Solution Methods

Reactions in liquid state
Goals :
- Decrease diffusion paths
- Shorten reaction times
- Decrease reaction temperatures

Intimate mixing of components in solution, precipitation, filtration, washing, drying, calcination

- High degree of homogenization
- Large contact area
- Reduction of diffusion distances
- Faster reaction rates
- Lower reaction temperatures
- Metastable phases, smaller grain size, larger surface area
- Shaping to fibers, films, nanoparticles

Precursor Coprecipitation Method

Coprecipitation applicable to nitrates, acetates, oxalates, hydroxides, alkoxides, beta-diketonates

Requires: similar salt/complex solubilities
                similar precipitation rates
                no supersaturation

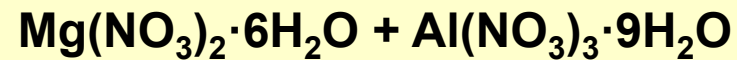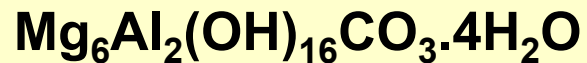Washing: water, organic solvents

Drying: evaporation
                azeotropic distillation
                freeze-drying

Disadvantage: difficult to prepare high purity, accurate stoichiometric phases if solubilities do not match

Coprecipitation Method

LDH = layered double hydroxides (hydrotalcites)

$Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$

$Mg(NO_3)_2 \cdot 6H_2O + Al(NO_3)_3 \cdot 9H_2O$
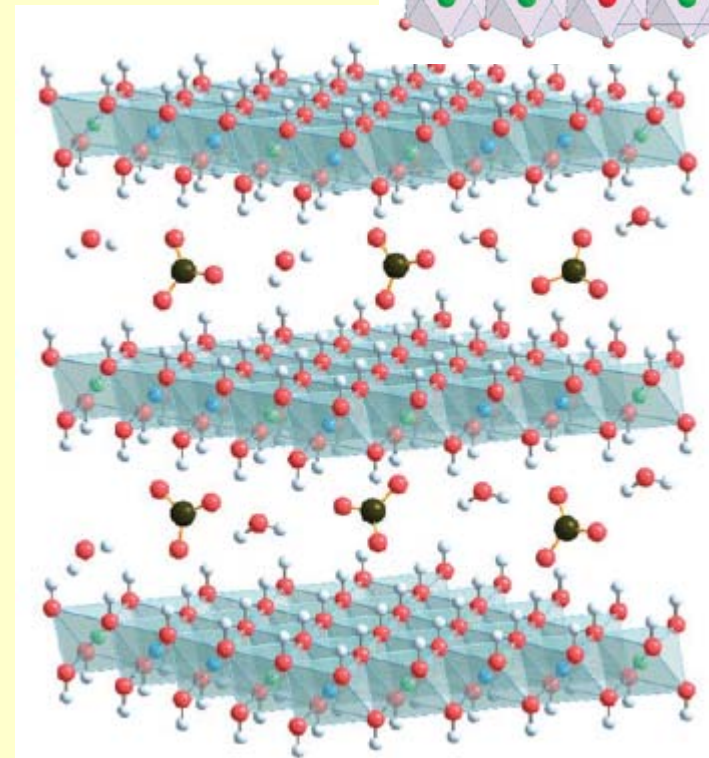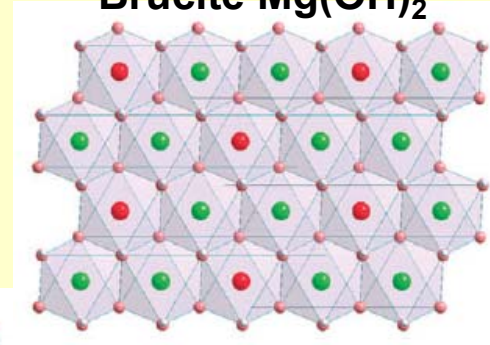**Aqueous solutions**
Low supersaturation

Addition of a NaOH solution
pH during precipitation kept constant at 9.0

Suspension aged at 373 K for 15 h w/stirring
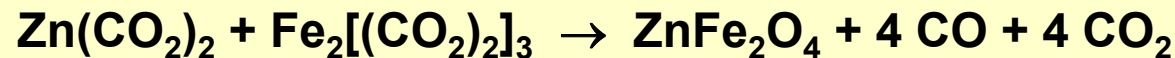
Centrifugation, washing, drying

Brucite $Mg(OH)_2$

Precursor Coprecipitation Method

Spinels

Oxalates: $Zn(CO_2)_2$ / $Fe_2[(CO_2)_2]_3$/H_2O, 1 : 1 mixing, H_2O evaporation, salts coprecipitation
Solid-solution mixing on atomic scale, filtration, calcination in air

$$Zn(CO_2)_2 + Fe_2[(CO_2)_2]_3 \rightarrow ZnFe_2O_4 + 4\ CO + 4\ CO_2$$

Al_2O_3 Bayer Process

bauxite + NaOH / pressure $\rightarrow$ $Al(OH)_4^-$ (+ insoluble $Fe(OH)_3$, TiO_2, SiO_2)
$Al(OH)_4^- + CO_2$ (g) $\rightarrow$ $Al(OH)_3$
2 $Al(OH)_3$ $\rightarrow$ α-Al_2O_3 + 3 H_2O

$BaTiO_3$

$BaCl_2 + TiOCl_2 + 2\ H_2C_2O_4 + 4\ H_2O + Ln^{3+}$ (dopants) $\rightarrow$
$$\rightarrow BaTiO(C_2O_4)2.4H_2O + 4\ HCl$$
Filtration, washing, drying, calcination @ 730 °C

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Coprecipitation Method

Spinel

$Al(NO_3)_3 + Mg(NO_3)_2 + H_2O$ Freeze-drying gives amorphous mixture

Calcination @ 800 °C (!!! low T)
Mixture-$Al(NO_3)_3$ / $Mg(NO_3)_2$ $\rightarrow$ random-$MgAl_2O_4$ + 6 NO_x + (10–3x) O_2

Ruby

Ion Exchange: $Al(NO_3)_3 + Cr(NO_3)_3$ $\rightarrow$ $Al(OH)_3 + Cr(OH)_3$ sol
Freeze drying gives solid $(Al/Cr)(OH)_3$ @ LN2 temperature, 5 Pa
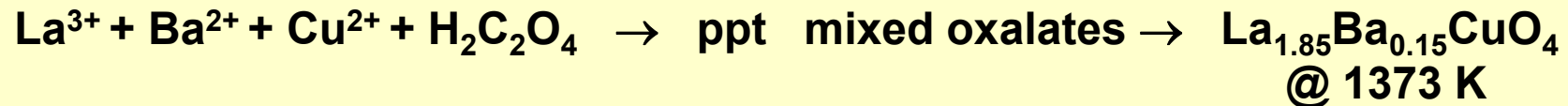Anealing @ 950 °C for 2.5 h gives solid solution $Al_{2-x}Cr_xO_3$

Zirconia (YSZ)

$ZrSiO_4$ (zircon) + NaOH $\rightarrow$ $Na_2ZrO_3 + Na_2SiO_3$
$Na_2ZrO_3 + Na_2SiO_3$ + HCl $\rightarrow$ $ZrOCl_2$ + SiO_2
$ZrOCl_2$ + NaOH + YCl_3 $\rightarrow$ $Zr(OH)_4$ / $Y(OH)_3$ $\rightarrow$ nano-Y/ZrO_2 (YSZ)

Coprecipitation Method

High-T_c Superconductors

$La^{3+} + Ba^{2+} + Cu^{2+} + H_2C_2O_4 \rightarrow$ ppt   mixed oxalates $\rightarrow$ $La_{1.85}Ba_{0.15}CuO_4$
@ 1373 K

Magnetic Garnets

$Y(NO_3)_3 + Gd(NO_3)_3 + FeCl_3 + NaOH \rightarrow$ ppt mixed $M(OH)_3 \rightarrow$ $Y_xGd_{3-x}Fe_5O_{12}$
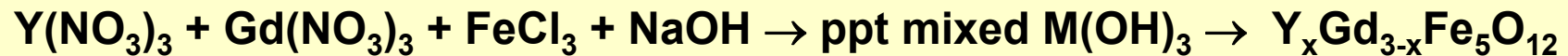
Firing @ 900 °C, 18-24 hrs, pellets, regrinding, repelletizing, repeated firings, removes $REFeO_3$ perovskite impurity

