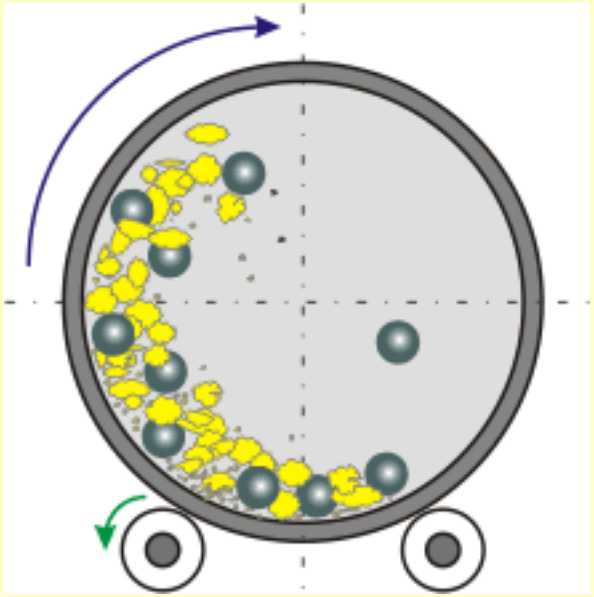
Mechanochemical Synthesis

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**

Ni + Nb $\longrightarrow$ **$Nb_{40}Ni_{60}$ amorphous**

Mechanochemical Synthesis

➔ **Preparation of mixed oxides**

Al_2O_3(corundum) + SiO_2 (xerogel) ⟶ mullite

Al_2O_3 + La_2O_3 ⟶ $LaAlO_3$ 120 min

Al_2O_3 + Mn_2O_3 ⟶ $LaMnO_3$ room temp., 180 min

$SnO + B_2O_3 + P_2O_5 + Li_2O \rightarrow (Li_2O)_2(Sn_2BPO_6)_4$ in dry N_2
anodic material for lithium batteries

➔ **Preparation of chalcogenides**

Fe (powder 4 μm) + S (50 μm) ⟶ FeS in Argon

$ZnCl_2 + Na_2S \longrightarrow ZnS + 2\ NaCl$

$CdCl_2 + Na_2S \longrightarrow CdS + 2\ NaCl$

Mechanochemical Synthesis

➔ **Preparation of carbides, borides, nitrides, silicides**

Nb + C (graphite) ⟶ NbC
(Fe impurities from abrasion)

Nb + C + Cu + Fe ⟶ NbC/Cu/Fe cermet

Ti + N_2 ⟶ TiN 60 h

Ti + C ⟶ TiC 35 h

Ti + 2 B ⟶ TiB_2 15 h

TiO_2 + 2 Mg + C ⟶ TiC + 2 MgO
(MgO removed by HCl)

WO_3 + 3 Mg + C ⟶ α-W + 3 MgO + C explosive

α-W + 3 MgO + C ⟶ WC 50 h
(4-20 nm, MgO removed by HCl)

Mechanochemical Synthesis

➔**Reactive milling**

$$Na_2CO_3 + SeO_2 \longrightarrow Na_2SeO_3 + CO_2$$

$$2In + 3\ urea.H_2O_2 + SnO_2 \longrightarrow In_2O_3 + SnO_2 + 3\ H_2O + 3\ urea$$

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

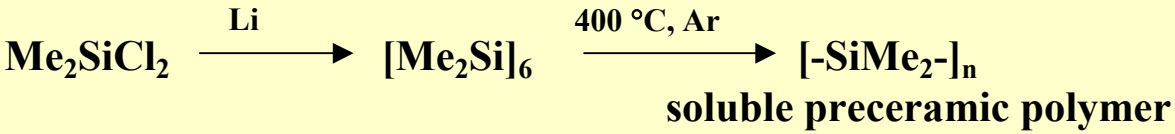
$$FeCl_2 + 2\ CpNa \longrightarrow 2\ NaCl + Cp_2Fe$$

