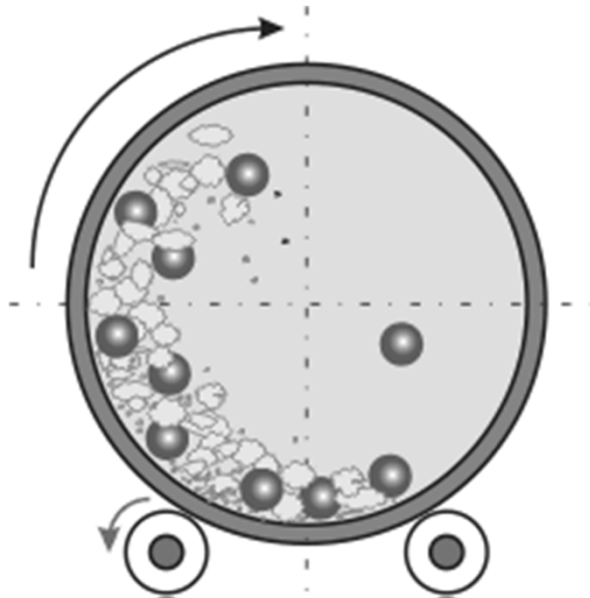
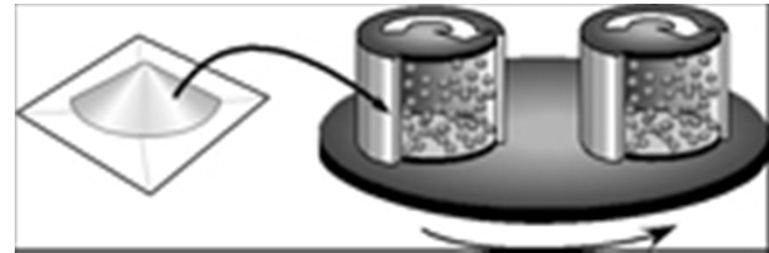


# Mechanochemical Synthesis

## 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 <sup>3</sup>	After	V, Å <sup>3</sup>
GeO <sub>2</sub>	quartz	40.3	rutile	27.6
TiO <sub>2</sub>	anatase	34.1	rutile	31.2
ZrO <sub>2</sub>	baddaleyite	35.2	fluorite	32.8

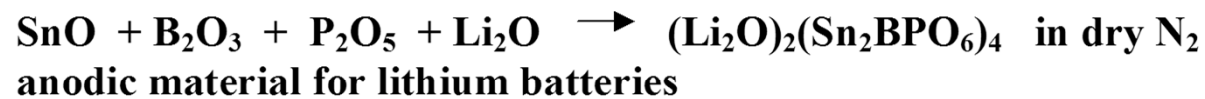
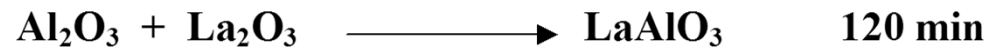
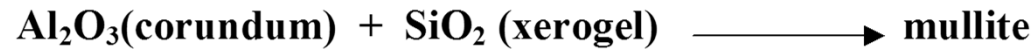
V = volume per formula unit

→ Mechanical Alloying

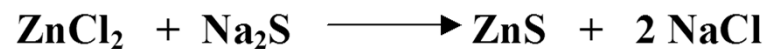
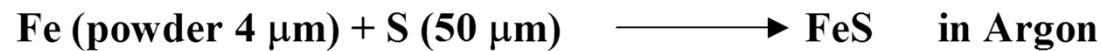


# Mechanochemical Synthesis

→ Preparation of mixed oxides

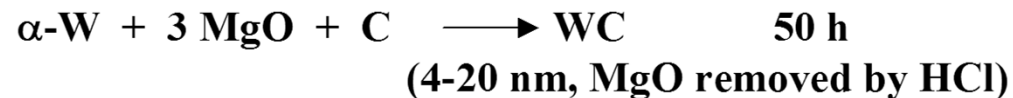
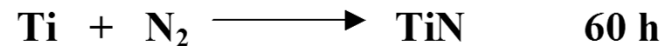
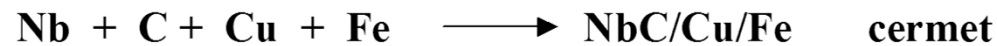
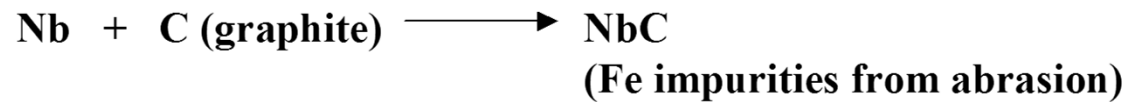