Isomorphous replacement of Y^{3+} for Gd^{3+} on dodecahedral sites, solid solution, similar rare earth ionic radii

Complete family accessible, $0 < x < 3$, $2Fe^{3+}$ O_h sites, $3Fe^{3+}$ T_d sites, $3RE^{3+}$ dodecahedral sites - tunable magnetic materials

Oxalate Coprecipitation

LiMPO$_4$ (M = Mn, Fe, Co, or Ni)
- olivine structure
- new cathode materials for lithium rechargeable batteries
- multicomponent olivine cathode materials LiMn$_{1/3}$Fe$_{1/3}$Co$_{1/3}$PO$_4$

Mn$_{1/3}$Fe$_{1/3}$Co$_{1/3}$(C$_2$O$_4$)$_3$ 2H$_2$O - stoichiometric, homogeneously mixed transition metal oxalate precursor
The differences in chemical behavior of Fe, Co, and Mn ions
- control of pH - different solubilities of MC$_2$O$_4$ 2H$_2$O
- control of atmosphere - Fe^{2+} get easily oxidized to Fe^{3+}
- control of temperature and aging time - FeC$_2$O$_4$·2H$_2$O and CoC$_2$O$_4$·2H$_2$O have temperature-dependent polymorphisms: monoclinic α (90 °C) and orthorhombic β (25 °C), MnC$_2$O$_4$·2H$_2$O forms only monoclinic

The final step:
Solid state reaction of Mn$_{1/3}$Fe$_{1/3}$Co$_{1/3}$(C$_2$O$_4$)$_3$ 2H$_2$O and LiH$_2$PO$_4$

Oxalate Coprecipitation

UO2 +ThO2 U1-xThxO2

- **Solutions of UIV (0.5 M, obtained by electroreduction of UO2(NO3)2 solution in 4 M HNO3 containing 0.5 M of hydrazine)**
- **ThIV (1.9 M in 8 M HNO3)**
- **Adding a stoichiometric amount of 1 M solution of oxalic acid**
- **precipitate was washed with water and dried**
- **Hydrothermal decomposition of**
- **under argon control of ox state of U 4+ vs 6+   addition of hydrazine**
- **different solubilities of MC_2O_4 $2H_2O$**
- **control of atmosphere – U^{4+} get easily oxidized to U^{6+}**
- **control of temperature and aging time 18 h at 250 °C in an autoclave**
- **Spark plasma sintering**

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Pechini and Citrate Gel Method

$$\text{HO} - \overset{\displaystyle -\text{COOH}}{\underset{\displaystyle -\text{COOH}}{\overline{}}} - \text{COOH}$$
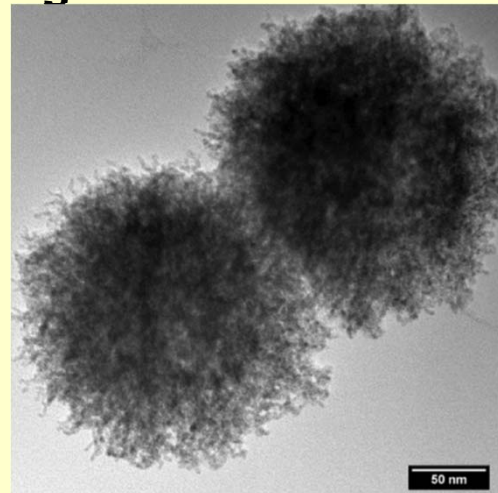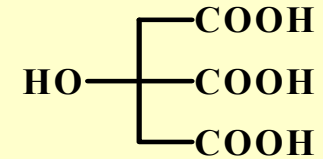
- **Aqueous solution of metal ions**
- **Chelate formation with citric acid**
- **Polyesterification with polyfunctional alcohol on heating**
- **Further heating leads water evaporation and to resin, transparent glassy gel**
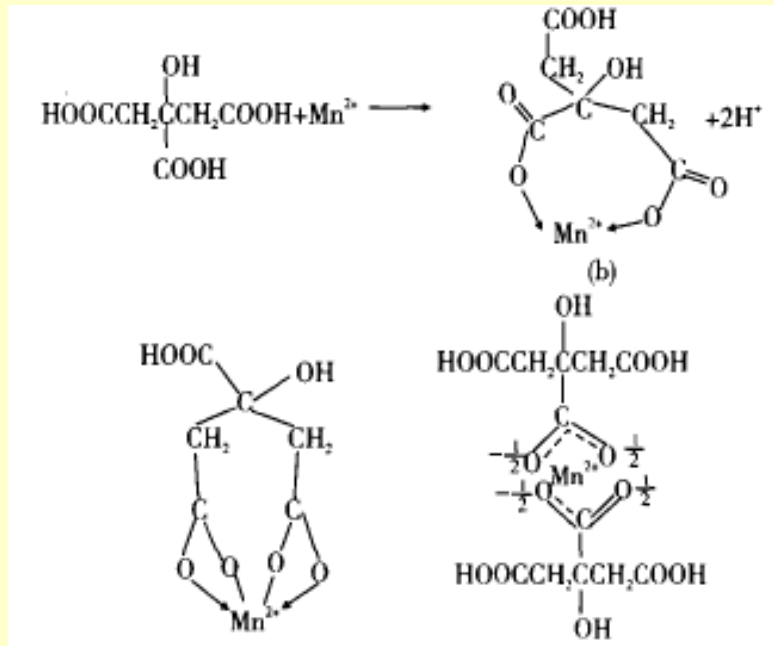- **Calcination provides oxide powder**

Control of stoichiometry by initial reagent ratio

Complex compositions, mixture of metal ions
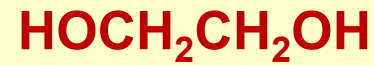
Good homogeneity, mixing at the molecular level

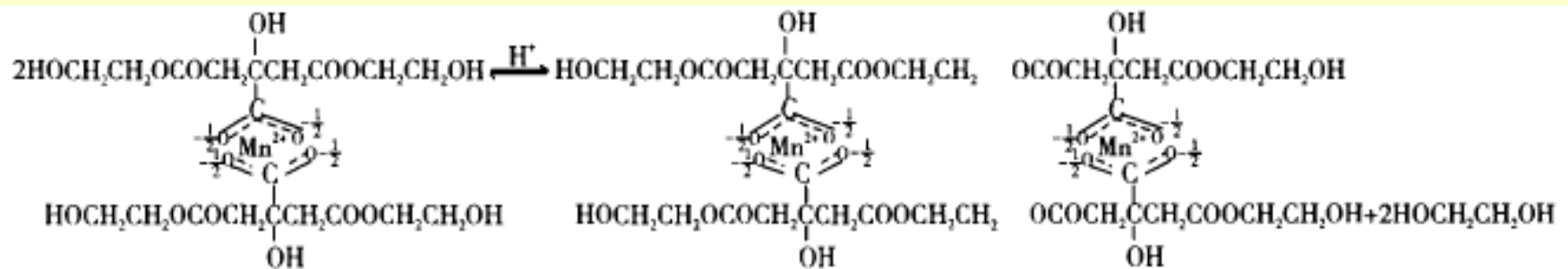**Low firing temperatures**

Pechini and Citrate Gel Method
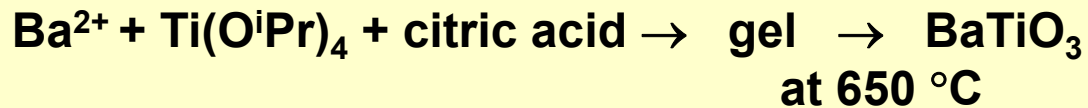

Chelation
Complexation-coordination polymers

HOCH₂CH₂OH

Polyesterification
polycondensation

Pechini and Citrate Gel Method

BaTiO$_3$
by conventional powder method at 1200 °C

Ba^{2+} + Ti(O^{i}Pr)$_4$ + citric acid $\rightarrow$ gel $\rightarrow$ BaTiO$_3$
at 650 °C

