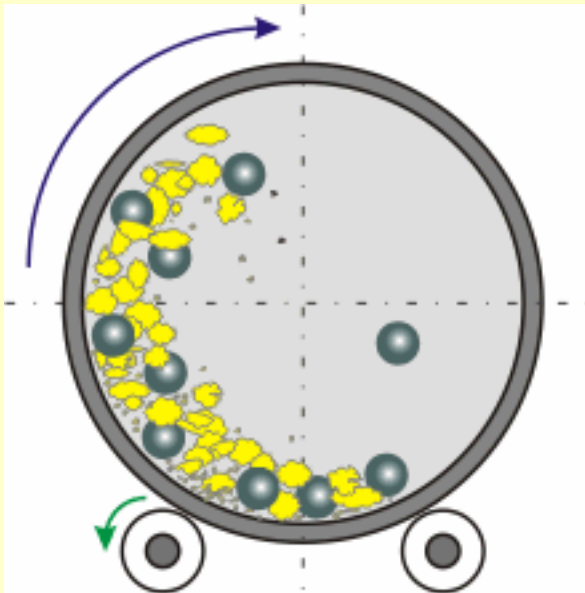


Mechanochemical Synthesis

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

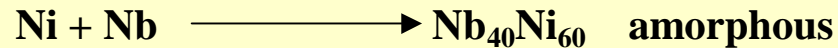
Mechanochemical Synthesis

➔ 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

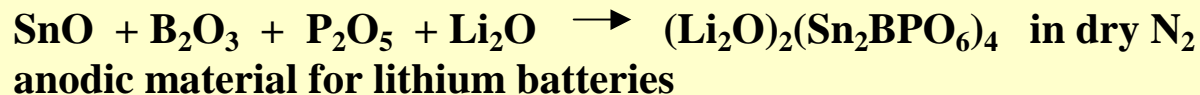
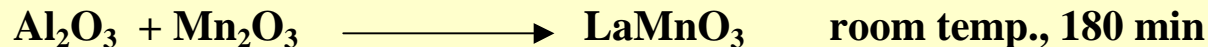
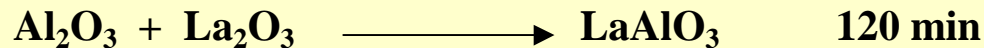
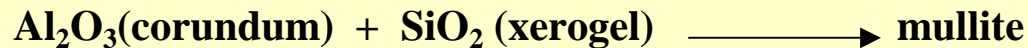
V = volume per formula unit

➔ Mechanical Alloying

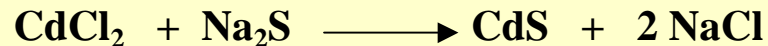
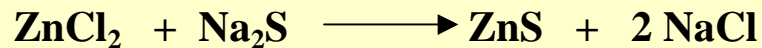
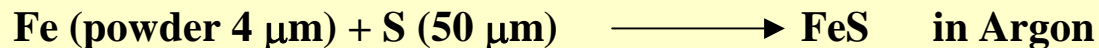


Mechanochemical Synthesis

→ Preparation of mixed oxides

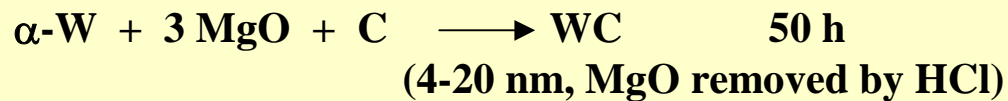
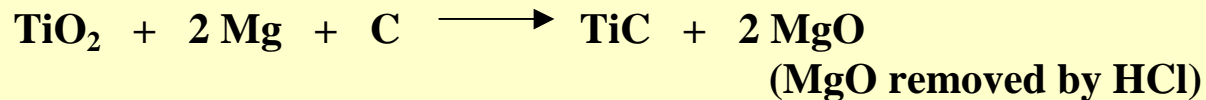
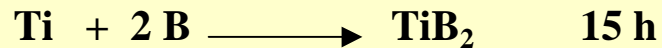
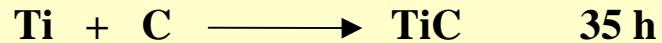
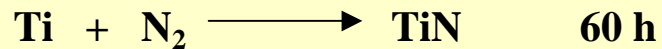
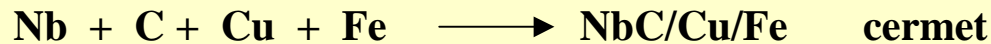
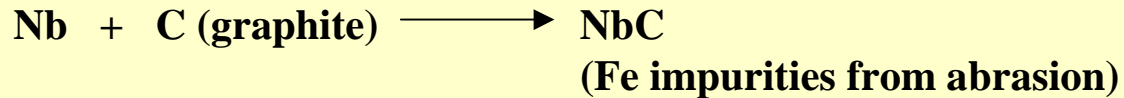