→ Preparation of chalcogenides



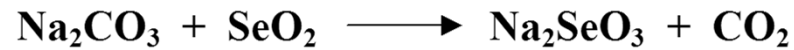
# Mechanochemical Synthesis

→ Preparation of carbides, borides, nitrides, silicides

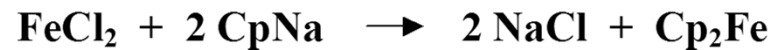


# Mechanochemical Synthesis

→ Reactive milling



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

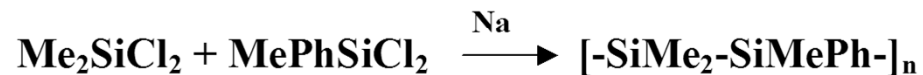
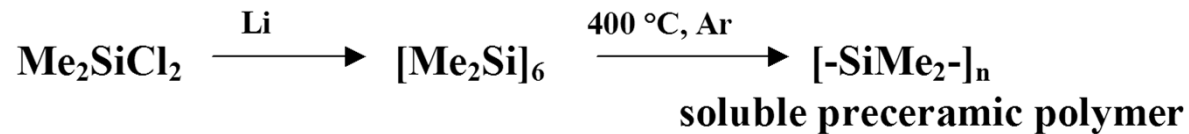


# Polymer Pyrolysis

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

**Example: SiC fibers**

☺ **polymer synthesis**

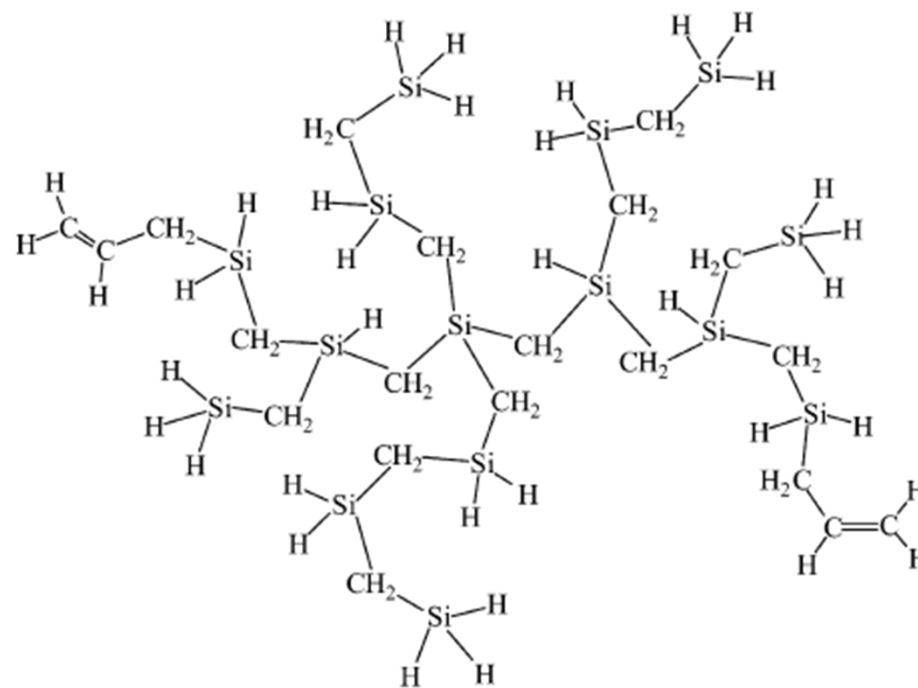
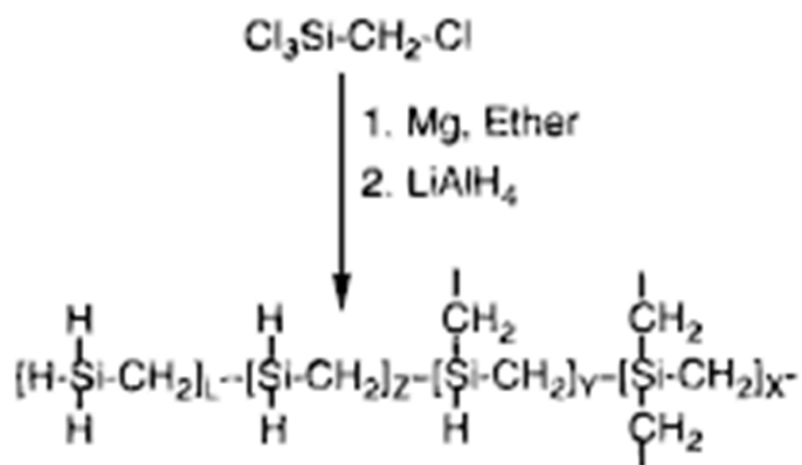
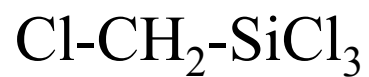


☺ **melt spinning or drawing from solution gives continuous polymer fiber**

☺ **curing in O<sub>2</sub>, heat to 400 - 500 °C, thermoset, crosslinking to prevent melting**