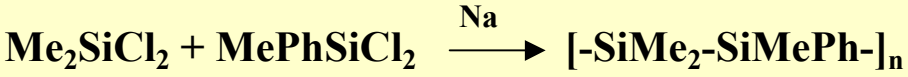
Polymer Pyrolysis

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

Example: SiC fibers

☺ polymer synthesis

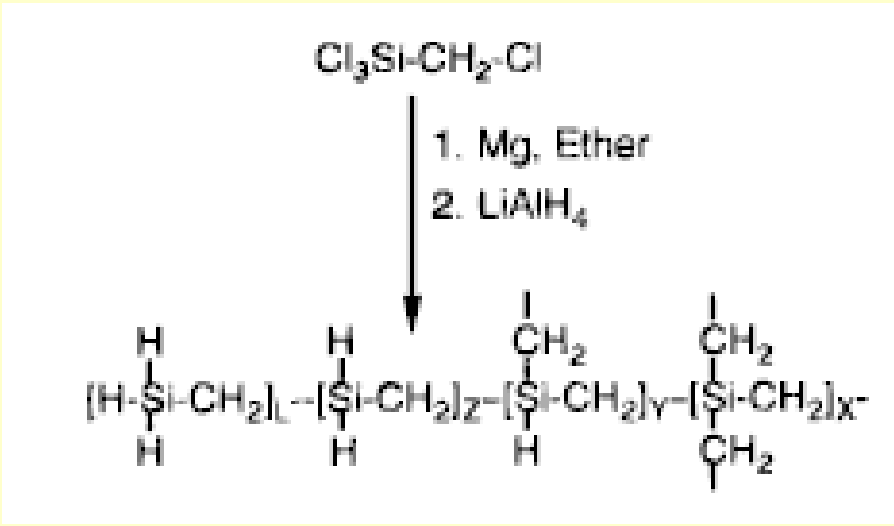


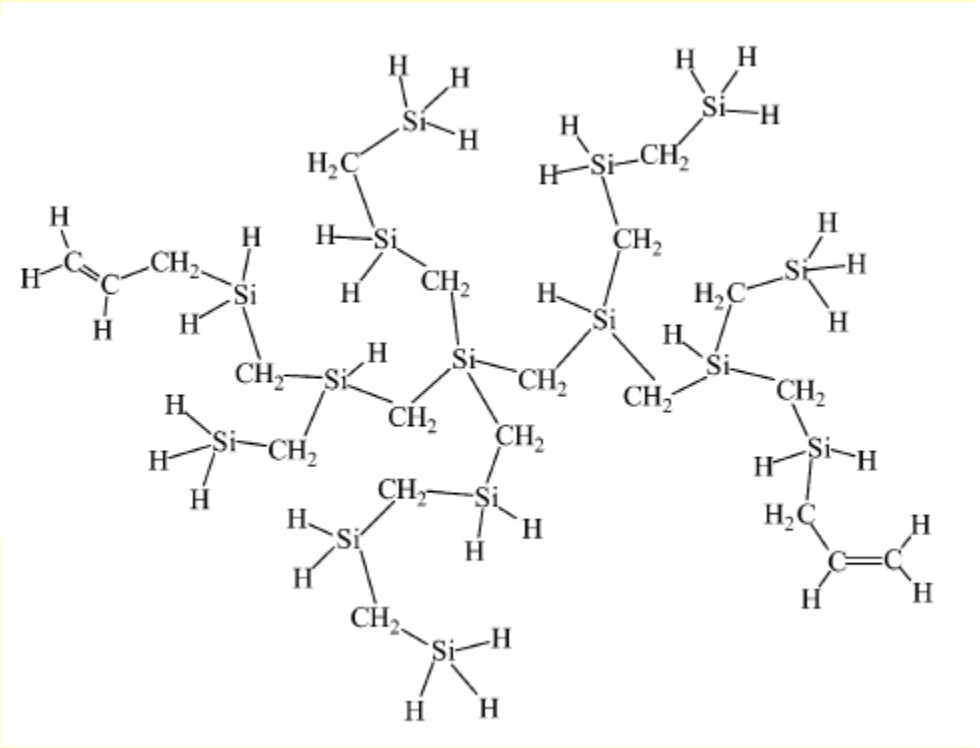


☺ melt spinning or drawing from solution gives continuous polymer fiber
☺ curing in O_2, heat to 400 - 500 °C, thermoset, crosslinking to prevent melting
☺ pyrolysis at 1000 - 1500 °C to polyxtalline β-SiC fiber