ScMnO$_3$
Sc$_2$O$_3$ + 6 HCOOH $\rightarrow$ 2 Sc(HCOO)$_3$ + 3 H$_2$O
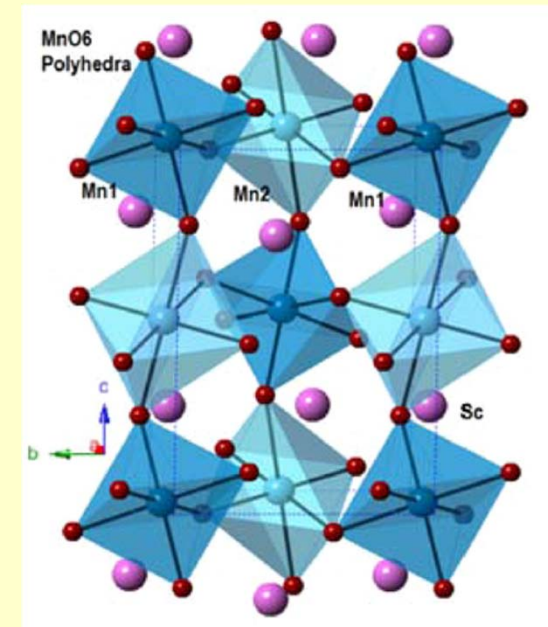**MnCO$_3$ + 2 HCOOH $\rightarrow$ Mn(HCOO)$_2$ + CO$_2$ + H$_2$O**
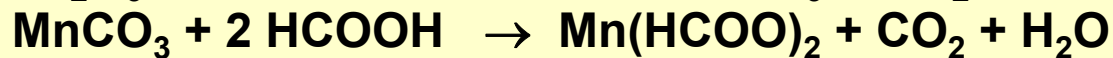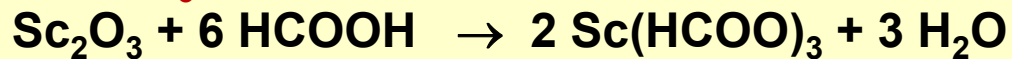
Added to citric acid, heating, water removal
Gel formation
Calcination @ 690 °C gives perovskite ScMnO$_3$

Without citric acid only a mixture of Sc$_2$O$_3$ and Mn$_2$O$_3$ is formed
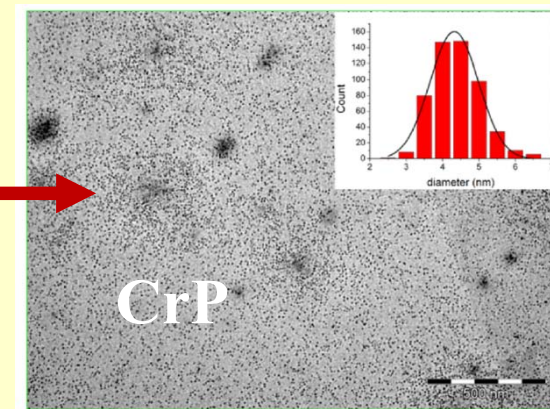

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Single Source Precursors

- Compounds containing desired elements in a proper **stoichiometric ratio**
- **Easy chemical pathway** for ligand removal
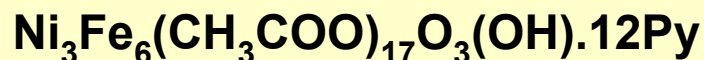

$$(M\text{-}O\text{-}SiO_3)_x$$
$$-\ H_2O$$
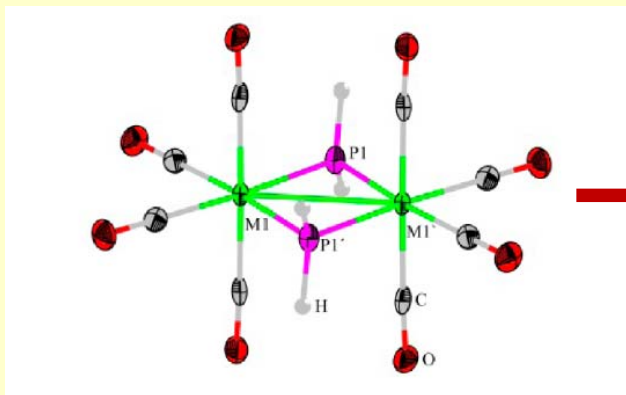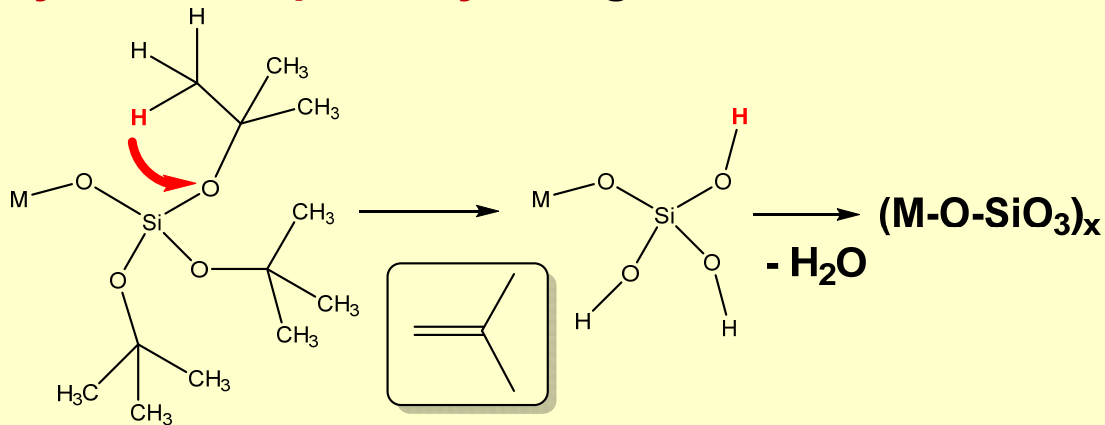
Thermolysis
180 °C for 1 h

Hexadecylamine (HDA)
Oleic acid (OlA)
Mesitylene

CrP

Known phases in Cr-P system: Cr_3P, Cr_2P, Cr_2P_7, CrP, CrP_2, CrP_4

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Double Salt Precursors

Double salts of known and controlled stoichiometry such as:
$Ni_3Fe_6(CH_3COO)_{17}O_3(OH).12Py$

Burn off organics 200-300 ^oC, then 1000 ^oC in air for 2-3 days
Product highly crystalline phase pure $NiFe_2O_4$ spinel
Good way to make chromite spinels, important tunable magnetic materials
Juggling the electronic-magnetic properties of the O_h and T_d ions in the spinel lattice

Chromite spinel	Precursor	Ignition T, ^oC
$MgCr_2O_4$	$(NH_4)_2Mg(CrO_4)_2.6H_2O$	1100-1200
$NiCr_2O_4$	$(NH_4)_2Ni(CrO_4)_2.6H_2O$	1100
$MnCr_2O_4$	$MnCr_2O_7.4C_5H_5N$	1100
$CoCr_2O_4$	$CoCr_2O_7.4C_5H_5N$	1200
$CuCr_2O_4$	$(NH_4)_2Cu(CrO_4)_2.2NH_3$	700-800
$ZnCr_2O_4$	$(NH_4)_2Zn(CrO_4)_2. 2NH_3$	1400
$FeCr_2O_4$	$(NH_4)_2Fe(CrO_4)_2$	1150

Vegard's Law in Solid-Solutions

Vegard law behavior:

A linear relationship exists between the concentration of the substitute element and a property of a solid-solution, e.g., the size of the lattice parameters, cell volume, band gap, transition temperatures, ……