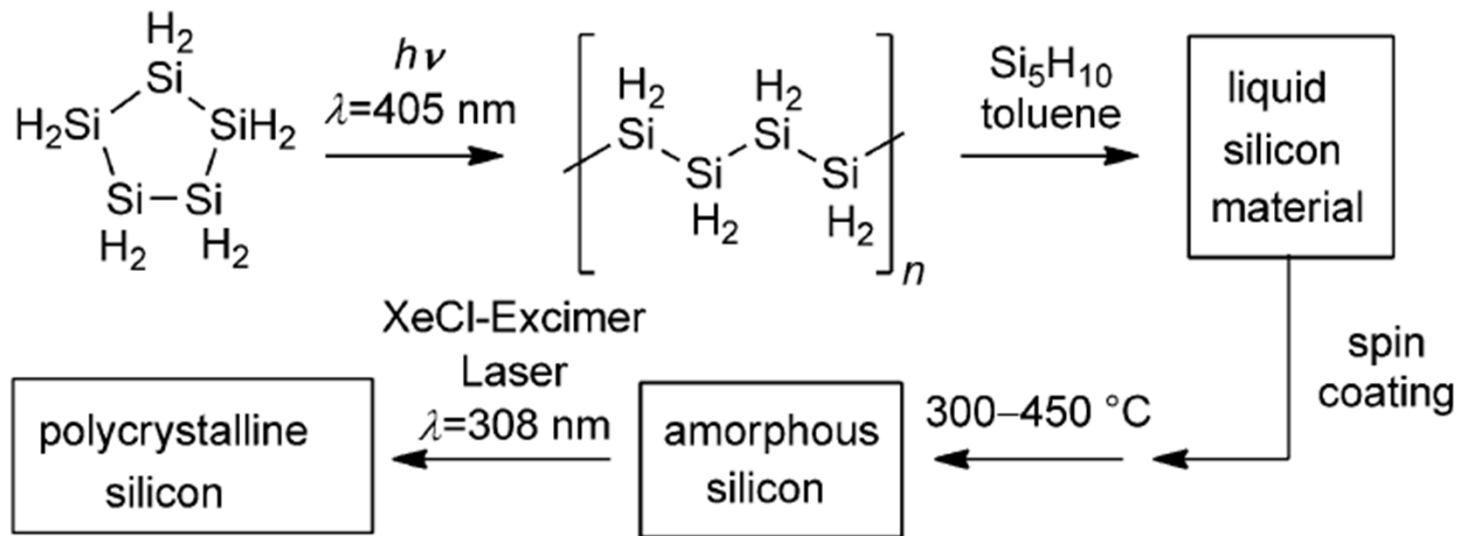
☺ **pyrolysis at 1000 - 1500 °C to polycrystalline β-SiC fiber**

# Polymer Pyrolysis



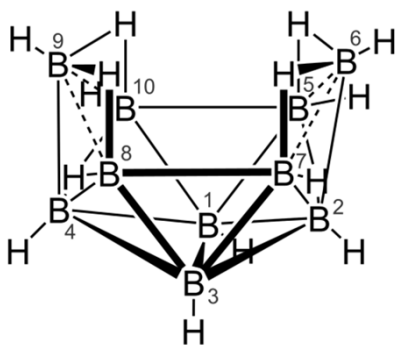


# Polymer Pyrolysis



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

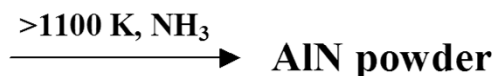
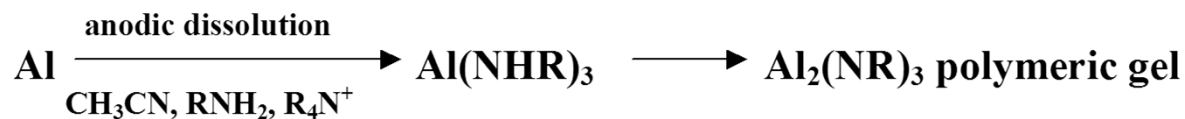
# Polymer Pyrolysis



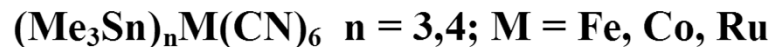
**BN**



**AlN**



## Thermolysis of Organometallic Coordination Polymers



thermolysis in Ar or H<sub>2</sub> gives intermetallics FeSn<sub>2</sub>, CoSn<sub>2</sub>, Ru<sub>3</sub>Sn<sub>7</sub>