Polymer Pyrolysis

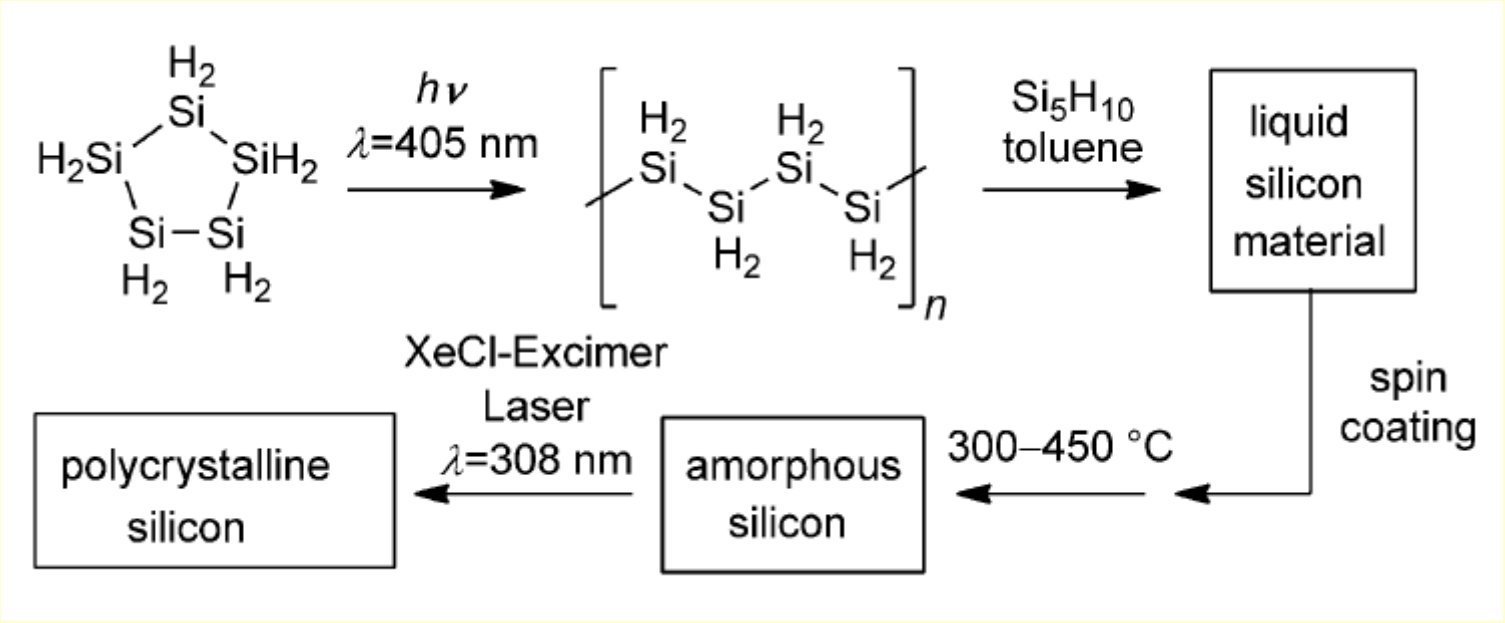
$Cl\text{-}CH_2\text{-}SiCl_3$





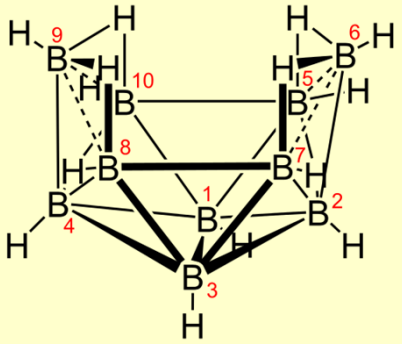
$(SiCH_4)_n$

Polymer Pyrolysis



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

Polymer Pyrolysis



BN

$$B_{10}H_{14} + en \longrightarrow \text{polymer} \xrightarrow{1300\ K,\ NH_3} \text{BN powder}$$

AlN

$$Al \xrightarrow[CH_3CN,\ RNH_2,\ R_4N^+]{\text{anodic dissolution}} Al(NHR)_3 \longrightarrow Al_2(NR)_3 \text{ polymeric gel}$$

$$\xrightarrow{>1100\ K,\ NH_3} \text{AlN powder}$$

Thermolysis of Organometallic Coordination Polymers

$(Me_3Sn)_nM(CN)_6$ n = 3,4; M = Fe, Co, Ru

thermolysis in Ar or H_2 gives intermetallics $FeSn_2$, $CoSn_2$, Ru_3Sn_7
thermolysis in air gives oxides Fe_2O_3/SnO_2, Co_2SnO_4, RuO_2

