

Precursor Methods

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**

Coprecipitation Method

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

Requires: **similar salt solubilities**
 similar precipitation rates
 no supersaturation

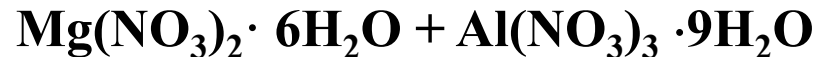
Washing: **water, organic solvents**

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)



aqueous solutions

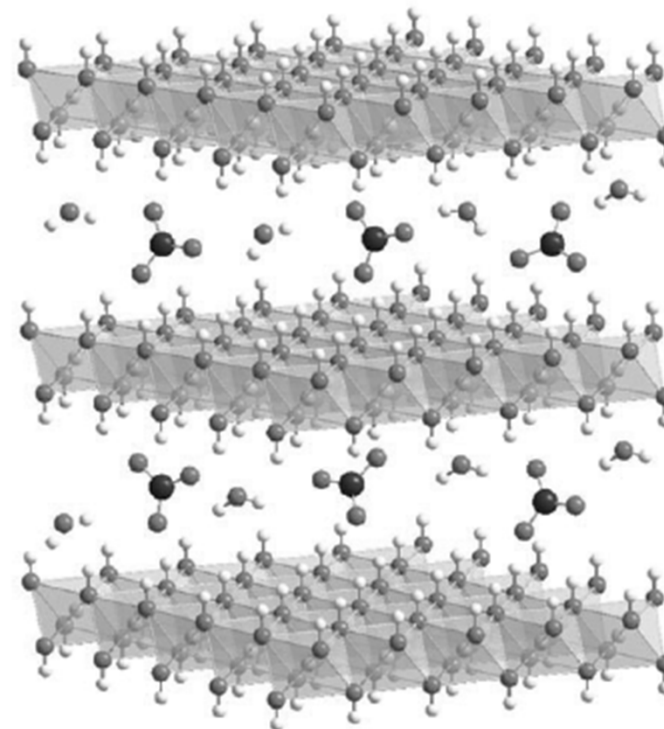
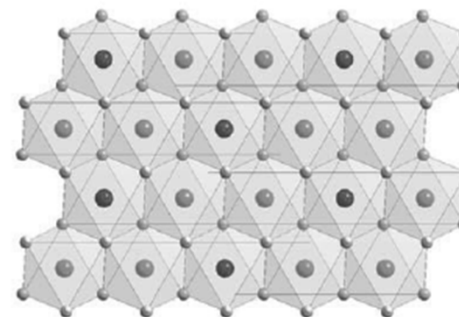
low supersaturation

addition of an NaOH solution

pH during precipitation kept constant at 9.0

suspension aged at 373 K for 15 h w/stirring

centrifugation, washing, drying

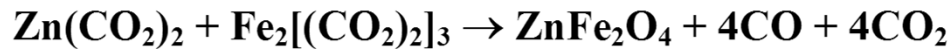


Coprecipitation Method

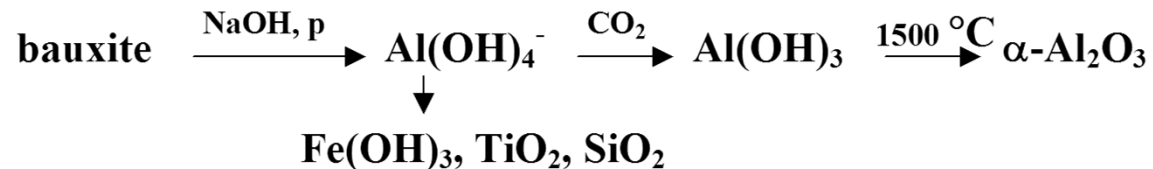
Spinels

oxalates: $\text{Zn}(\text{CO}_2)_2/\text{Fe}_2[(\text{CO}_2)_2]_3/\text{H}_2\text{O}$ 1 : 1 mixing, H_2O evaporation,
salts coprecipitation

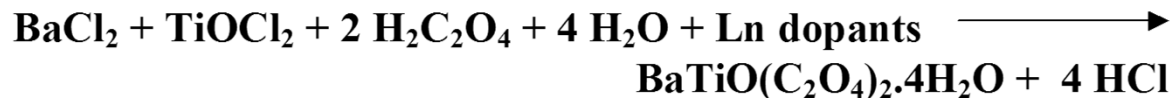
Solid-solution mixing on atomic scale, filter, calcine in air



Al_2O_3 Bayer Process



BaTiO_3

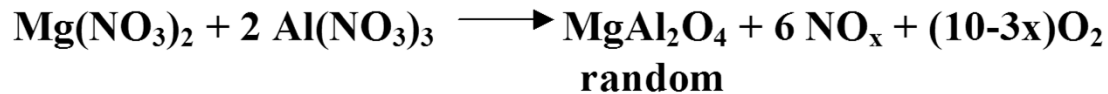


filtration, washing, drying, calcination @ 730°C

Coprecipitation Method

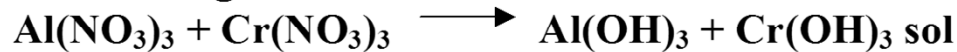
Spinel

$\text{Al}(\text{NO}_3)_3 + \text{Mg}(\text{NO}_3)_2 + \text{H}_2\text{O}$ freeze-drying gives amorphous mixture, calcination @ 800 °C !!! low T



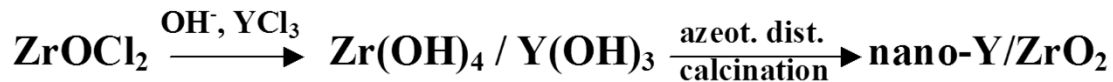
Ruby

Ion exchange



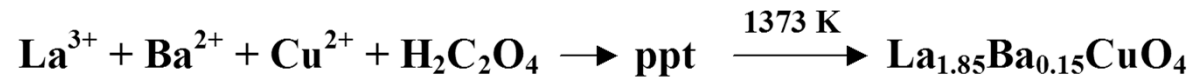
freeze drying gives solid $(\text{Al}/\text{Cr})(\text{OH})_3$ @ LN₂ temperature, 5 Pa
annealing @ 950 °C for 2.5 h gives solid solution $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$

Zirconia

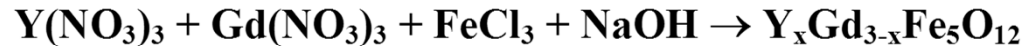


Coprecipitation Method

High- T_c Superconductors



Magnetic garnets, tunable magnetic materials



**Firing @ 900 °C, 18-24 hrs, pellets, regrinding, repelletizing,
repeated firings, removes REFeO₃ perovskite impurity**

**Isomorphous replacement of Y³⁺ for Gd³⁺ on dodecahedral sites,
solid solution, similar rare earth ionic radii**

**complete family accessible, 0 < x < 3, 2Fe³⁺ O_h sites, 3Fe³⁺ T_d sites,
3RE³⁺ dodecahedral sites**

Oxalate Coprecipitation

LiMPO₄ (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}PO₄**

Mn_{1/3}Fe_{1/3}Co_{1/3}(C₂O₄)₃·2H₂O

stoichiometric, homogeneously mixed transition metal oxalate precursor

the differences in chemical behavior of Fe, Co, and Mn ions

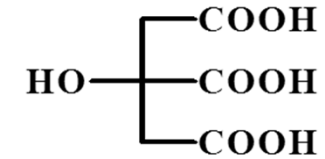
- control of pH - different solubilities of **MC₂O₄·2H₂O**
- control of atmosphere - **Fe²⁺** get easily oxidized to **Fe³⁺**
- control of temperature and aging time - **FeC₂O₄·2H₂O** and **CoC₂O₄·2H₂O** have temperature-dependent polymorphisms: monoclinic **α** (90 °C) and orthorhombic **β** (25 °C), **MnC₂O₄·2H₂O** forms only monoclinic