→ Preparation of chalcogenides



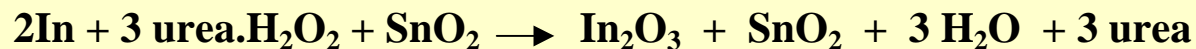
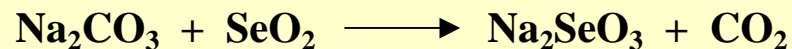
Mechanochemical Synthesis

→ Preparation of carbides, borides, nitrides, silicides

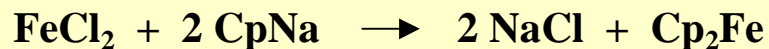


Mechanochemical Synthesis

→ **Reactive milling**



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

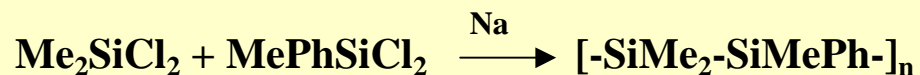
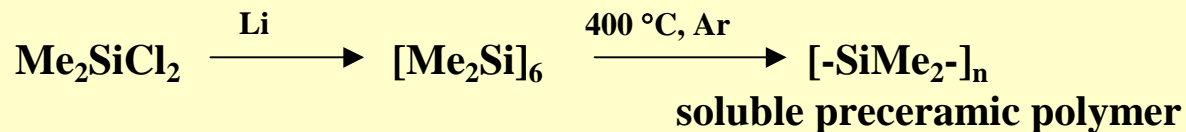


Polymer Pyrolysis

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

Example: SiC fibers

☺ polymer synthesis

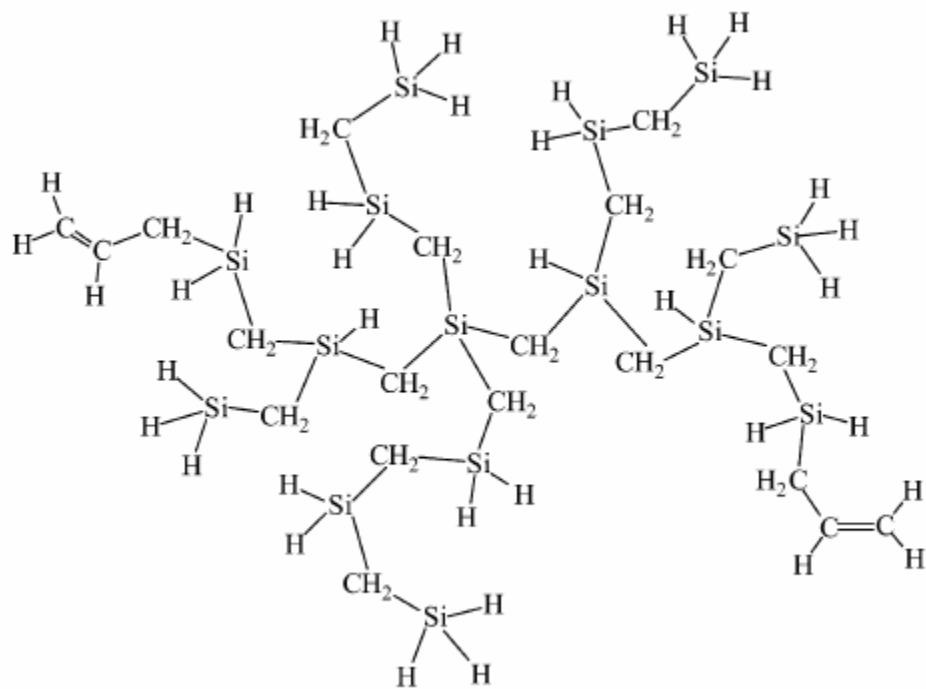
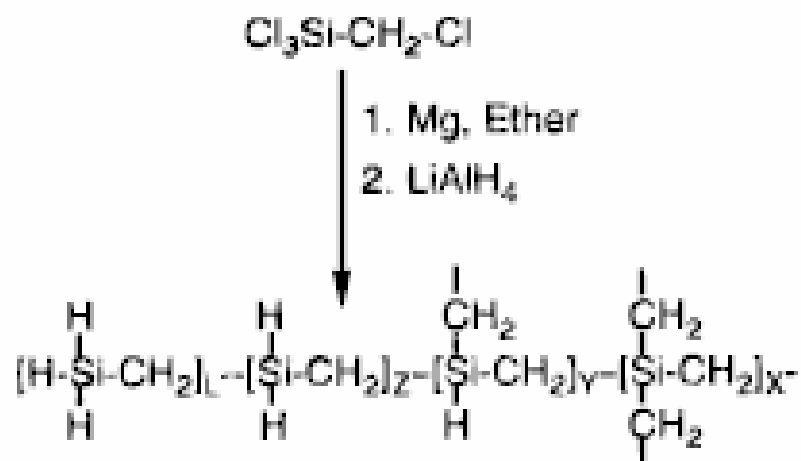
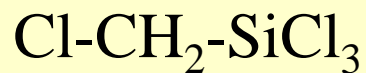