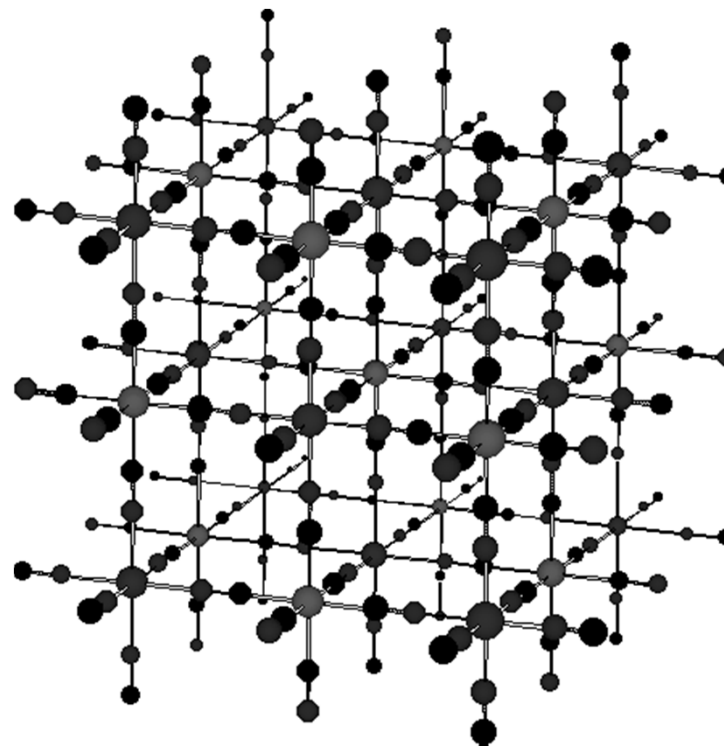
thermolysis in air gives oxides Fe<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub>, Co<sub>2</sub>SnO<sub>4</sub>, RuO<sub>2</sub>

# Thermolysis of Organometallic Coordination Polymers

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

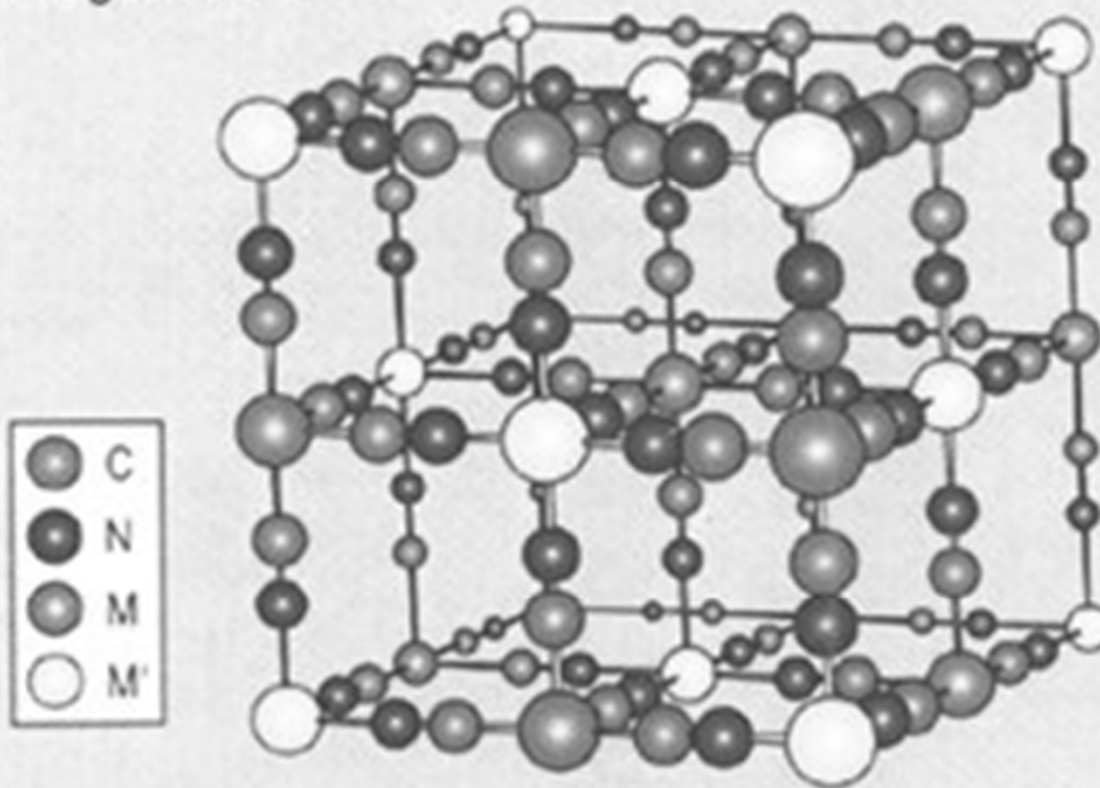
thermolysis in Ar or  $\text{H}_2$  gives intermetallics  
 $\text{FeSn}_2, \text{CoSn}_2, \text{Ru}_3\text{Sn}_7$

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

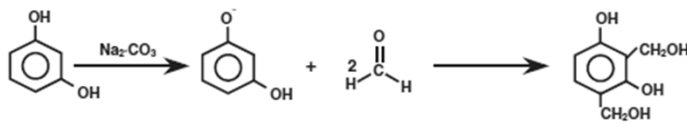
An idealised structure of Prussian Blue with  $M \leftarrow C \equiv N \rightarrow M'$  linkages in 3-D