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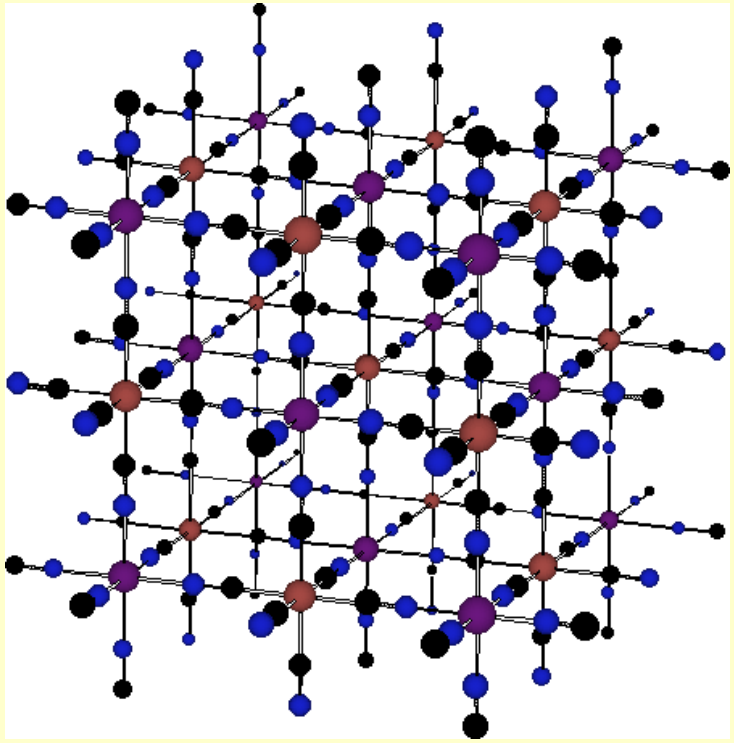
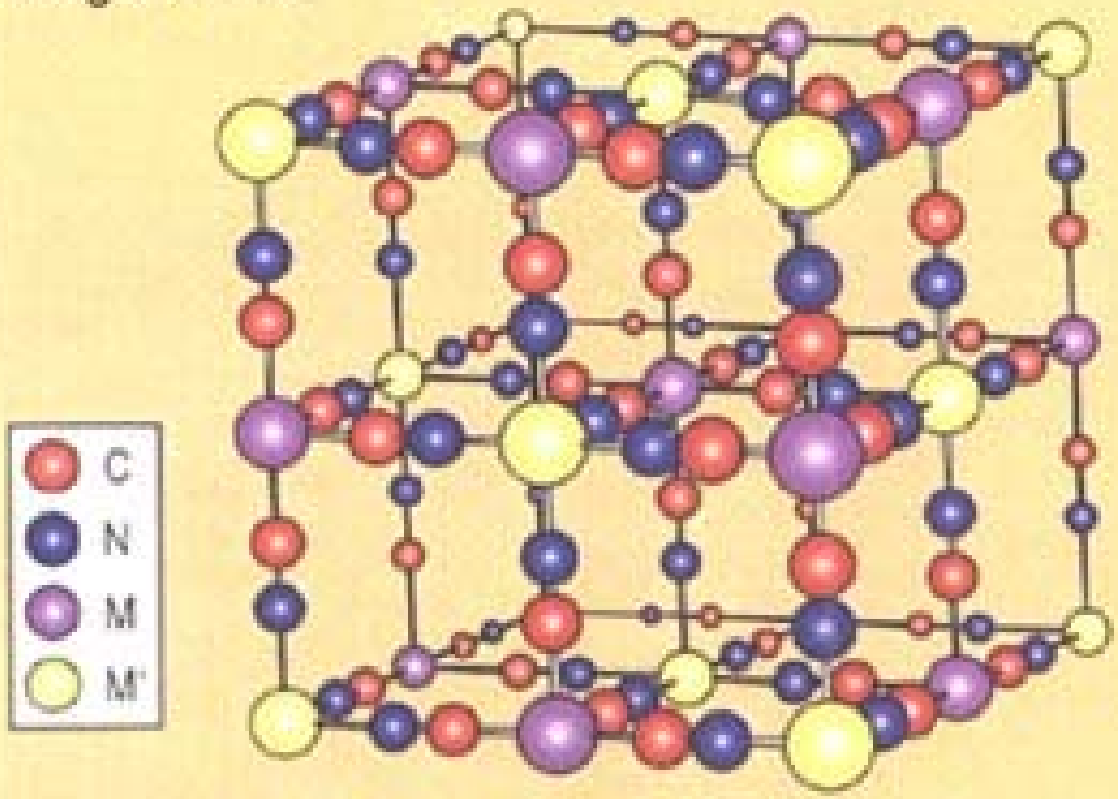