Any property P of a solid-solution member $A_{1-x}B_x$ (x = 0–1) is the atom fraction weighted average of the end-members
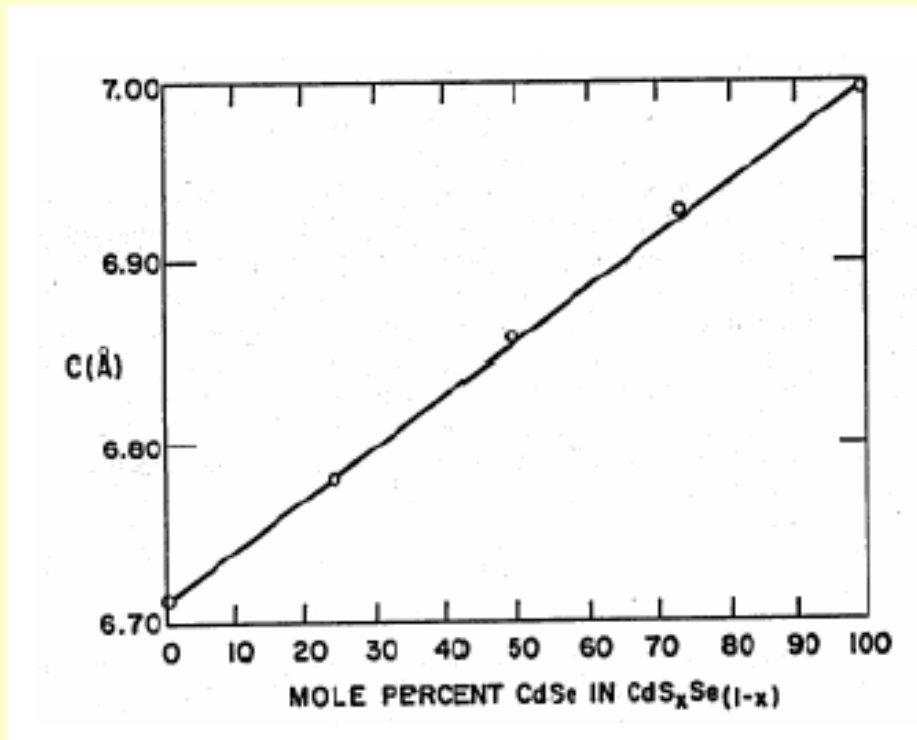
The composition of the $A_{1-x}B_x$ phase can be calculated from Vegard's law

The lattice parameter of a solid solution alloy _a_ will be given by a linear dependence of lattice parameter on composition:

$a(A_{1-x}B_x) = x\,a(B) + (1 - x)\,a(A)$

Vegard's Law in $CdSe_{1-x}S_x$

$c(CdSe_{1-x}S_x) = x\, c(CdS) + (1 - x)\, c(CdSe)$

Anion radius

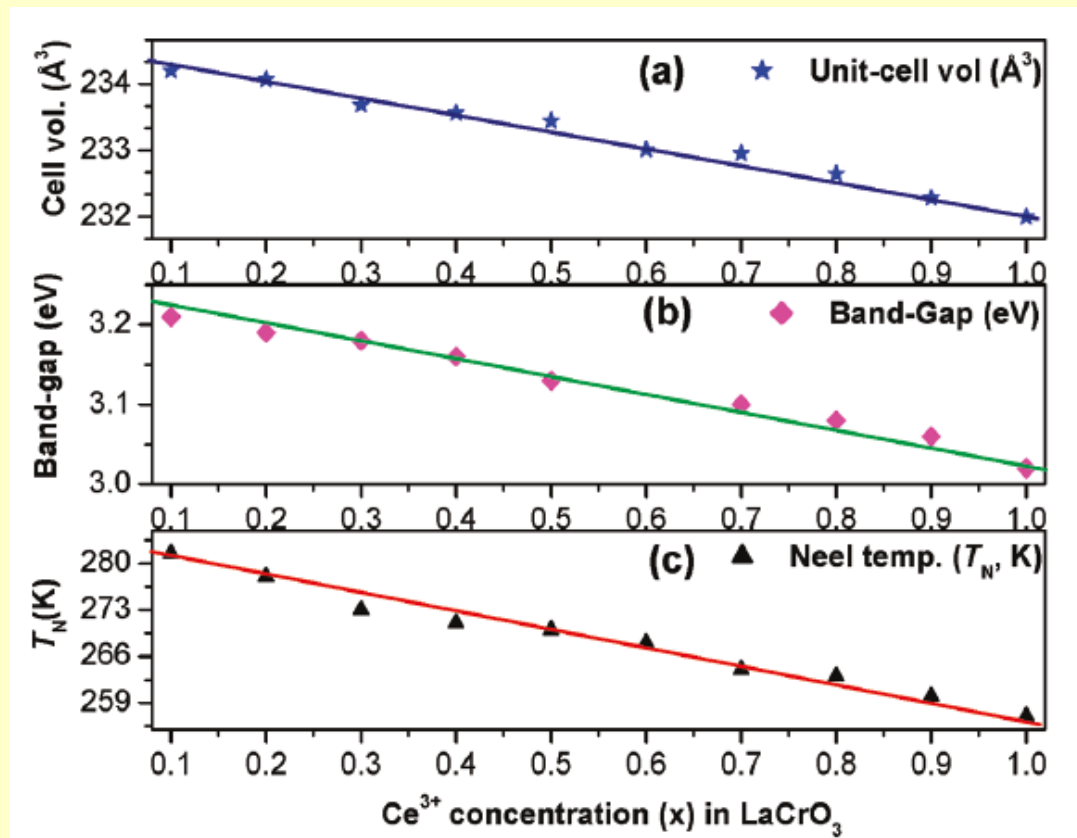**S^{2-} 1.84 Å**

Se^{2-} 1.98 Å

a hexagonal wurzite structure
a cubic zinc blende
a high pressure form with the NaCl structure

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Vegard's Law in $La_{1-x}Ce_xCrO_3$

Any property P of a solid-solution member is the atom fraction weighted average of the end-members:

$P(A_{1-x}B_x) = x\, P(B) + (1 - x)\, P(A)$

Flux Method

LiCl - LiF , 1 atm
Data from FTsalt - FACT salt databases
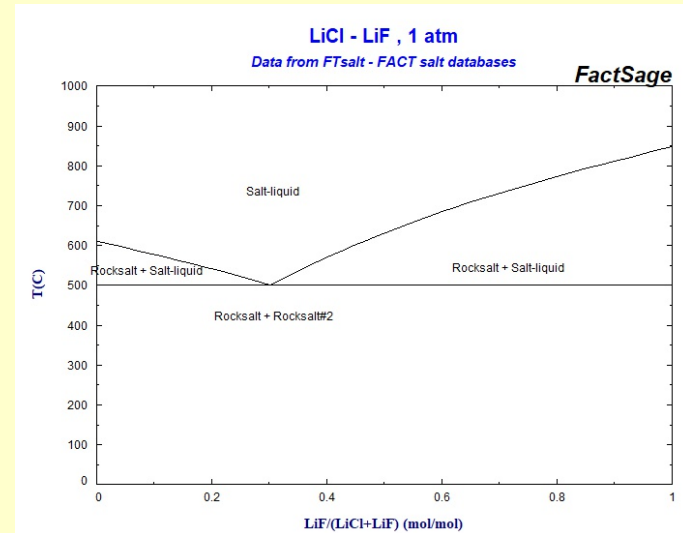FactSage

Molten salts (inert or reactive)

Metals, metal oxides

MNO_3, MOH, (M = alkali metal)

M_2Q_x (M = alkali metal, Q = S, Se, Te)

FLINAK: LiF-NaF-KF

FLIBE: $LiF-BeF_2$

- Molten salts - ionic, low mp, eutectics, completely ionized
- Act as solvents or reactants, T = 250-550 °C
- Enhanced diffusion, reduced reaction temperatures in comparison with direct powder method
- Products finely divided solids, powders of high surface area (SA)
- Slow cooling to grow single crystals
- Separation of water insoluble product from a water soluble flux
- Incorporation of the molten salt ions in products prevented by using salts with ions of much different sizes than the ones in the product
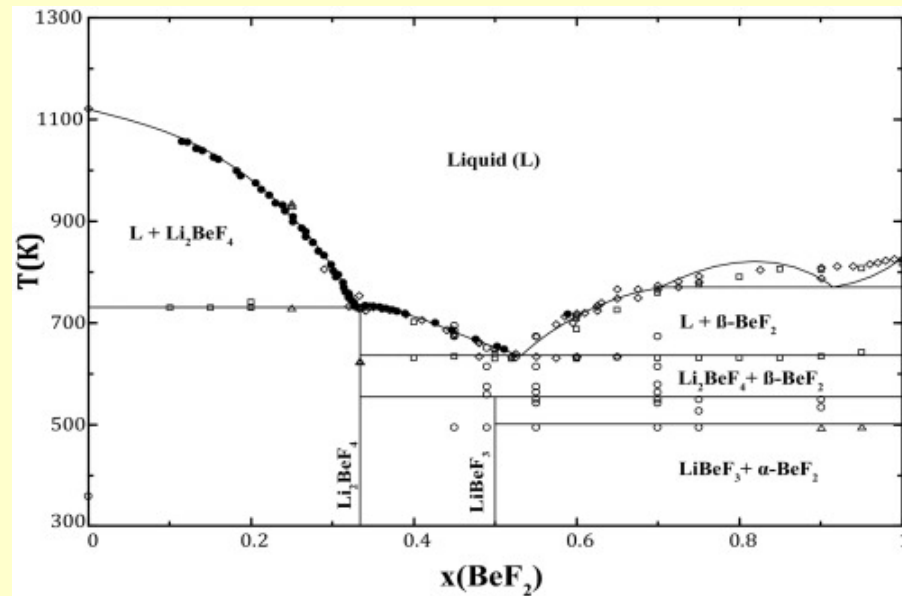($PbZrO_3$ in a B_2O_3 flux)