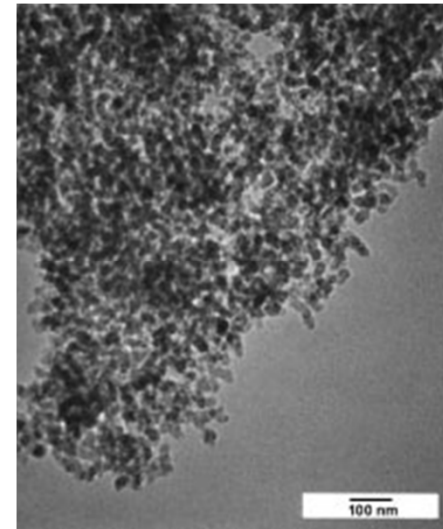
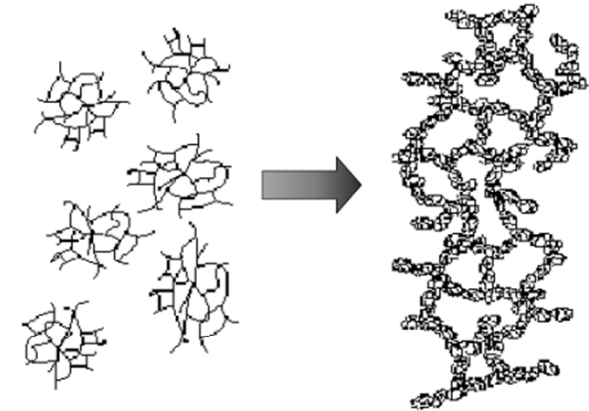
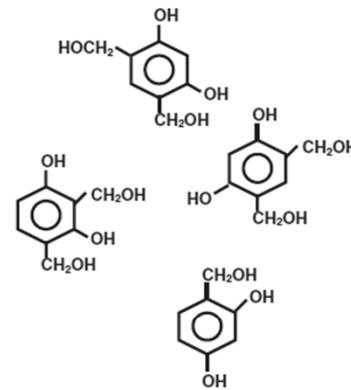
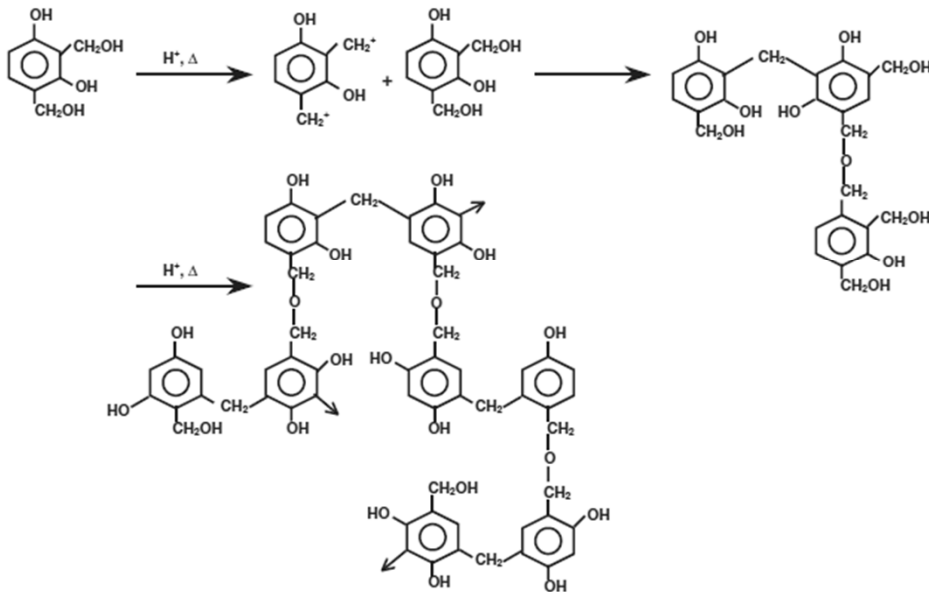
When  $M = Cr$ ,  $M' = Ni$  material is a ferromagnet,  $T_c = 90K$   
When  $M = V$ ,  $M' = Mn$  material is a ferrimagnet,  $T_c = 125K$   
When  $M = Cr$ ,  $M' = V$  material is a ferrimagnet,  $T_c = 315K$