Prussian Blue structure

11

An idealised structure of Prussian Blue with M←C≡N→M' linkages in 3-D



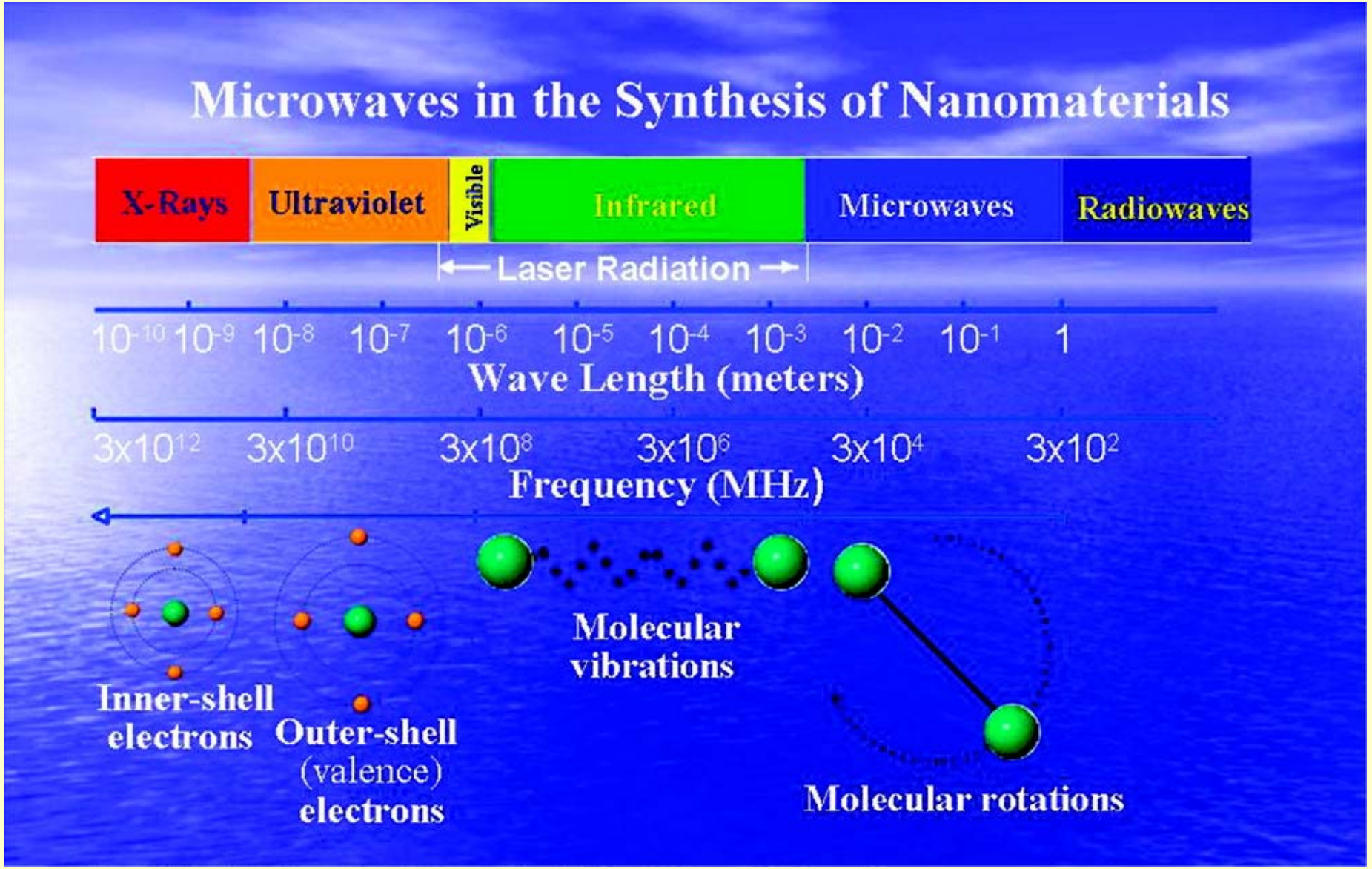
When M = Cr, M' = Ni material is a ferromagnet, T_c = 90K
When M= V, M' = Mn material is a ferrimagnet, T_c = 125K
When M= Cr, M' = V material is a ferrimagnet, T_c = 315K

Microwave-Assisted Synthesis