Solid state reaction of Mn_{1/3}Fe_{1/3}Co_{1/3}(C₂O₄)₃·2H₂O and LiH₂PO₄

Pechini and Citrate Gel Method

Aqueous solution of metal ions

Chelate formation with citric acid



Polyesterification with polyfunctional alcohol on heating

**Further heating leads to resin, transparent glassy gel
calcination provides oxide powder**

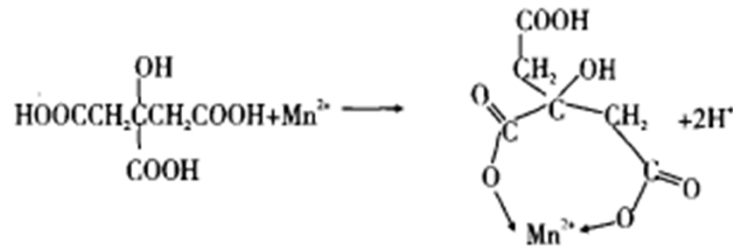
Control of stoichiometry by initial reagent ratio

Complex compositions, mixture of metal ions

Good homogeneity, mixing at the molecular level

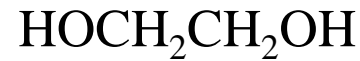
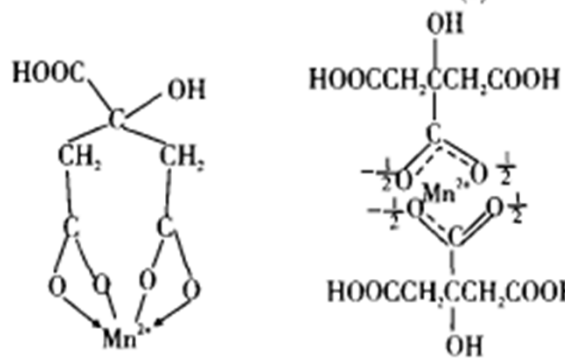
Low firing temperatures

Pechini and Citrate Gel Method

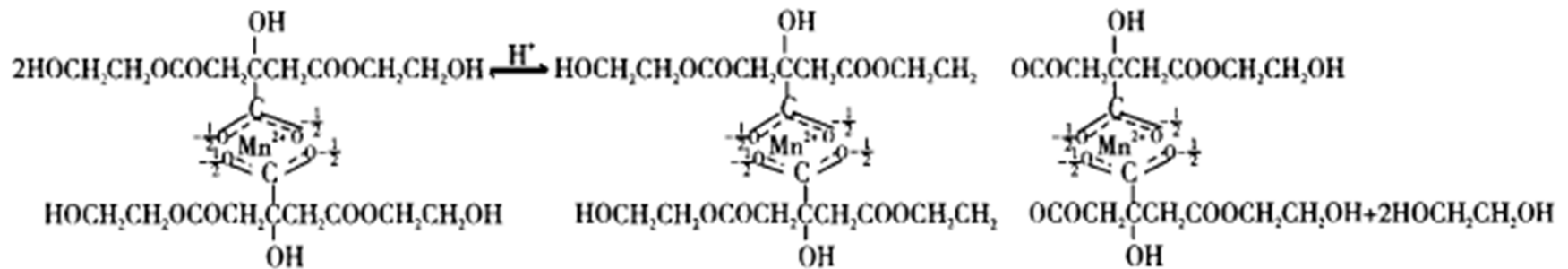


Chelation

Complexation-coordination polymers



Polyesterification polycondensation

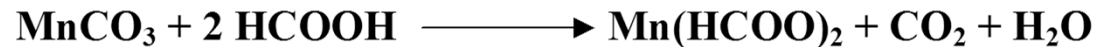
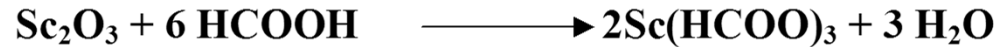


Pechini and Citrate Gel Method

BaTiO₃

by conventional powder method at 1200 °C

Ba²⁺ + Ti(OⁱPr)₄ + citric acid at 650 °C



added to citric acid, water removal, calcination @ 690 °C gives
ScMnO₃

without citric acid only mixture of Sc₂O₃ and Mn₂O₃ is formed

Double Salt Precursors

Double salts of known and controlled stoichiometry such as:



Burn off organics 200-300 °C, then 1000 °C in air for 2-3 days

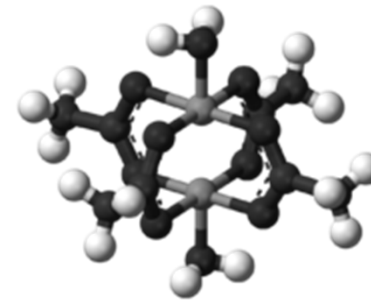
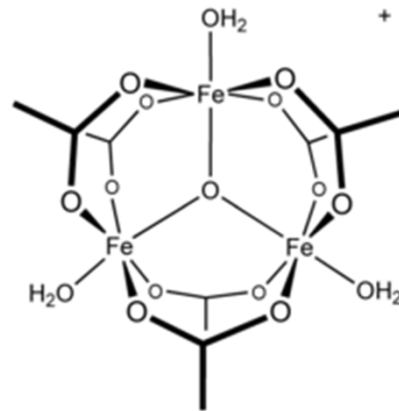
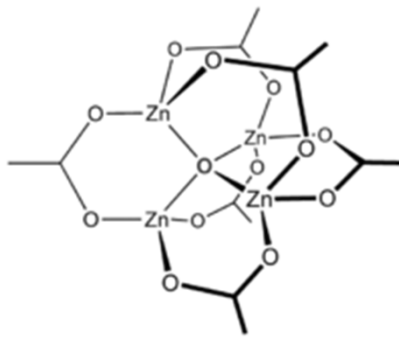
Product highly crystalline phase pure NiFe_2O_4 spinel