☺ melt spinning or drawing from solution gives continuous polymer fiber

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

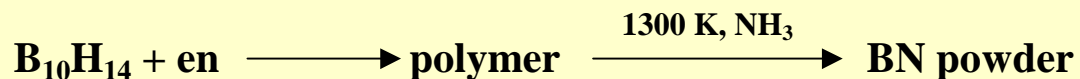
☺ pyrolysis at 1000 - 1500 °C to polyxtalline β-SiC fiber

Polymer Pyrolysis

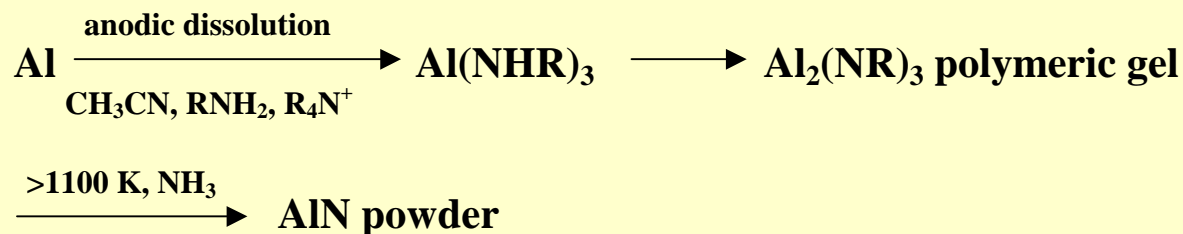


Polymer Pyrolysis

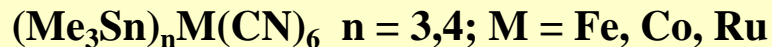
BN



AlN



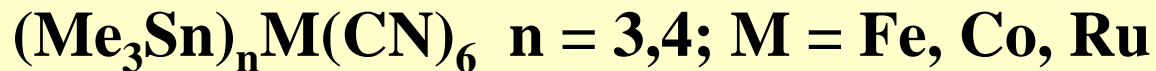
Thermolysis of Organometallic Coordination Polymers



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

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

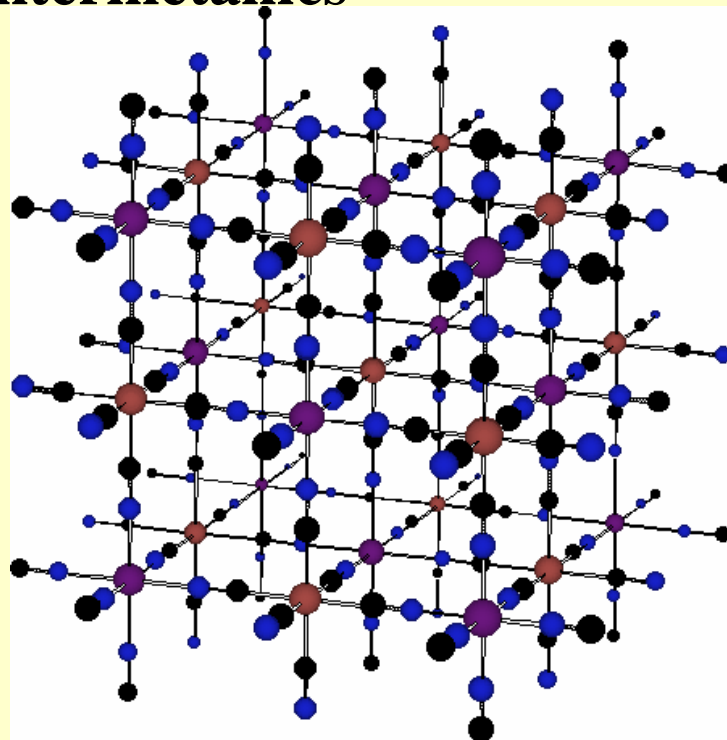
Thermolysis of Organometallic Coordination Polymers