Microwave radiation = electromagnetic radiation Microwaves:
λ = 1 mm to 1m, ν = 0.3 to 300 GHz
Microwave ovens 2.45 GHz, λ = 12.24 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

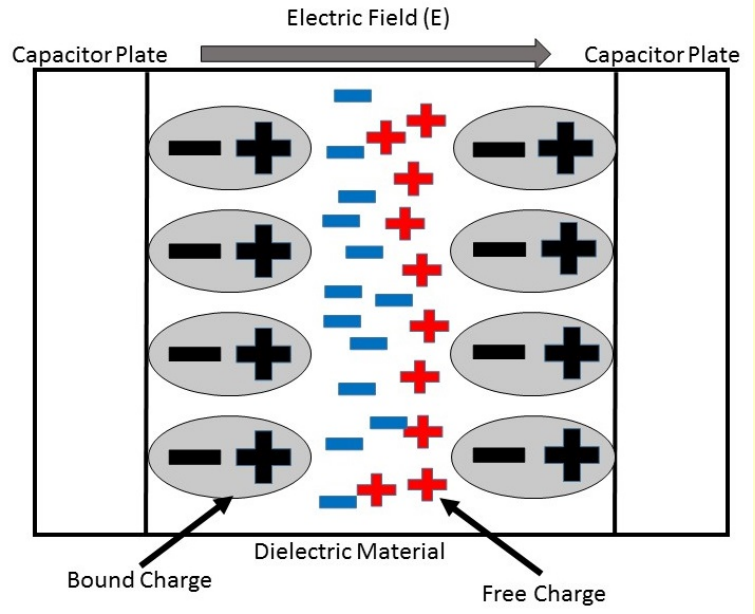
Rotational excitation: weak bonds (interlayer bonds in graphite and other layer materials