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

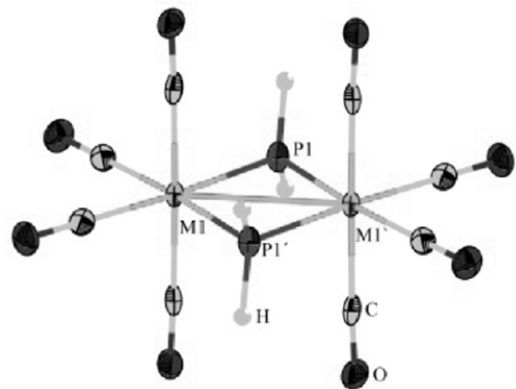
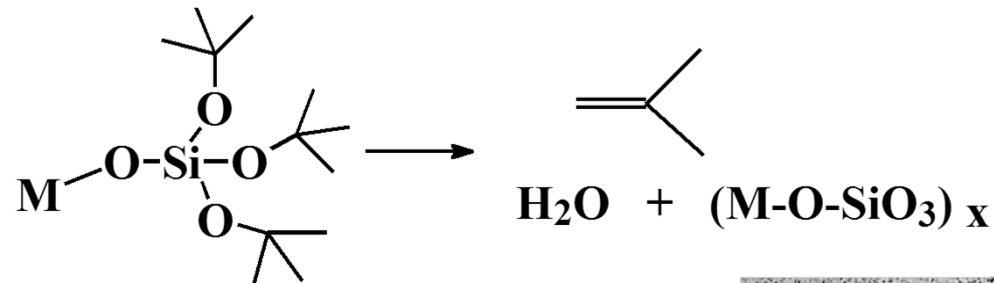
Chromite spinel	Precursor	Ignition T, °C
MgCr_2O_4	$(\text{NH}_4)_2\text{Mg}(\text{CrO}_4)_2\cdot 6\text{H}_2\text{O}$	1100-1200
NiCr_2O_4	$(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2\cdot 6\text{H}_2\text{O}$	1100
MnCr_2O_4	$\text{MnCr}_2\text{O}_7\cdot 4\text{C}_5\text{H}_5\text{N}$	1100
CoCr_2O_4	$\text{CoCr}_2\text{O}_7\cdot 4\text{C}_5\text{H}_5\text{N}$	1200
CuCr_2O_4	$(\text{NH}_4)_2\text{Cu}(\text{CrO}_4)_2\cdot 2\text{NH}_3$	700-800
ZnCr_2O_4	$(\text{NH}_4)_2\text{Zn}(\text{CrO}_4)_2\cdot 2\text{NH}_3$	1400
FeCr_2O_4	$(\text{NH}_4)_2\text{Fe}(\text{CrO}_4)_2$	1150

Double Salt Precursors



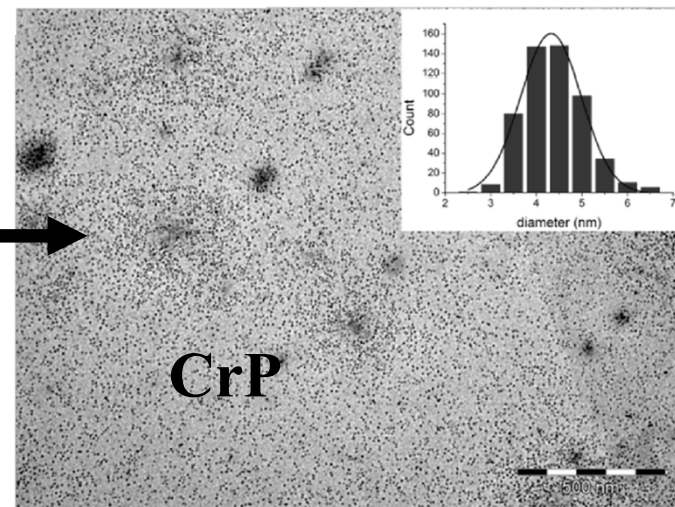
Single Source Precursors

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



Thermolysis
180 °C for 1 h

Hexadecylamine (HDA)
Oleic acid (OLA)
Mesitylene



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

Vegard's Law

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.

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

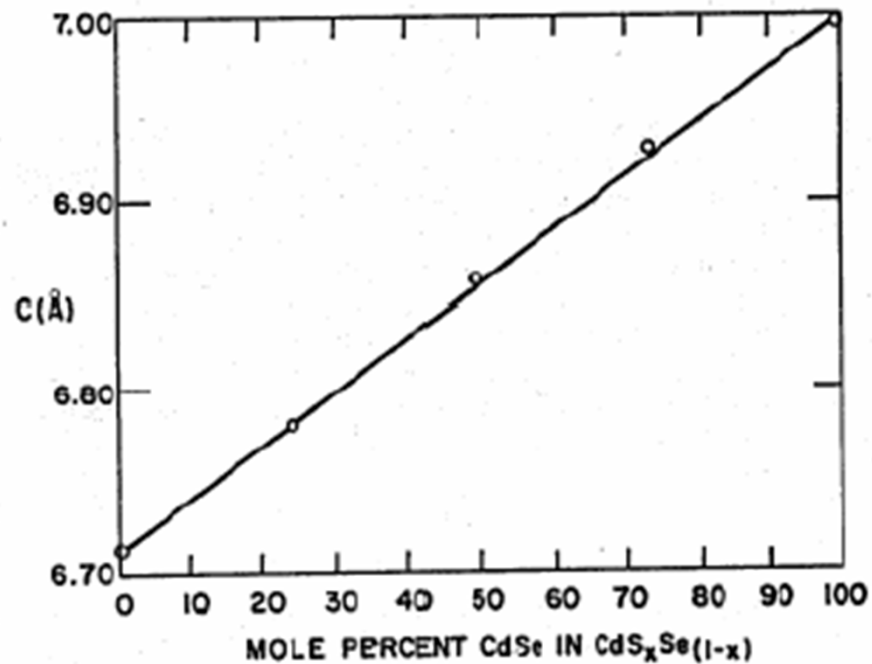
The composition of the $A_{1-x}B_x$ alloy can be calculated from Vegard's law