thermolysis in Ar or H_2 gives intermetallics

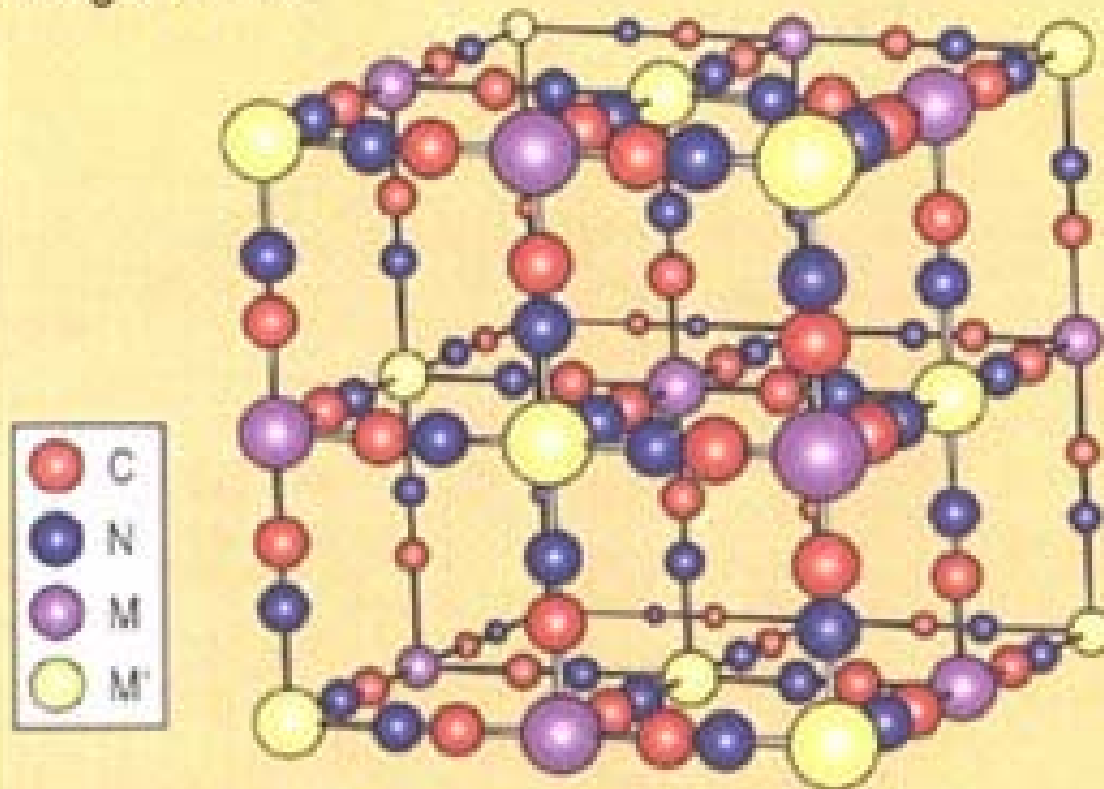


thermolysis in air gives oxides



Prussian Blue structure

An idealised structure of Prussian Blue with $M \leftarrow C \equiv N \rightarrow M'$ 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.

Microwave-Assisted Synthesis

The energy of the microwave photon in this frequency region

**too low to break chemical bonds (0.0016 eV)
lower than the energy of Brownian motion**

Microwaves cannot induce chemical reactions

Microwave-enhanced chemistry is based on 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

Interaction of materials with microwaves:

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

✦ transmitters: quartz, zircon, glasses, ceramics (no TM), Teflon

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

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

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 and, in the process, 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.

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 heating

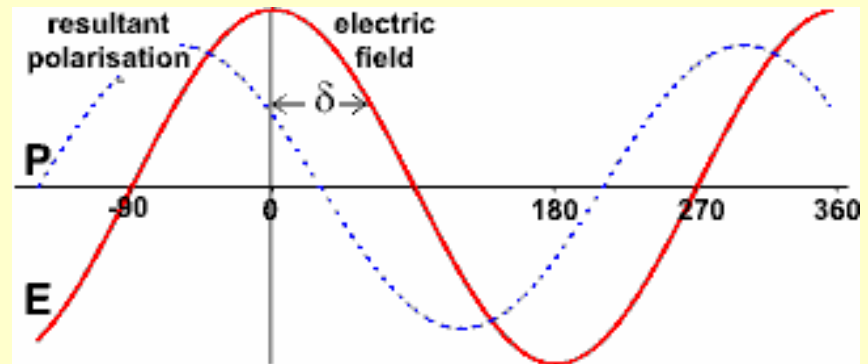
The applied field potential E of electromagnetic radiation