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

$$P = \varepsilon_0(\varepsilon_r - 1)E$$



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: $\varepsilon^* = \varepsilon_0\varepsilon_r$ $\varepsilon^* = \varepsilon' + i\varepsilon''$

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 tanδ $\tan \delta = \varepsilon''/\varepsilon'$

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 tanδ value required for efficient absorption and for rapid heating

Loss factors (tanδ) of different solvents (2.45 GHz, 20 °C)

Solvent	tanδ	Solvent	tanδ
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

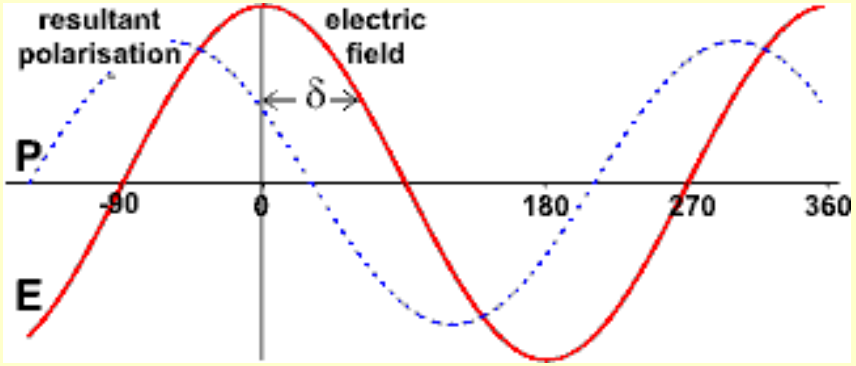
microwave absorbing properties

high	tanδ > 0.5
medium	tanδ 0.1–0.5
low	tanδ < 0.1

Dielectric Heating

The applied field potential E of electromagnetic radiation

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



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

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

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

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

λ = wavelength of the microwave radiation.
D_p = several micrometers for metals and several tens of meters for low-loss polymers