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FLINAK and FLIBE
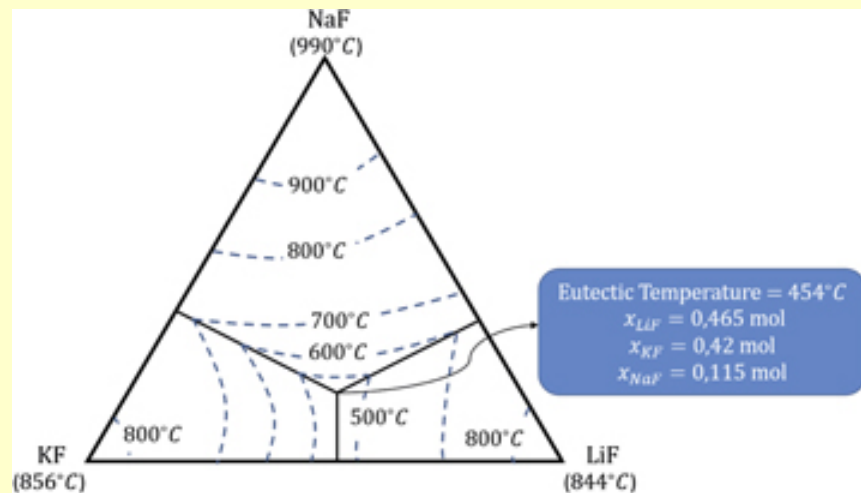
FLINAK: LiF-NaF-KF

Melting point 454 °C
Eutectic (46.5 - 11.5 - 42 mol %)
A coolant in the molten salt reactors

FLIBE: LiF-BeF$_2$

Melting point of 360 °C
Eutectic (50% BeF$_2$)
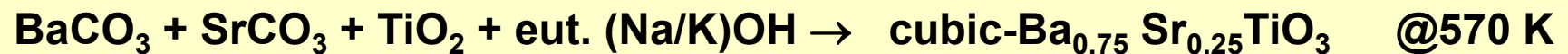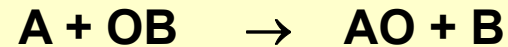**A neutron moderator and coolant in the nuclear reactors**

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Flux Method

Lux-Flood formalism

oxide = strong base

acid = oxide acceptor $A + OB \rightarrow AO + B$

base = oxide donor

$Zr(SO_4)_2$ + eut. (Li/K)$NO_3 \rightarrow$ ZrO_2 @700 K

$Zr(SO_4)_2$ + eut. (Li/K)$NO_2 \rightarrow$ ZrO_2 @540 K

$ZrOCl_2$ + eut. (Na/K)$NO_3 \rightarrow$ ZrO_2 amorph. @540 K   calcine $\rightarrow$ t-ZrO_2

$ZrOCl_2$ + YCl_3 + eut. (Na/K)$NO_3 \rightarrow$ ZrO_2 (YSZ)   @720 K

$BaCO_3$ + $SrCO_3$ + TiO_2 + eut. (Na/K)OH $\rightarrow$ cubic-$Ba_{0.75}Sr_{0.25}TiO_3$ @570 K
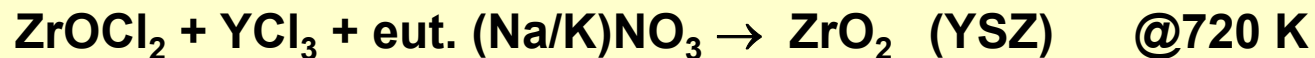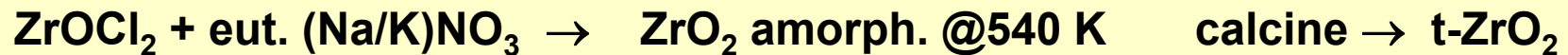
Flux Method

Zeolites

Fly ash (aluminosilicates) + NaOH, NH$_4$F, NaNO$_3$ → sodalite, cancrinite

Metal phosphates

NH$_4$H$_2$PO$_4$ + (Na/K)NO$_3$ + M(NO$_3$)$_2$ → (Na/K)MPO$_4$

β cage

● Si
◉ Al
○ O

8.9 Å

Mixed-metal oxides
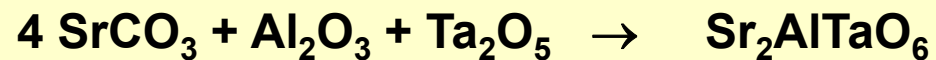
4 SrCO$_3$ + Al$_2$O$_3$ + Ta$_2$O$_5$ → Sr$_2$AlTaO$_6$
900 °C in SrCl$_2$ flux
1400 °C required for a direct reaction

Chalcogenides

K$_2$Te$_x$ + Cu → K$_2$Cu$_5$Te$_5$ K$_2$Te$_x$ reactive flux, 350 °C

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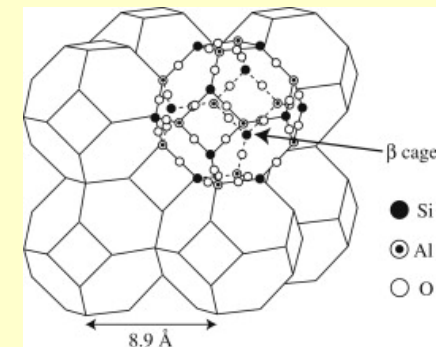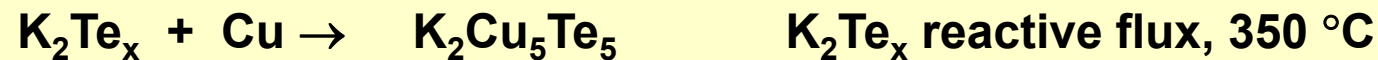
Flux Method

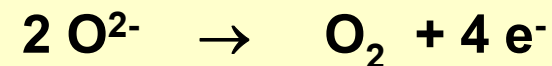**Electrolysis in molten salts**

Reduction of TiO$_2$ pellets to Ti sponge in a CaCl$_2$ melt at 950 °C

O^{2-} dissolves in CaCl$_2$, diffuses to the graphite anode

insulating TiO$_2$ $\rightarrow$ **TiO$_{2-x}$ conductive**

Graphite anode
anodic oxidation   **2 O^{2-}** $\rightarrow$ **O$_2$ + 4 e$^-$**

Cathode TiO$_2$ pellet
cathodic reduction   **Ti^{4+} + 4 e$^-$** $\rightarrow$ **Ti**
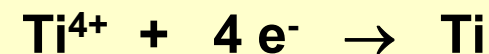
Ionic Liquids

Organic cations (containing N, P)
Ammonium, imodazolium, pyridinum,....
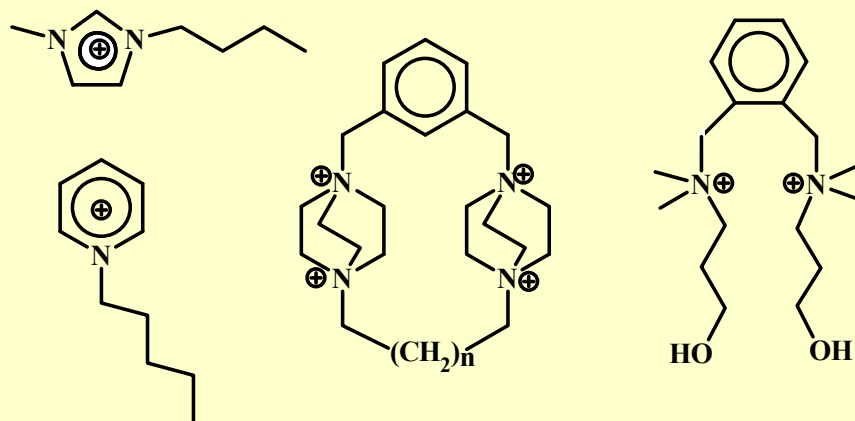
Inorganic anions: Cl^-, $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, PF_6^-, $SnCl_3^-$, BCl_3^-, BF_4^-, NO_3^-, $OSO_2CF_3^-$ (triflate), $CH_3C_6H_4SO_3^-$, $N(SO_2CF_3)_2^-$, PO_4^{3-}