# Resorcinol-Formaldehyde Polymers

## 1. Addition Reaction



## 2. Condensation Reaction



TEM of carbon xerogel carbonized at 1200 °C

# Microwave-Assisted Synthesis

**Microwave radiation = electromagnetic radiation** **Microwaves:**

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

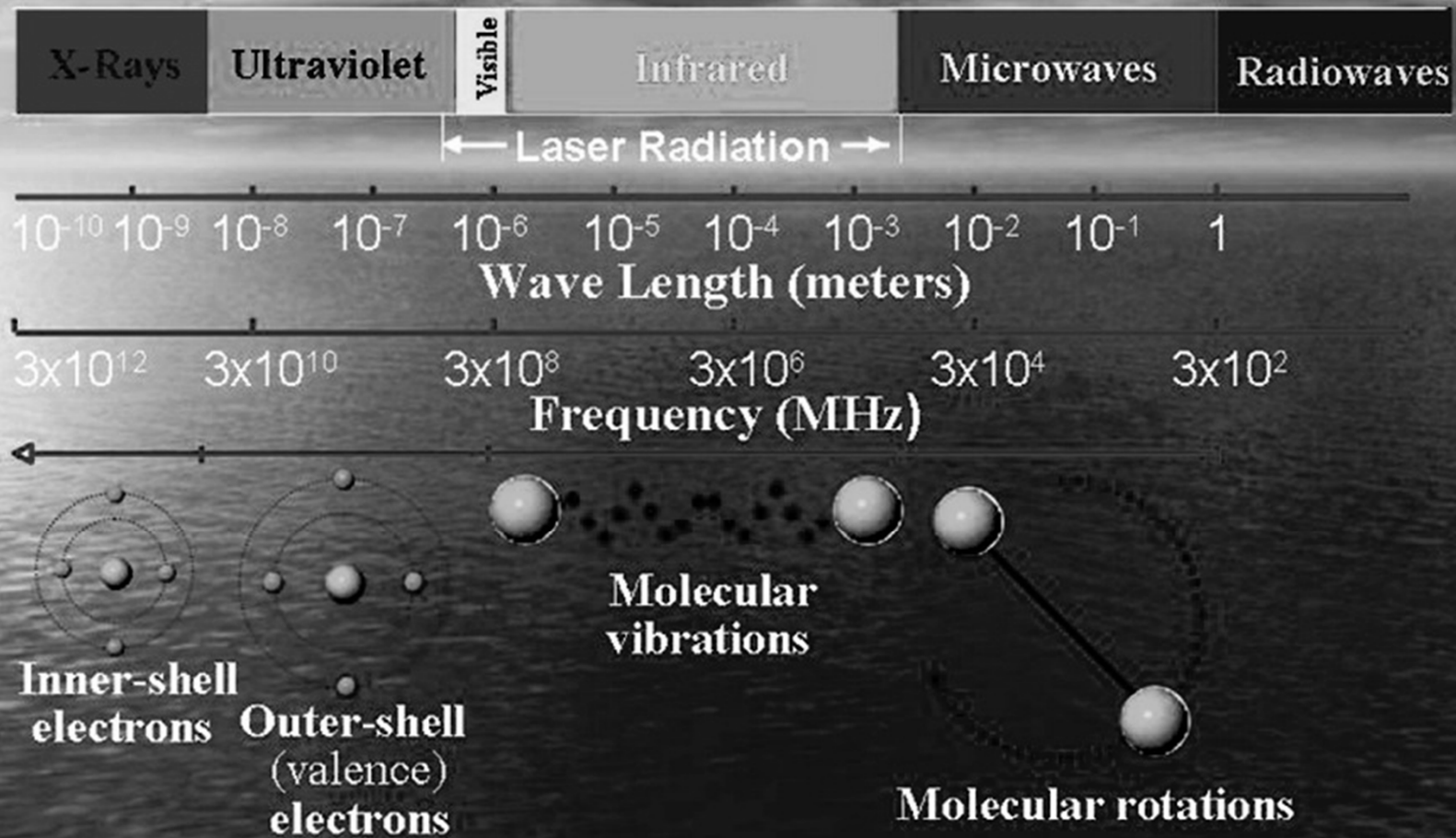
**Microwave ovens 2.45 GHz,  $\lambda = 12.24 \text{ cm}$**

**power up to 1 kW, pulses, magnetron, waveguide, 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

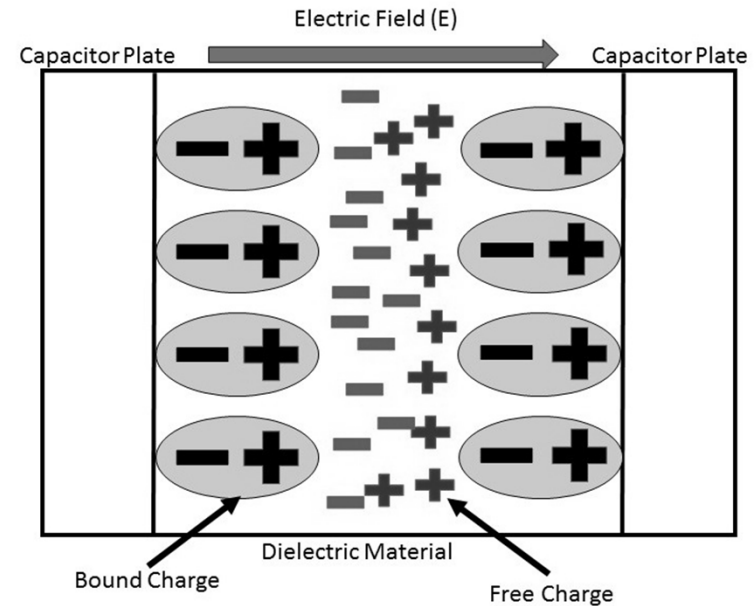
## Dipolar polarization, $P$

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

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

$\epsilon_0$  = permittivity of free space

$\epsilon_r$  = relative permittivity of a material



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

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

$\epsilon''$  = 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  $\tan\delta$                        $\tan \delta = \epsilon''/\epsilon'$**