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

$$c(\text{CdSe}_{1-x}\text{S}_x) = x c(\text{CdS}) + (1-x) c(\text{CdSe})$$



Anion radius

S^{2-} 1.84 Å

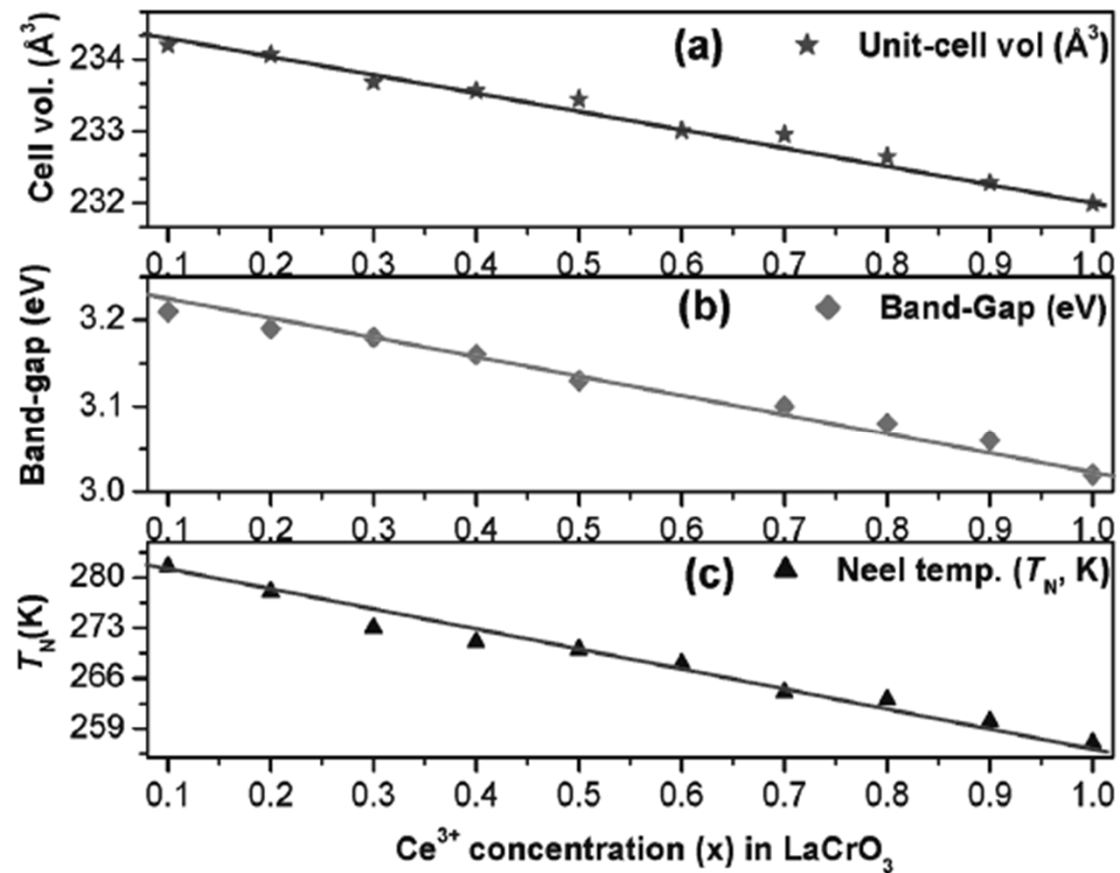
Se^{2-} 1.98 Å

a hexagonal wurzite structure

a cubic zinc blende

a high pressure form with the NaCl structure

$\text{La}_{1-x}\text{Ce}_x\text{CrO}_3$



Flux Method

Molten salts (inert or reactive), oxides, metals

MNO_3 , MOH , ($M = \text{alkali metal}$)

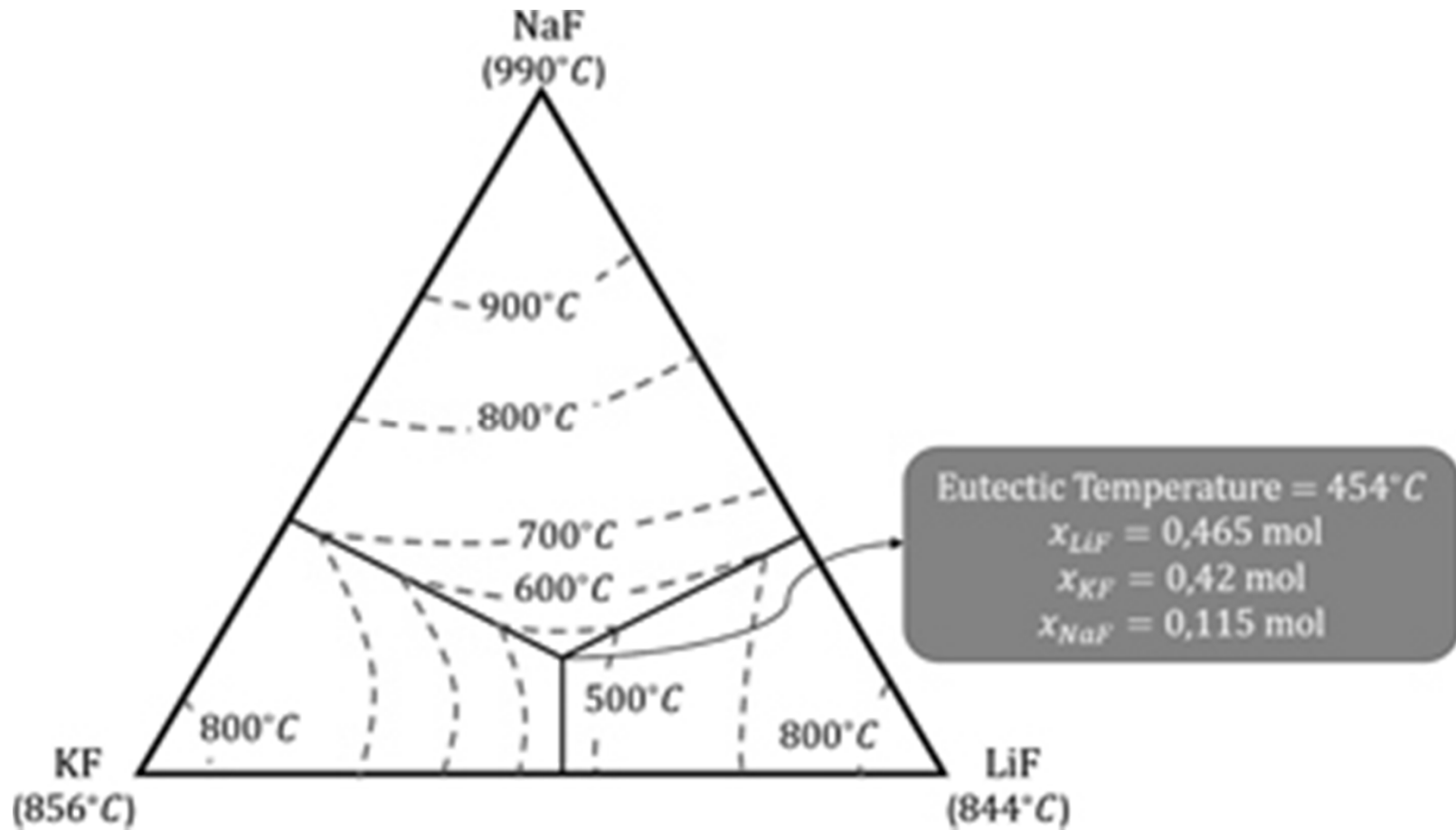
FLINAK: $LiF-NaF-KF$

M_2Q_x ($M = \text{alkali metal}$, $Q = S, Se, Te$)

- **molten salts - ionic, low mp, eutectics, completely ionized**
- **act as solvents or reactants, $T = 250-550\text{ }^\circ\text{C}$**
- **enhanced diffusion, reduced reaction temperatures in comparison with powder method**
- **products finely divided solids, high surface area (SA)**
- **slow cooling to grow crystals**
- **separation of water insoluble product from a water soluble flux**
- **incorporation of the molten salt ions in product prevented by using salts with ions of much different sizes than the ones in the product**

($PbZrO_3$ in a B_2O_3 flux)

FLINAK: LiF-NaF-KF



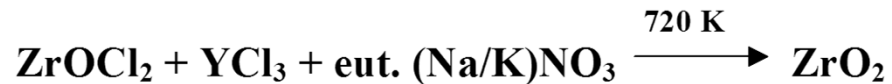
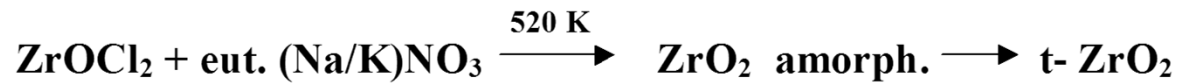
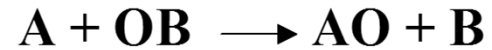
Flux Method