Ionic Liquids (IL)

Oldest known (1914): $EtNH_3^+ NO_3^-$ mp 12 $^\circ$C

- **Liquids at room temperature or low mp**

- **Thermal operating range from -40 $^\circ$C to 400 $^\circ$C**

- **Higly polar, noncoordinating, completely ionized**

- **Nonvolatile – no detectable vapor pressure**

- **Nonflamable, nonexplosive, nonoxidizing, high thermal stability**

- **Electrochemical window > 4 V (not oxidized or reduced)**

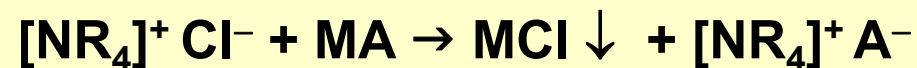- **IL immiscible with organic solvents**

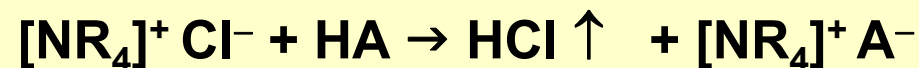- **Hydrophobic IL immiscible with water**

Synthesis of Ionic Liquids

NR_3 + RCl $\rightarrow$ $[NR_4]^+ Cl^-$

Aluminates
$[NR_4]^+ Cl^-$ + $AlCl_3$ $\rightarrow$ $[NR_4]^+ [AlCl_4]^-$
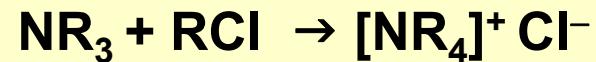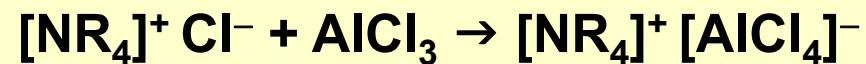
Metal halide elimination
$[NR_4]^+ Cl^-$ + MA $\rightarrow$ MCl $\downarrow$ + $[NR_4]^+ A^-$

Reaction with an acid
$[NR_4]^+ Cl^-$ + HA $\rightarrow$ HCl $\uparrow$ + $[NR_4]^+ A^-$

Ion exchange
$[NR_4]^+ Cl^-$ + Ion exchanger A $\rightarrow$ $[NR_4]^+ A^-$
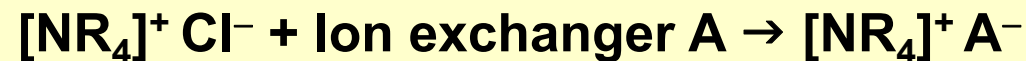
Halogenoaluminate(III) Ionic Liquids

The most widely studied class of IL

**High sensitivity to moisture – handling under vacuum
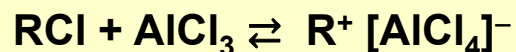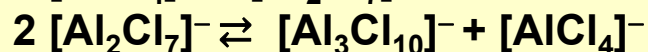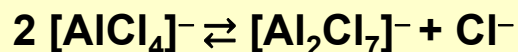or inert atmosphere in glass/teflon**

Equilibria in Halogenoaluminate(III) IL

$$RCl + AlCl_3 \rightleftarrows R^+ [AlCl_4]^-$$

Autosolvolysis K_{eq} = 10^{-16} to 10^{-17} at 40 ºC

$$2\,[AlCl_4]^- \rightleftarrows [Al_2Cl_7]^- + Cl^-$$
$$2\,[Al_2Cl_7]^- \rightleftarrows [Al_3Cl_{10}]^- + [AlCl_4]^-$$

Acidic: excess of $AlCl_3$ $x(AlCl_3)$ > 0.5
Basic: excess of Cl^- $x(AlCl_3)$ < 0.5
Neutral: $[AlCl_4]^-$ $x(AlCl_3)$ = 0.5

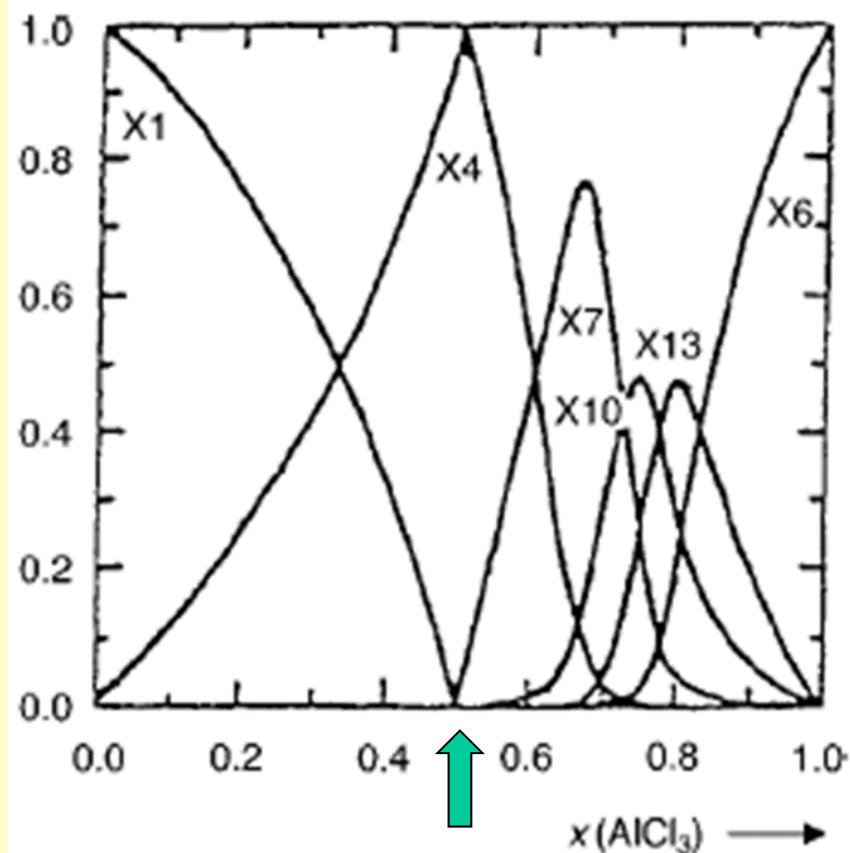**X1 = Cl^- X10 = $[Al_3Cl_{10}]^-$**
X4 = $[AlCl_4]^-$ X13 = $[Al_4Cl_{13}]^-$
X7 = $[Al_2Cl_7]^-$ X6 = Al_2Cl_6

Halogenoaluminate(III) Ionic Liquids

$2\ [AlCl_4]^- \rightleftarrows [Al_2Cl_7]^- + Cl^-$
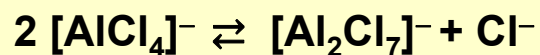
Autosolvolysis K_{eq} = 10^{-16} to 10^{-17} at 40 °C

Superacidity Scale, H_0

Acidic IL with an excess of $AlCl_3$

$HCl\ +\ [Al_2Cl_7]^- \rightleftarrows\ H^+ +\ 2\ [AlCl_4]^-$
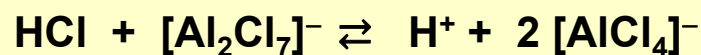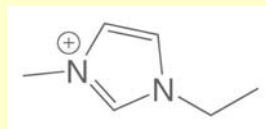
Proton extremely poorly solvated high reactivity

Superacid   [EMIM]Cl/$AlCl_3$/HCl
H_0 = -19
(HSO_3F: H_0 = -15)