**$\epsilon''$  is the dielectric loss, the efficiency of radiation-to-heat conversion**

**$\epsilon'$  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

<b>high</b>	$\tan\delta > 0.5$
<b>medium</b>	$\tan\delta 0.1\text{--}0.5$
<b>low</b>	$\tan\delta < 0.1$

# Dielectric Heating

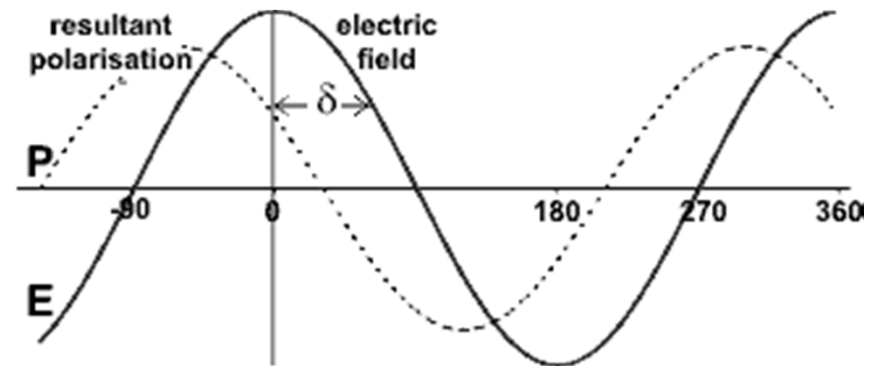
The applied field potential  $E$  of electromagnetic radiation

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

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

$\omega$  = the angular frequency ( $\text{rad s}^{-1}$ )

$\tau$  = the time (s)



If the polarization lags behind the field by the phase ( $\delta$ , 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

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

$\lambda$  = 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:

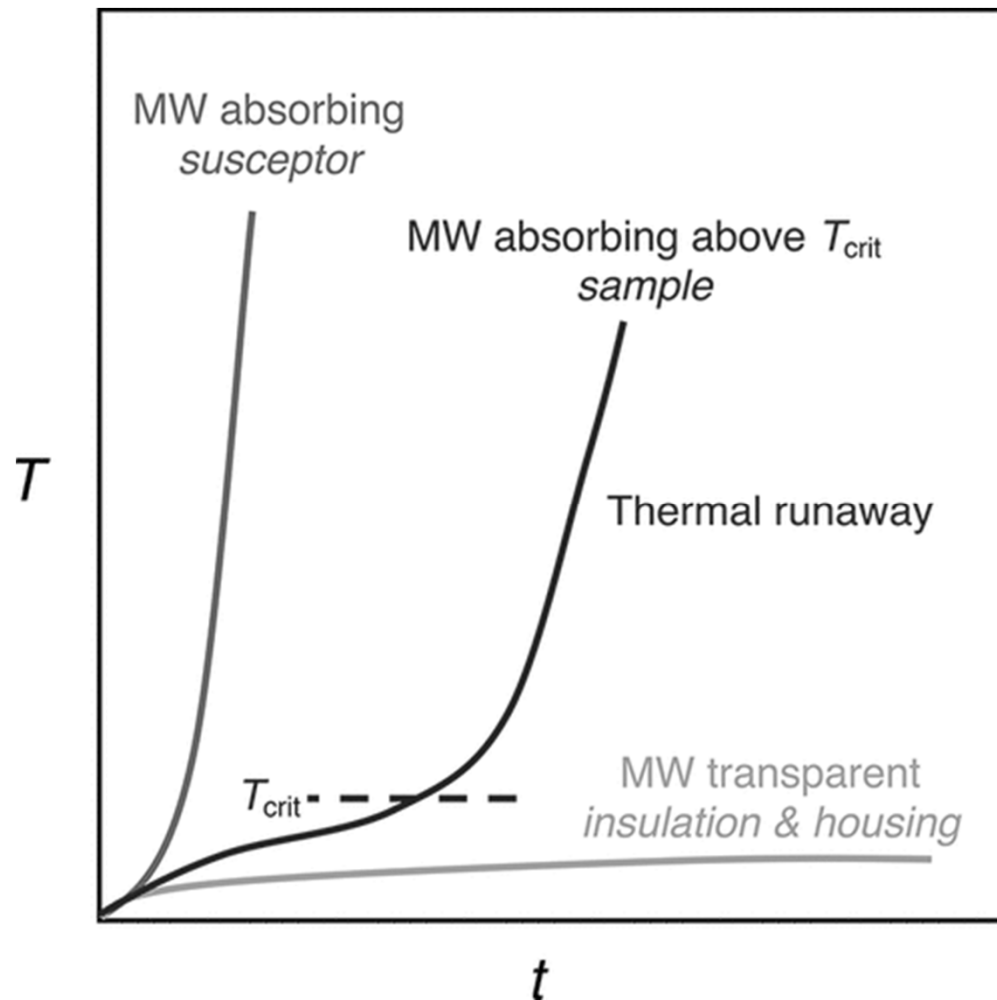
✦ reflectors: metals, alloys ( $\delta$  skin depth, large E gradients, discharges)