Lux-Flood formalism

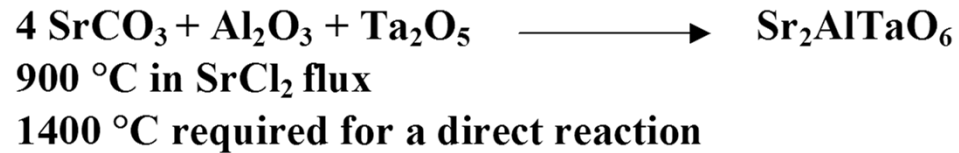
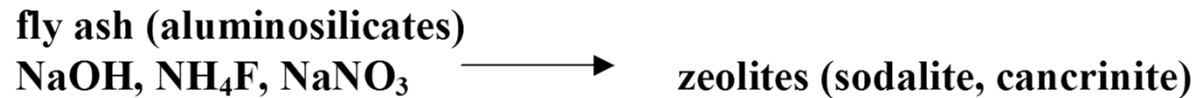
oxide = strong base

acid = oxide acceptor

base = oxide donor



Flux Method



Flux Method

Electrolysis in molten salts

Reduction of TiO₂ pellets to Ti sponge in a CaCl₂ melt at 950 °C

O²⁻ dissolves in CaCl₂, diffuses to the graphite anode

insulating TiO₂ → TiO_{2-x} conductive

**graphite anode
anodic oxidation**



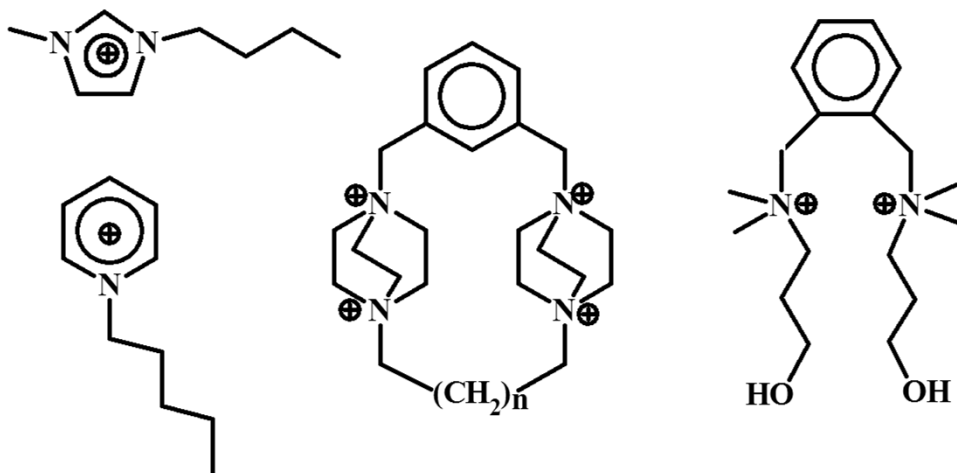
**cathode TiO₂ pellet
cathodic reduction**



Ionic Liquids

Organic cations (containing N, P)

Inorganic anions: Cl^- , AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$, PF_6^- , SnCl_3^- , BCl_3^- , BF_4^- , NO_3^- , $\text{OSO}_2\text{CF}_3^-$ (triflate), $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$, $\text{N}(\text{SO}_2\text{CF}_3)_2^-$, PO_4^{3-}

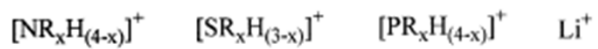


Ionic Liquids

Oldest known (1914) : $\text{EtNH}_3^+\text{NO}_3^-$ mp 12 °C

- Liquids at room temperature or low mp
- Thermal operating range from -40 °C to 400 °C
- Highly polar, noncoordinating, completely ionized
- Nonvolatile – no detectable vapor pressure
- Nonflammable, nonexplosive, nonoxidizing, high thermal stability
- Electrochemical window > 4V (not oxidized or reduced)
- Immiscible with organic solvents
- Hydrophobic IL immiscible with water

Ionic Liquids



1

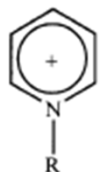
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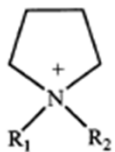
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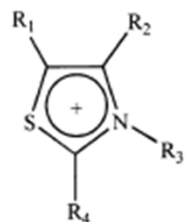
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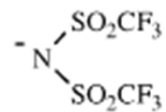
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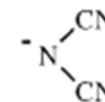
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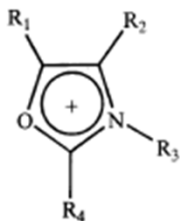
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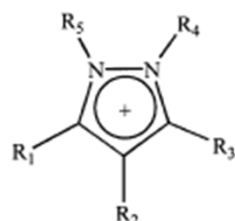
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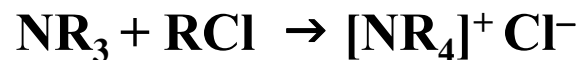


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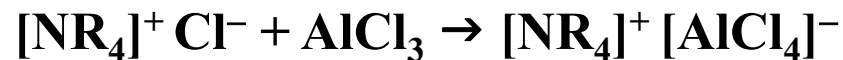


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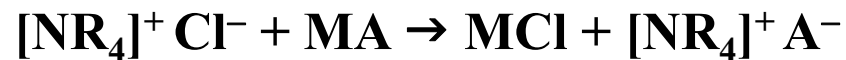
Synthesis of Ionic Liquids