Latent acidity

$MCl\ +\ [Al_2Cl_7]^- \rightleftarrows\ M^+ +\ 2\ [AlCl_4]^-$
buffered IL

$B\ +\ M^+ +\ [AlCl_4]^- \rightleftarrows\ MCl\ +\ B\text{-}AlCl_3$

Liquid	$-H_0$	Solid
HF-SbF$_5$	28	
FSO$_3$H-SbF$_5$ (magic acid)		
	24	
acidic ionic liquid	20	
HF-TaF$_5$		
	16	SO$_4{}^{2-}$/ZrO$_2$
FSO$_3$H		
CF$_3$SO$_3$H		H$_3$PW$_{12}$O$_{40}$
100% H$_2$SO$_4$	12	Nafion
HF		
	8	

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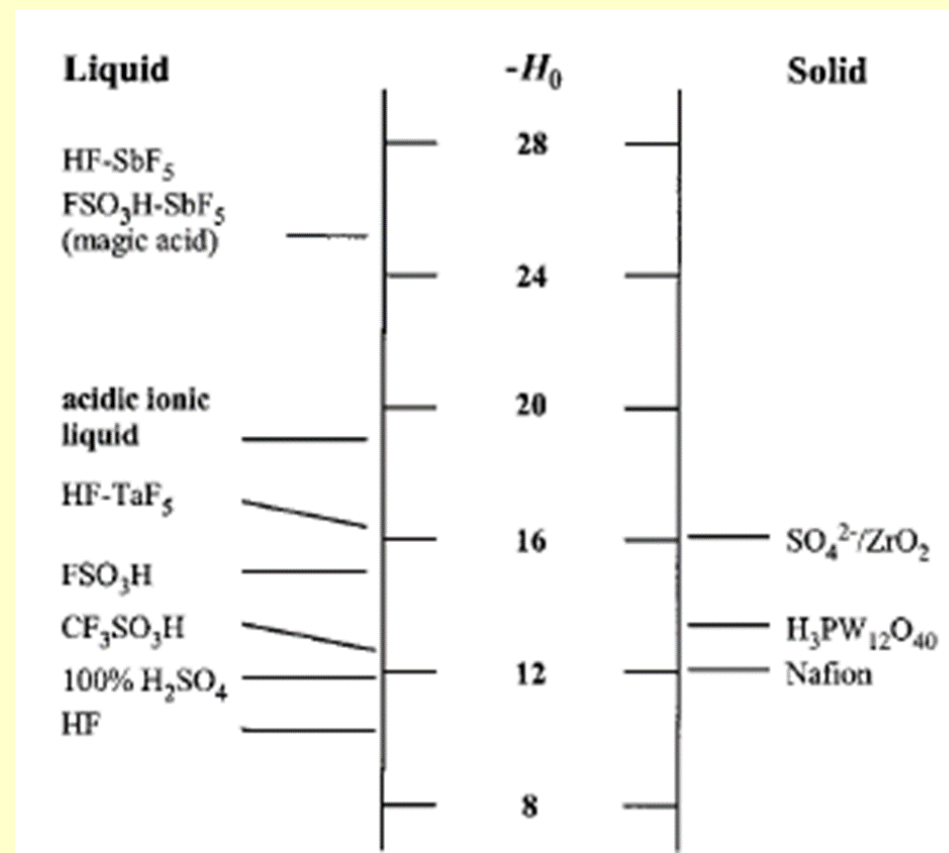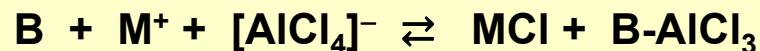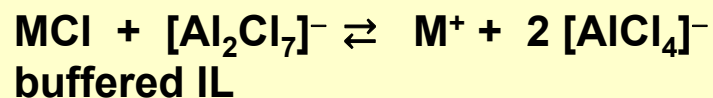
Superacidic [EMIM]Cl/AlCl$_3$/HCl
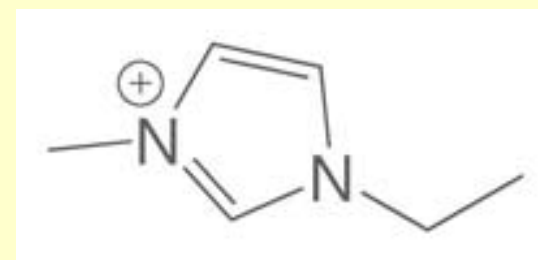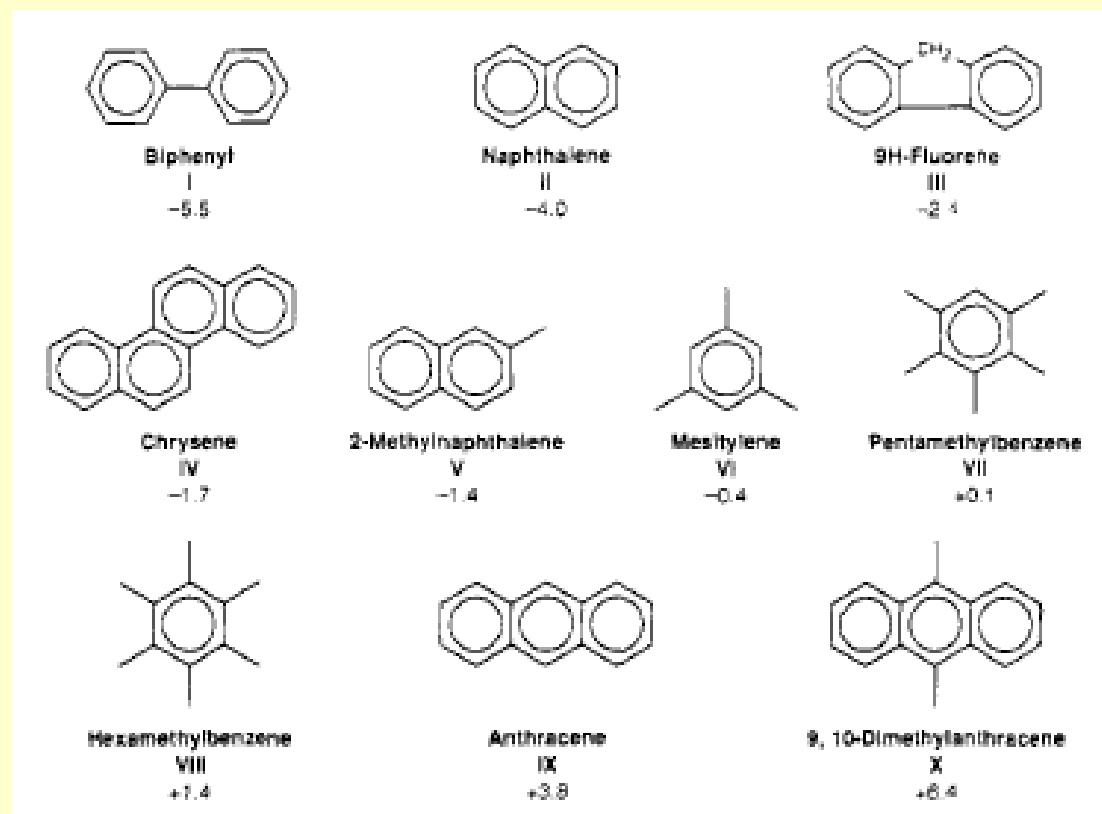
I = not protonated
II = slightly protonated
III and IV = 10-20 %
V = 75-90%
VI-VIII = nearly completely
IX and X = completely

log K$_b$ in HF

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Melting Point of Ionic Liquids

Melting point is influenced by:
Cation – low symmetry, weak imtermolecular interactions, good distribution of charge
Anion – increasing size leads to lower mp
Composition – Phase diagram