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

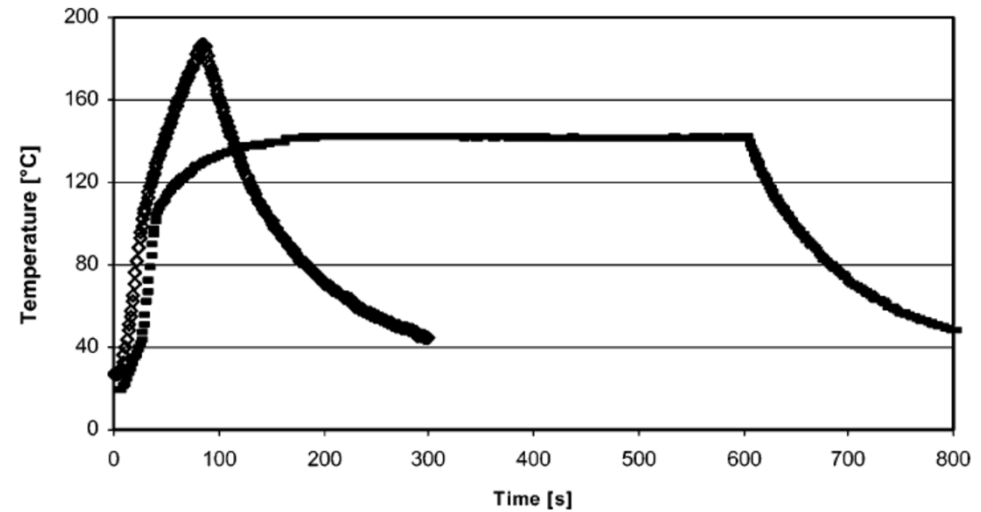
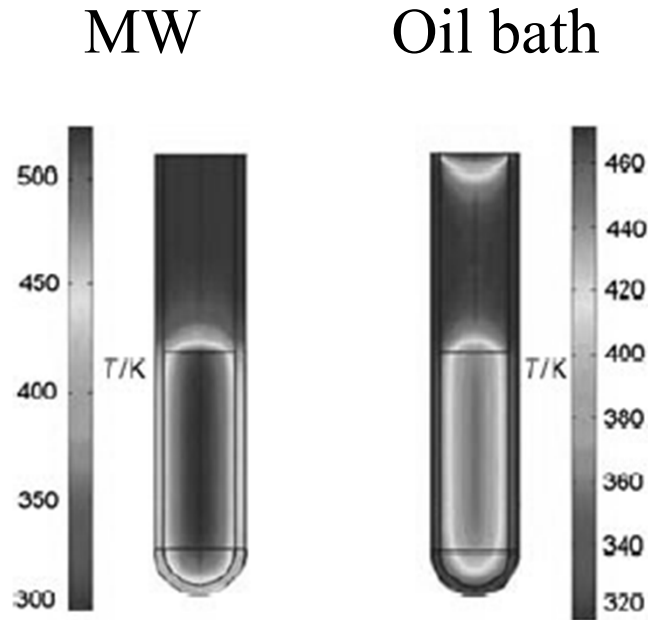
✦ absorbers: amorphous carbon, graphite, powdered metals, metal oxides, sulfides, halides, water



# Microwave-Assisted Synthesis



# Temperature Gradients

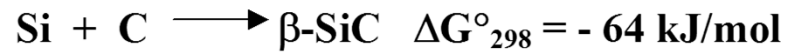


Microwave heating profiles for  
 pure water (■)  
 0.03 M sodium chloride solution (◆)  
 at constant 150 W power

Solvent	T, °C	$\epsilon'$	$\epsilon''$	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 (I<sub>2</sub>),  
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<sub>2</sub>S



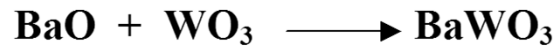
high mp, oxidation and carbidation resistance, metallic conductivity,  
heating elements and high-T engine parts

# Microwave-Assisted Synthesis

Mixed oxides



200 W, 25 min



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



$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  good MW susceptor, rotational excitation of water, dehydrates to  $\text{NaPO}_3$ , melts, 700 °C in 5 min

$\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{KH}_2\text{PO}_4$  no MW heating



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

# Microwave-Assisted Synthesis