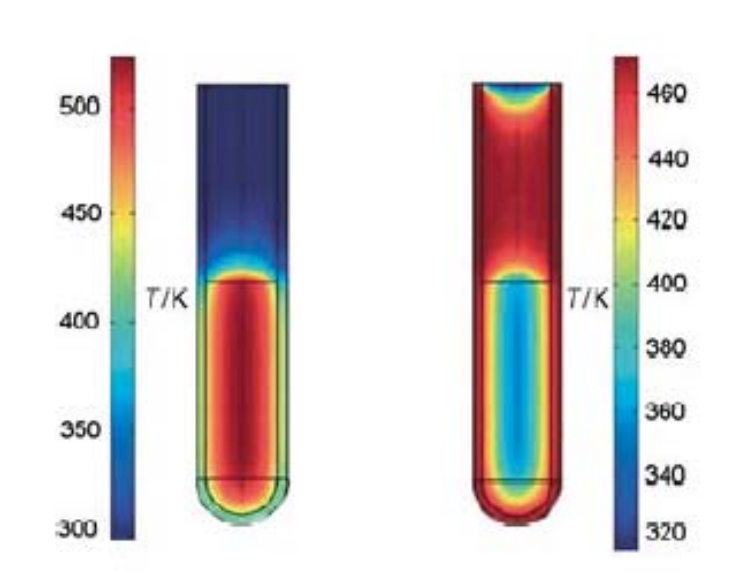
Microwave-Assisted Synthesis

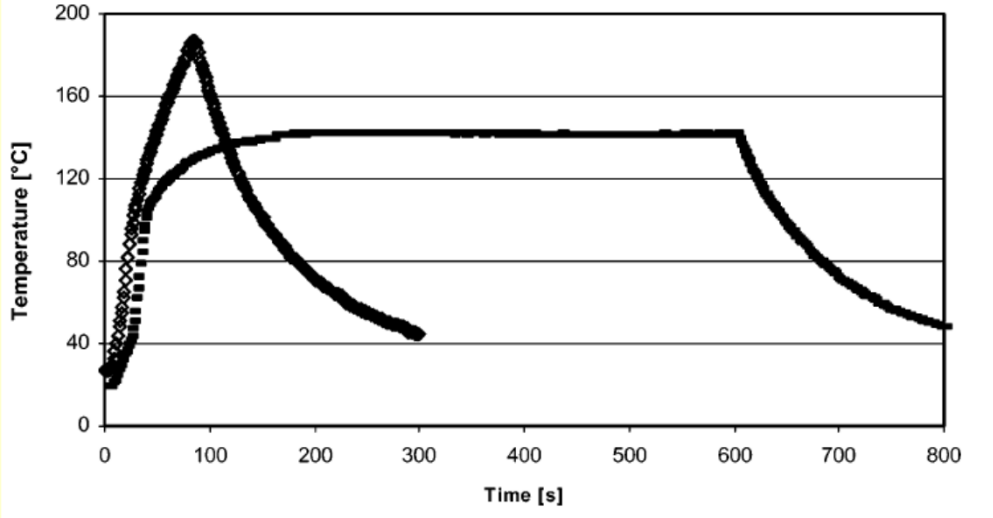
Interaction of materials with microwaves:

- **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 δ
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

Si + C $\longrightarrow$ β-SiC $\Delta G°_{298}$ = - 64 kJ/mol
silica crucible, 1 kW, 4-10 min, 900 °C, inert ambient (I_2),
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, Ag_2S

Mo + Si + graphite $\longrightarrow$ $MoSi_2$
high mp, oxidation and carbidation resistance, metallic conductivity,
heating elements and high-T engine parts

Microwave-Assisted Synthesis

Mixed oxides

$Y_2O_3 + BaO + CuO \longrightarrow YBa_2Cu_3O_{7-x}$

200 W, 25 min

$BaO + WO_3 \longrightarrow BaWO_3$

500 W, 30 min

Amorphous carbon is a secondary susceptor, does not react with reagents or products (carbothermal reduction)

C burns and initiates decomposition of carbonates or nitrates

$BaCO_3 + TiO_2 + C \longrightarrow BaTiO_3 + CO_2$

$PbNO_3 + TiO_2 + C \longrightarrow PbTiO_3 + CO_2$

$NaH_2PO_4.2H_2O$ good MW susceptor, rotational excitation of water, dehydrates to $NaPO_3$, melts, 700 °C in 5 min

$Na_2HPO_4.2H_2O$, KH_2PO_4 no MW heating

$NaH_2PO_4.2H_2O + ZrO_2 \longrightarrow NaZr_2(PO_4)_3$

NASICON superionic conductor, 8 min

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_2O_5	11	987
C (graphite, < 1 μm)	1.75	1346	WO_3	6	1543
Co	3	970	Ag_2S	5.5	925
Fe	7	1041	Cu_2S	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_2O_3	3	1563	CuCl	13	892
CuO	6.25	1285	$ZnBr_2$	7	847
Fe_3O_4 (magnetite)	2.75	1531	$ZnCl_2$	7	882

Microwave-Assisted Synthesis