Phase diagram of [EMIM]Cl/AlCl$_3$
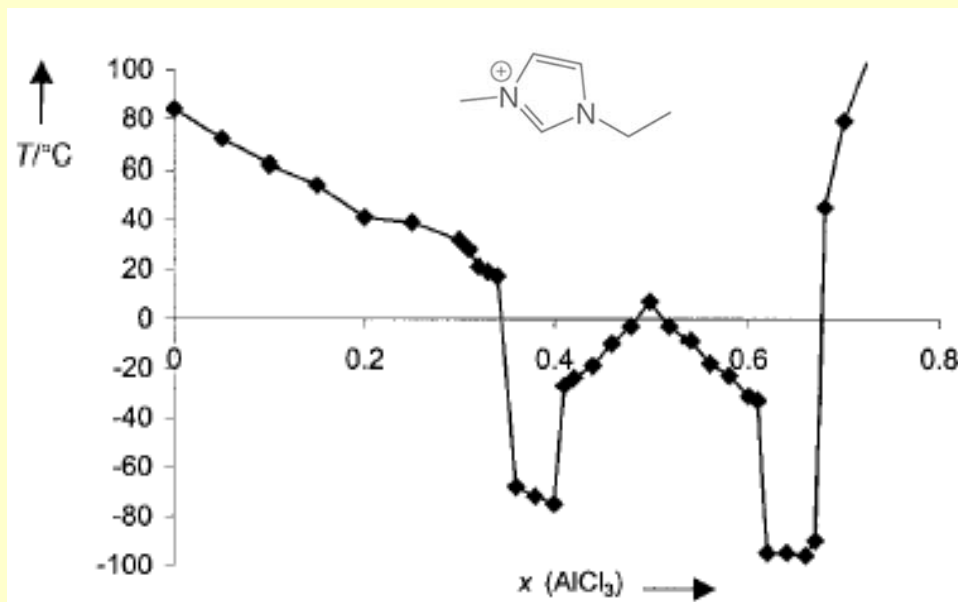
R	X	mp/°C
Me	Cl	125
Et	Cl	87
n-Bu	Cl	65
Et	NO$_3$	38
Et	AlCl$_4$	7
Et	BF$_4$	6
Et	CF$_3$SO$_3$	−9
Et	(CF$_3$SO$_3$)$_2$N	−3
Et	CF$_3$CO$_2$	−14
n-Bu	CF$_3$SO$_3$	16

Density and Viscosity of Ionic Liquids

The density of IL decreases as the bulkiness of the organic cation increases:
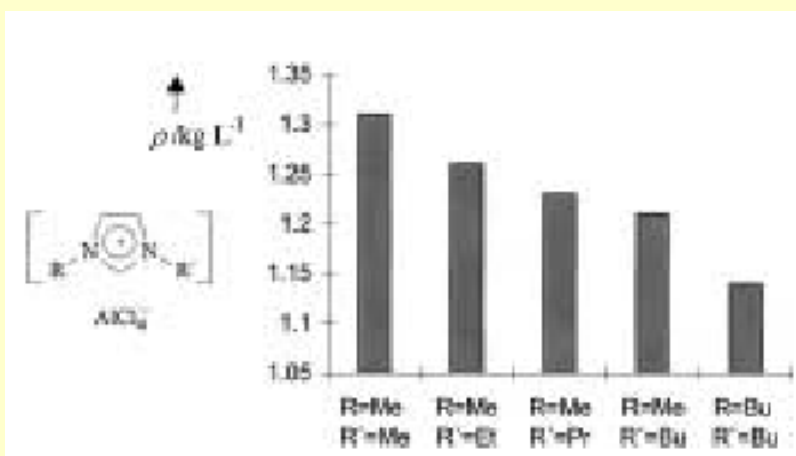
The viscosity of IL depends on van der Waals interactions and H-bonding

[BMIM]	Anion $[A]^-$	$\eta\ [cP]$
	$CF_3SO_3^-$	90
	$n\text{-}C_4F_9SO_3^-$	373
	CF_3COO^-	73
	$n\text{-}C_3F_7COO^-$	182
	$(CF_3SO_2)_2N^-$	52

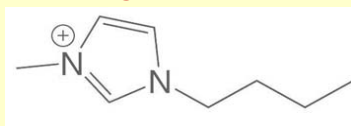# Solubility in/of Ionic Liquids

Variation of the alkyl group
Increasing nonpolar character of the cation increases solubility of nonpolar solutes

Water solubility depends on the anion
[BMIM]   **Water-soluble: Br, CF_3COO, CF_3SO_3**
                      Water-immiscilble: PF_6, $(CF_3SO_2)_2N$

IL are miscible with organic solvent if their dielectric constant is above a certain limit given by the cation/anion combination

Polarity by $E_{(T)}(30)$ scale

$[EtNH_3][NO_3]$ 0.95
between CF_3CH_2OH and water

[BMIM] PF_6 as methanol

1-hexene / IL (wt.%)

- $(CF_3SO_2)_2N$
- CF_3COO^-
- $CF_3SO_3^-$
- PF_6^-
- NO_3^-
- BF_4^-

30
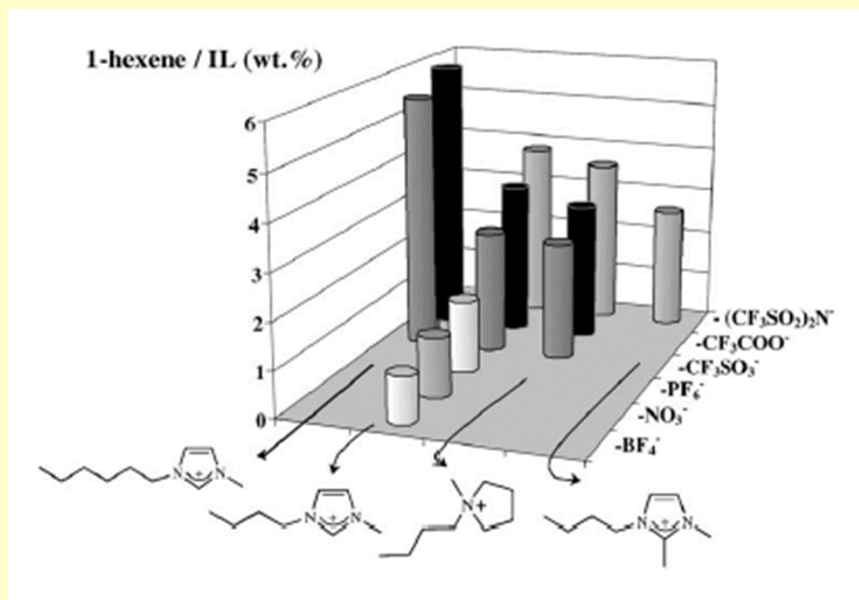
Applications of Ionic Liquids

Electrodeposition

Metals and alloys (also nanoscopic): Al, $CoAl_x$, $CuAl_x$, $FeAl_x$, $AlTi_x$
Semiconductors Si, Ge, GaAs, InSb, CdTe

Electrodeposition of a Bi-Sr-Ca-Cu alloy (precursor to SC oxides)

Melt of MeEtImCl at 120 ºC
$BiCl_3$, $SrCl_2$, $CaCl_2$, $CuCl_2$ dissolve well

Constituent	$BiCl_3$	$SrCl_2$	$CaCl_2$	$CuCl_2$
Concentration	0.068	0.50	0.18	0.050
(mol kg^{-1} MeEtImCl)				

Substrate Al
-1.72 V vs the Ag/Ag^+ reference electrode

Applications of Ionic Liquids

Olefin polymerization

Ethene + TiCl$_4$ + AlEtCl$_2$ in acidic IL $\rightarrow$ Polyethylene

Ethene + Cp$_2$TiCl$_2$ + Al$_2$Me$_3$Cl$_3$ in acidic IL $\rightarrow$ Polyethylene

Cp$_2$TiCl$_2$ + [cation]$^+$[Al$_2$Cl$_7$]$^-$ $\rightleftarrows$ [Cp$_2$TiCl]$^+$ + [cation]$^+$ + 2 [AlCl$_4$]$^-$
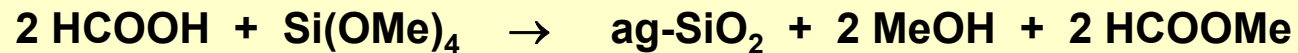
Olefin hydrogenation

Cyclohexene + H$_2$ + [RhCl(PPh$_3$)$_3$] (Wilkinson's catalyst) $\rightarrow$ Cyclohexne

Applications of Ionic Liquids

Biphasic solvent systems: IL / organic solvent

Preparation of aerogels

$2 \text{ HCOOH} + \text{Si(OMe)}_4 \rightarrow \text{ag-SiO}_2 + 2 \text{ MeOH} + 2 \text{ HCOOMe}$

Natural gas sweetening (H_2S, CO_2 removal)

Electrolytes in batteries or solar cells

Dissolving spent nuclear fuel (U^{4+} oxidized to U^{6+})

Extraction

Enyzme activity