surface value

$$D_p = \frac{\lambda \sqrt{\epsilon''}}{2\pi \epsilon'}$$

λ = wavelength of the microwave radiation.

D_p = several micrometers for metals and several tens of meters for low-loss polymers

Microwave-Assisted Synthesis

Interaction of materials with microwaves:

✦ reflectors: metals, alloys (δ skin depth, large E gradients, discharges)

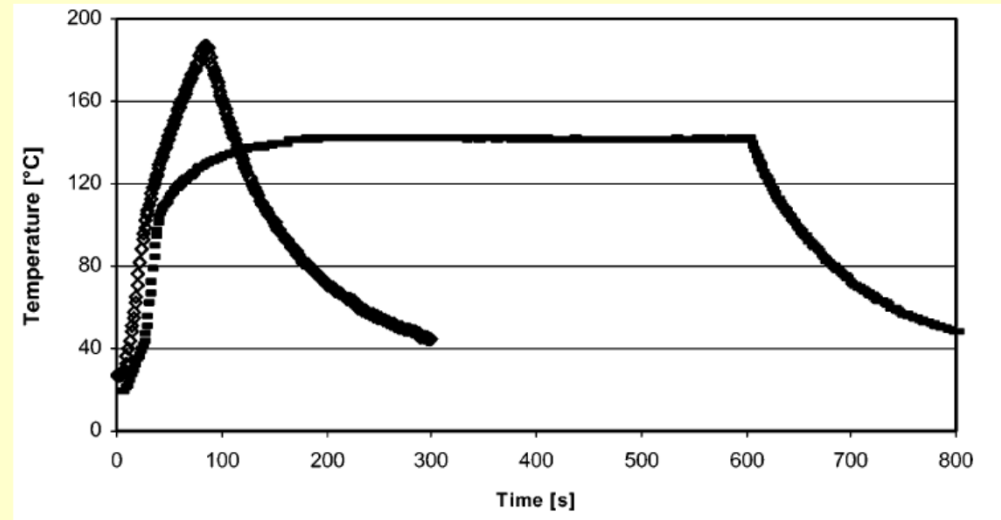
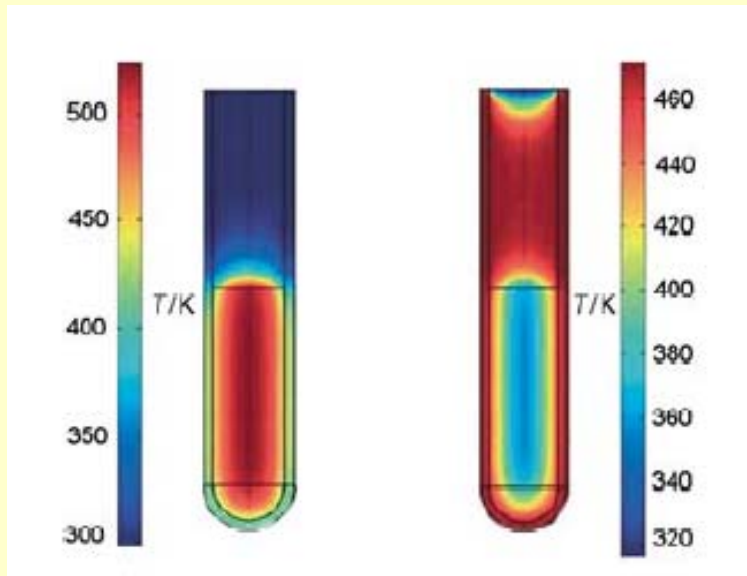
✦ transmitters: quartz, zircon, glasses, ceramics (TM free), Teflon

✦ absorbers: amorphous carbon, graphite, powdered metals, metal oxides, sulfides, halides, water

Temperature Gradients

MW

Oil bath

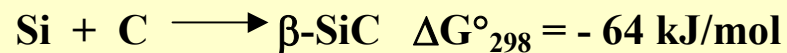


Microwave heating profiles for
 pure water (■)
 0.03 M sodium chloride solution (◆)
 at constant 150 W power

Solvent	T, °C	ϵ'	ϵ''	Skin, cm	$\tan \delta$
ethylene glycol	25	37	49.95	0.55	1.35
water	25	78	10.33	3.33	0.13

Microwave-Assisted Synthesis

Examples of Microwave-assisted syntheses



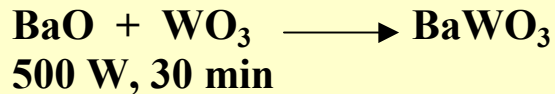
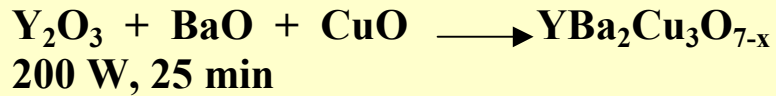
silica crucible, 1 kW, 4-10 min, 900 °C, inert ambient (I₂),
conventional process requires 1400 °C

metal + chalcogenide \longrightarrow ME evacuated quartz ampoules,
5-10 min, 900 W, melting, light emission
PbSe, PbTe, ZnS, ZnSe, ZnTe, Ag₂S

Mo + Si + graphite \longrightarrow MoSi₂
high mp, oxidation and carbidation resistance, metallic conductivity,
heating elements and high-T engine parts

Microwave-Assisted Synthesis

Mixed oxides

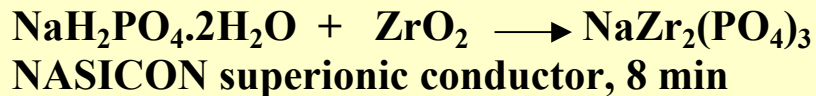


**Amorphous carbon is a secondary susceptor, does not react with reagents or products (carbothermal reduction)
C burns and initiates decomposition of carbonates or nitrates**



NaH₂PO₄·2H₂O good MW susceptor, rotational excitation of water, dehydrates to NaPO₃, melts, 700 °C in 5 min

Na₂HPO₄·2H₂O, KH₂PO₄ no MW heating



Microvawe-Active Elements, Natural Minerals, and Compounds (2.45 GHz, 1 kW)

element/ mineral/compound	time (min) of microvawe exposure	T, K	element/ mineral/compound	time (min) of microvawe exposure	T, K
Al	6	850	MnO ₂	6	1560
C (amorphous, < 1 μm)	1	1556	NiO	6.25	1578
C (graphite, 200 mesh)	6	1053	V ₂ O ₅	11	987
C (graphite, < 1 μm)	1.75	1346	WO ₃	6	1543
Co	3	970	Ag ₂ S	5.5	925
Fe	7	1041	Cu ₂ S	7	1019
Mo	4	933	CuFeS ₂ (chalcopyrite)	1	1193
V	1	830	FeS ₂ (pyrite)	6.75	1292
W	6.25	963	MoS ₂	7	1379
Zn	3	854	PbS	1.25	1297
TiB ₂	7	1116	CuBr	11	995
Co ₂ O ₃	3	1563	CuCl	13	892
CuO	6.25	1285	ZnBr ₂	7	847
Fe ₃ O ₄ (magnetite)	2.75	1531	ZnCl ₂	7	882

Microwave-Assisted Synthesis