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

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) 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

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

Dielectric Properties

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

Loss factor $\tan\delta$

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

ϵ'' is the dielectric loss, indicative of 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

solvents can be classified as microwave absorbing

high ($\tan\delta > 0.5$)

medium ($\tan\delta = 0.1 - 0.5$)

low ($\tan\delta < 0.1$)

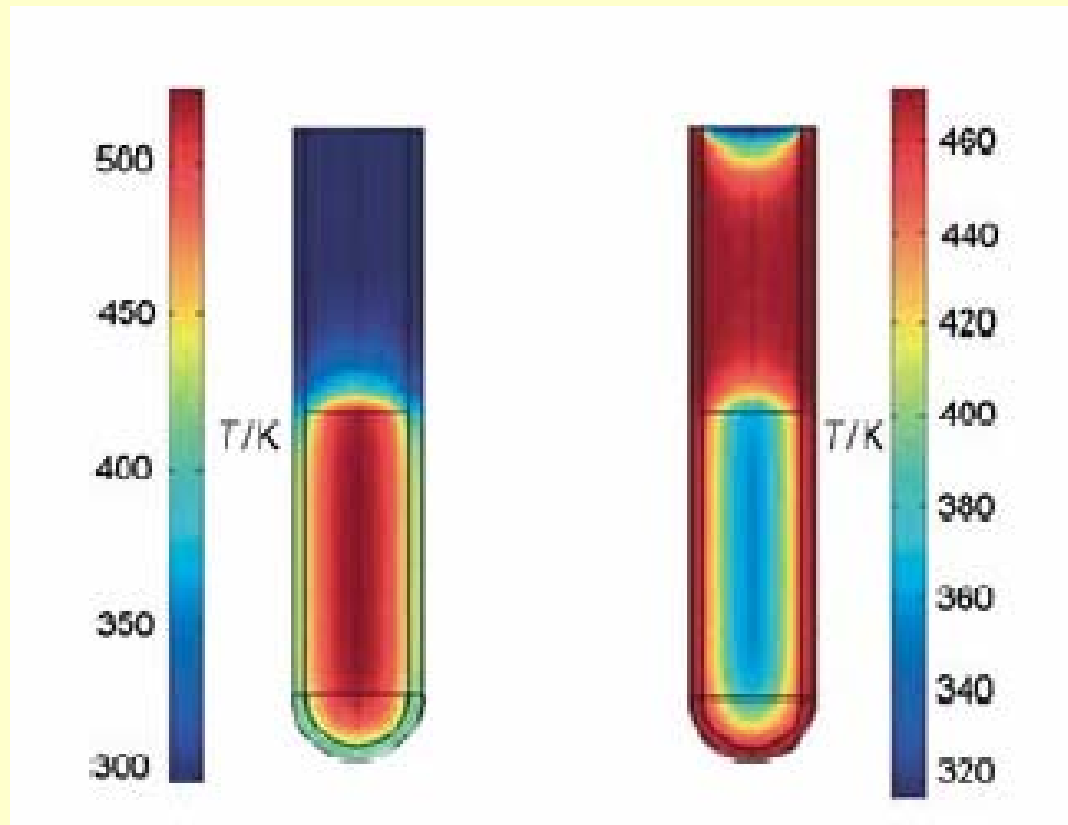
Loss factors ($\tan\delta$) of different solvents (2.45 GHz, 20 °C)

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

Temperature Gradients

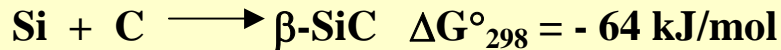
MW

Oil bath



Microwave-Assisted Synthesis

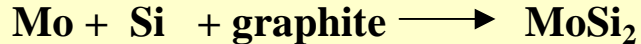
Examples of Microwave-assisted syntheses



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

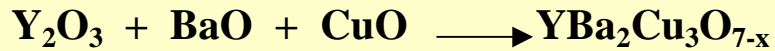
PbSe, PbTe, ZnS, ZnSe, ZnTe, Ag₂S



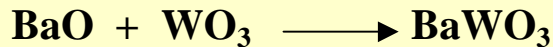
high mp, oxidation and carbidation resistance, metallic conductivity,
heating elements and high-T engine parts

Microwave-Assisted Synthesis

Mixed oxides



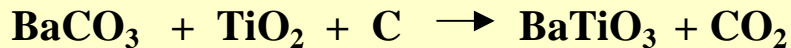
200 W, 25 min



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



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

Na₂HPO₄·2H₂O, KH₂PO₄ 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 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