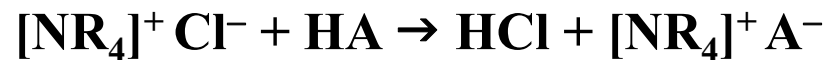
Aluminates



Metal halide elimination



Reaction with an acid



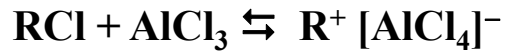
Ion exchange



Halogenoaluminate(III) Ionic Liquids

The most widely studied class of IL

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



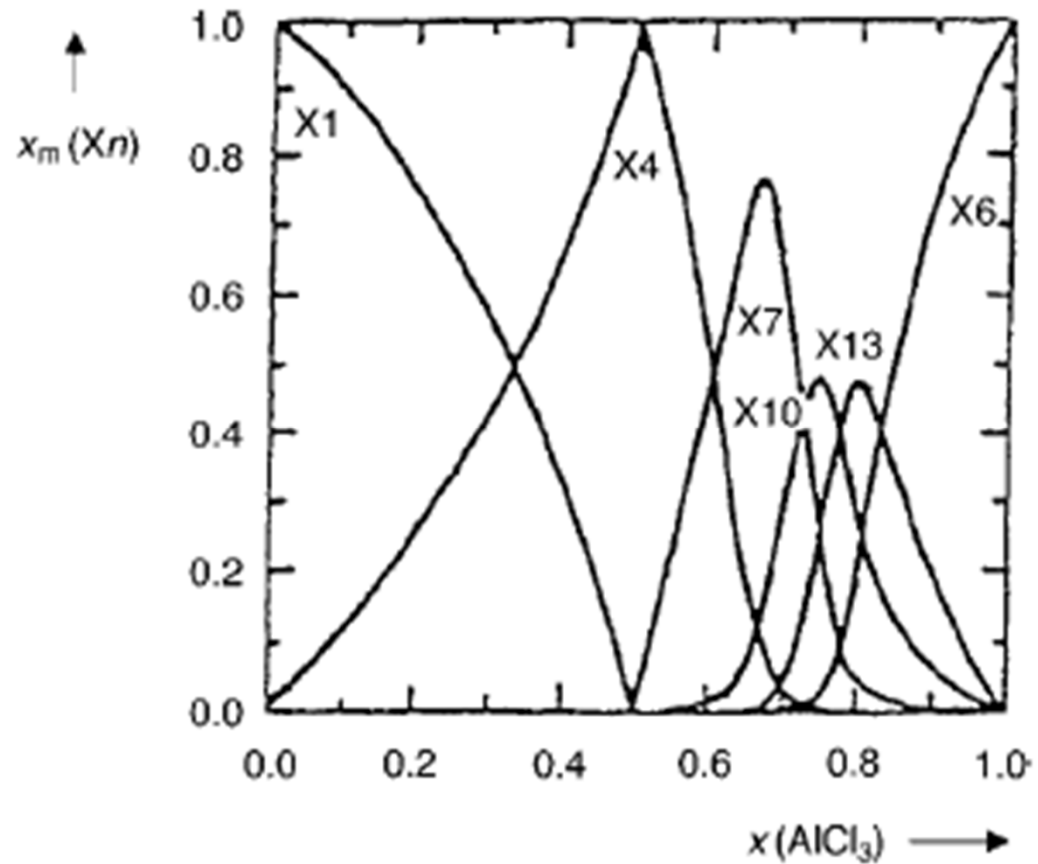
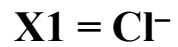
Acidic: excess of $AlCl_3$ as $[Al_2Cl_7]^-$ $x(AlCl_3) > 0.5$

Basic: excess of Cl^- $x(AlCl_3) < 0.5$

Neutral: $[AlCl_4]^-$ $x(AlCl_3) = 0.5$

Equilibria in Halogenoaluminate(III) IL

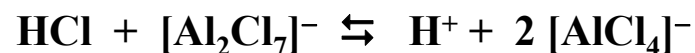
Equilibria in IL



Halogenoaluminate(III) Ionic Liquids



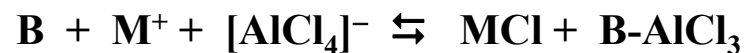
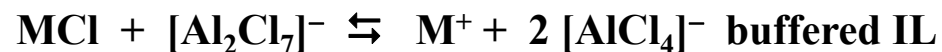
Acidic IL with an excess of AlCl_3



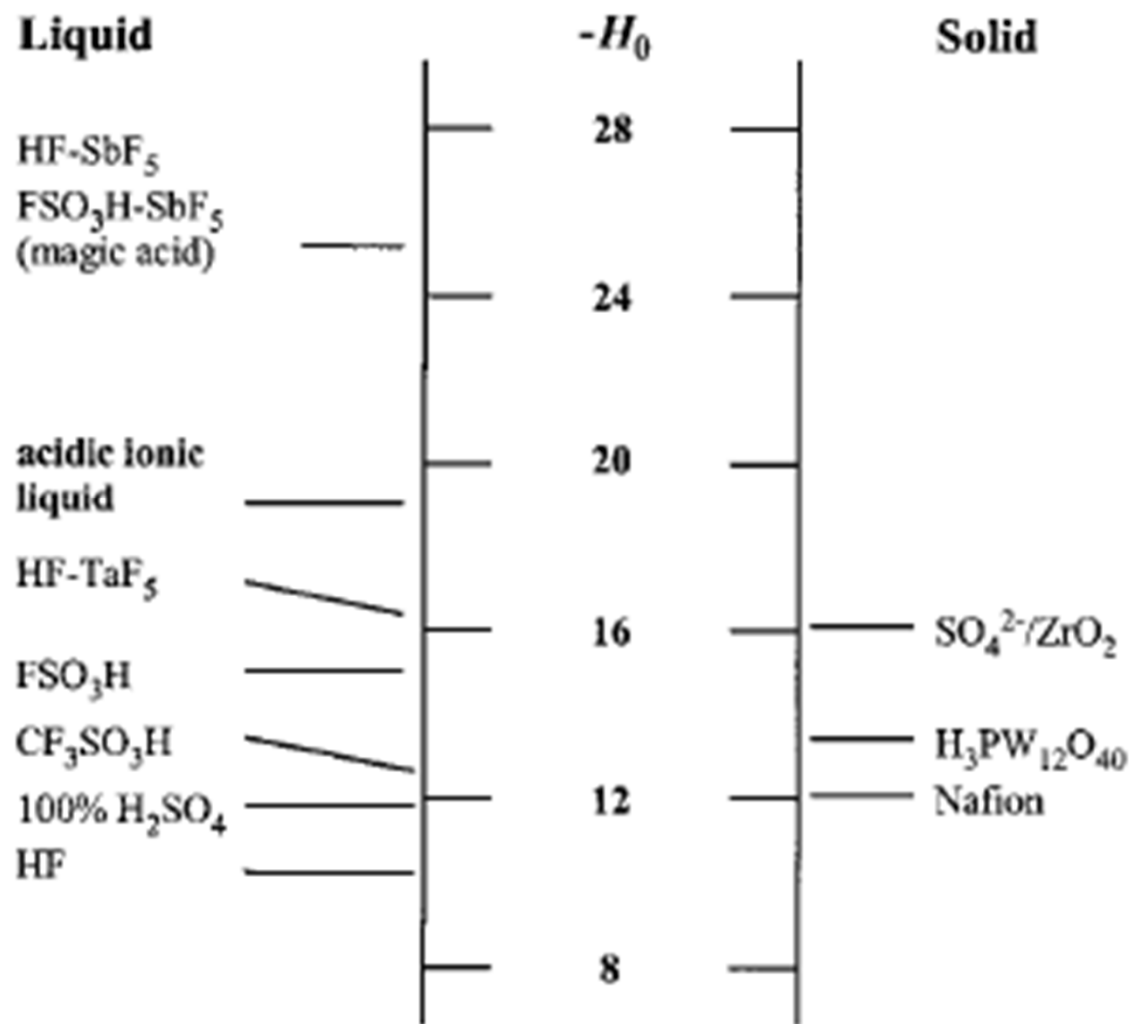
Proton extremely poorly solvated = high reactivity

Superacid $[\text{EMIM}]\text{Cl}/\text{AlCl}_3/\text{HCl}$ $H_0 = -19$ (HSO₃F: $H_0 = -15$)

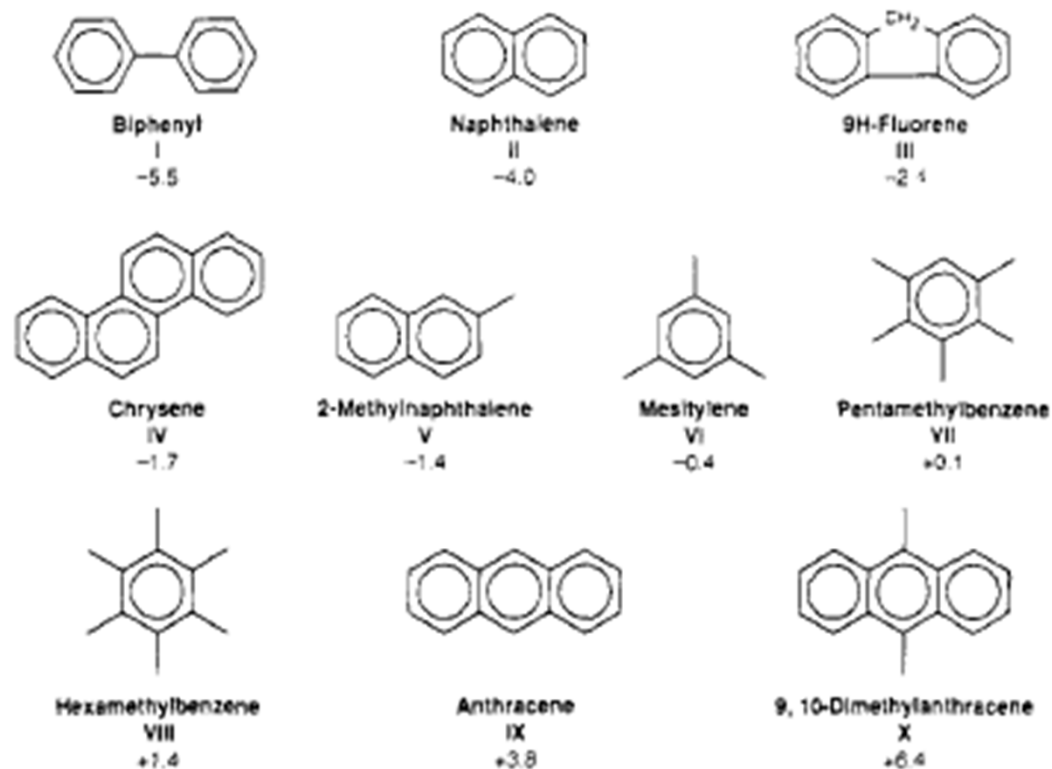
Latent acidity



Superacidity



Superacidic [EMIM]Cl/AlCl₃/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

Ionic Liquids

Completely inorganic ionic liquids

Compound	mp (K)	Compound	mp (K)
$\text{Na}_{13}[\text{La}(\text{TiW}_{11}\text{O}_{39})_2]$	253.0	$\text{Na}_{13}[\text{Tm}(\text{TiW}_{11}\text{O}_{39})_2]$	260.2
$\text{Na}_{13}[\text{Ce}(\text{TiW}_{11}\text{O}_{39})_2]$	263.0	$\text{Na}_{13}[\text{Yb}(\text{TiW}_{11}\text{O}_{39})_2]$	267.2
$\text{Na}_{13}[\text{Pr}(\text{TiW}_{11}\text{O}_{39})_2]$	253.0	$\text{Na}_5[\text{CrTiW}_{11}\text{O}_{39}]$	261.5
$\text{Na}_{13}[\text{Sm}(\text{TiW}_{11}\text{O}_{39})_2]$	256.0	$\text{Na}_5[\text{MnTiW}_{11}\text{O}_{39}]$	253.0
$\text{Na}_{13}[\text{Gd}(\text{TiW}_{11}\text{O}_{39})_2]$	265.1	$\text{Na}_5[\text{FeTiW}_{11}\text{O}_{39}]$	257.6
$\text{Na}_{13}[\text{Dy}(\text{TiW}_{11}\text{O}_{39})_2]$	265.2	$\text{Na}_6[\text{ZnTiW}_{11}\text{O}_{39}]$	257.4
$\text{Na}_{13}[\text{Er}(\text{TiW}_{11}\text{O}_{39})_2]$	261.0		

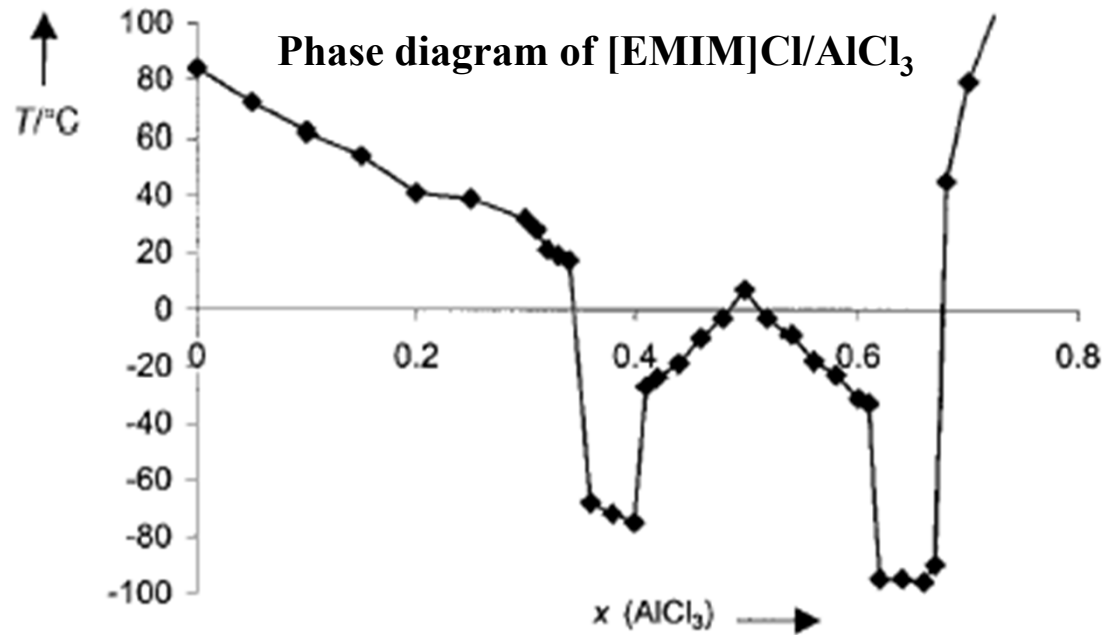
Melting Point of Ionic Liquids

Melting point is influenced by:

Cation – low symmetry, weak intermolecular interactions, good distribution of charge

Anion – increasing size leads to lower mp

Composition – Phase diagram



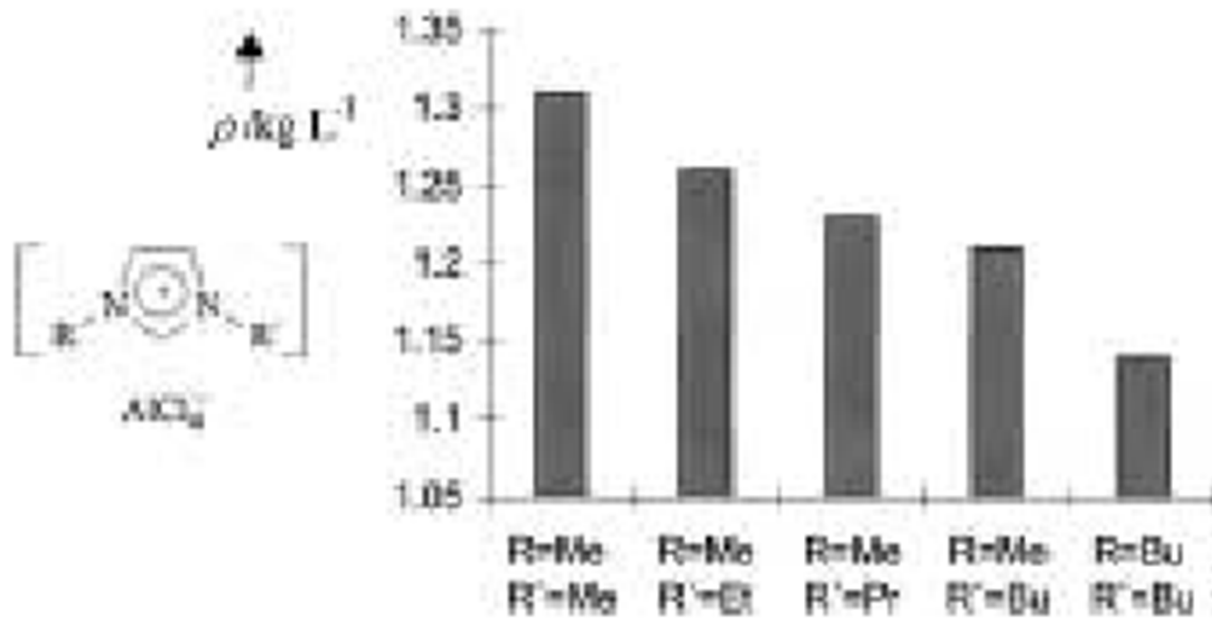
Melting Point of Ionic Liquids



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 of Ionic Liquids

The density of IL decreases as the bulkiness of the organic cation increases:

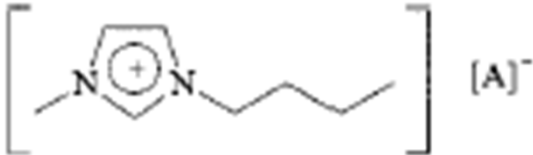


Viscosity of Ionic Liquids

The viscosity of IL depends on:

van der Waals interactions

H-bonding

	Anion [A] ⁻	η [cP]
	CF ₃ SO ₃ ⁻	90
	<i>n</i> -C ₄ F ₉ SO ₃ ⁻	373
	CF ₃ COO ⁻	73
	<i>n</i> -C ₃ F ₇ COO ⁻	182
	(CF ₃ SO ₂) ₂ N ⁻	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

water-soluble [BMIM] Br, CF₃COO, CF₃SO₃

Water-immiscible [BMIM] PF₆ (CF₃SO₂)₂N

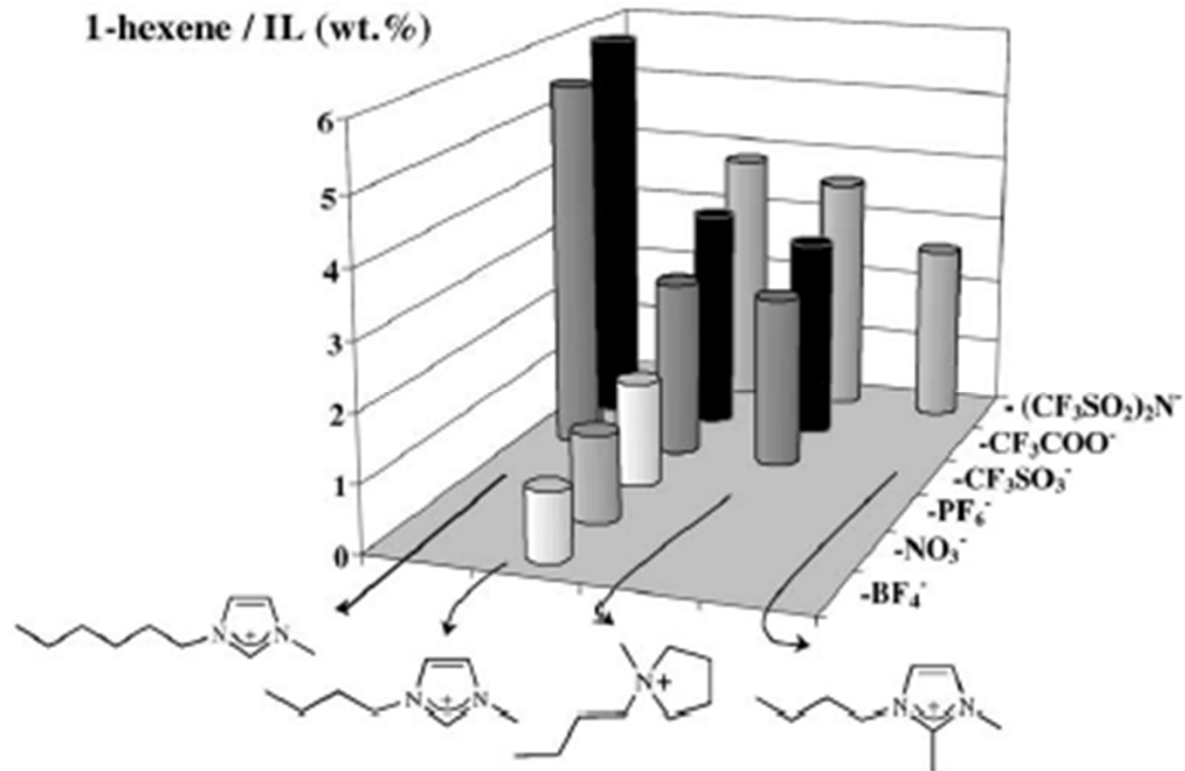
IL miscible with organic solvent IF their dielectric constant is above a certain limit given by the cation/anion combination

Polarity by E_(T)(30) scale

[EtNH₃][NO₃] 0.95 between CF₃CH₂OH and water

[BMIM] PF₆ as methanol

Solubility in/of Ionic Liquids



Applications of Ionic Liquids

Electrodeposition of 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 °C

BiCl₃, SrCl₂, CaCl₂, CuCl₂ dissolve well

Constituent	BiCl₃	SrCl₂	CaCl₂	CuCl₂
Concentration (mol kg⁻¹ MeEtImCl)	0.068	0.50	0.18	0.050

Substrate Al

-1.72 V vs the Ag/Ag⁺ reference electrode

Applications of Ionic Liquids

Biphasic solvent systems

Preparation of aerogels



Natural gas sweetening (H₂S, CO₂ removal)

Electrolytes in batteries or solar cells

Dissolving spent nuclear fuel (U⁴⁺ oxidized to U⁶⁺)

Extraction

Enzyme activity

Applications of Ionic Liquids

Olefin polymerization

Ethene + TiCl_4 + AlEtCl_2 in acidic IL

Ethene + Cp_2TiCl_2 + $\text{Al}_2\text{Me}_3\text{Cl}_3$ in acidic IL



Olefin hydrogenation

Cyclohexene + H_2 + $[\text{RhCl}(\text{PPh}_3)_3]$ (Wilkinson's catalyst)