

# Precursor Methods

**Goals – decrease diffusion paths, shorten reaction times and 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**

# 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**

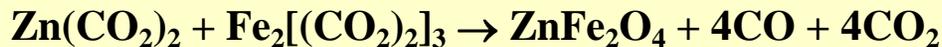
**Disadvantage: difficult to prepare high purity, accurate stoichiometric phases if solubilities do not match**

# Coprecipitation Method

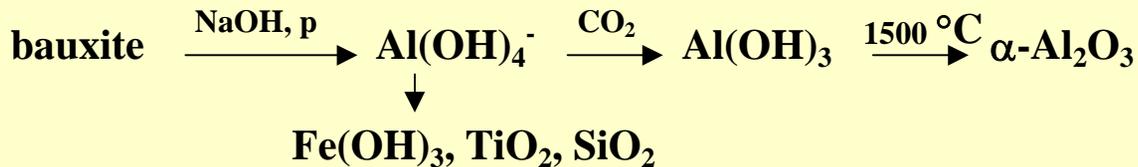
## Spinels

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

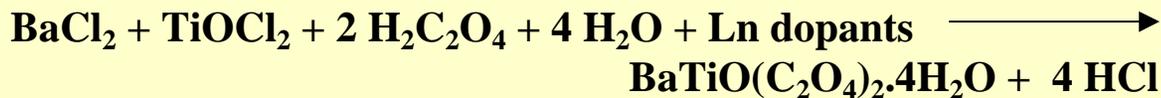
Solid-solution mixing on atomic scale, filter, calcine in air



## $\text{Al}_2\text{O}_3$ Bayer Process



## $\text{BaTiO}_3$

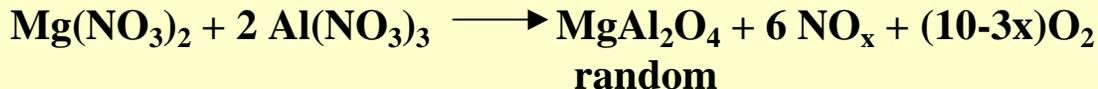


filtration, washing, drying, calcination @  $730^\circ\text{C}$

# 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



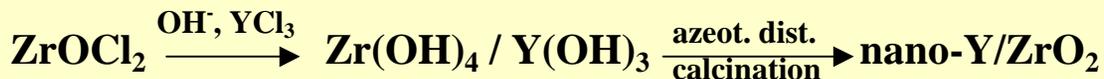
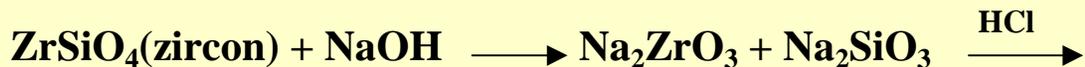
## Ruby

### Ion exchange



freeze drying gives solid (Al/Cr)(OH)<sub>3</sub> @ LN<sub>2</sub> temperature, 5 Pa  
annealing @ 950 °C for 2.5 h gives solid solution Al<sub>2-x</sub>Cr<sub>x</sub>O<sub>3</sub>

## Zirconia



# Coprecipitation Method

## High- $T_c$ Superconductors



## Magnetic garnets, tunable magnetic materials



**Firing @ 900 °C, 18-24 hrs, pellets, regrinding, repelletizing,  
repeated firings, removes REFeO<sub>3</sub> perovskite impurity**

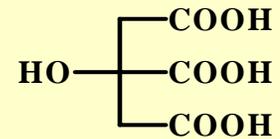
**Isomorphous replacement of Y<sup>3+</sup> for Gd<sup>3+</sup> on dodecahedral sites,  
solid solution, similar rare earth ionic radii**

**complete family accessible, 0 < x < 3, 2Fe<sup>3+</sup> O<sub>h</sub> sites, 3Fe<sup>3+</sup> T<sub>d</sub> sites,  
3RE<sup>3+</sup> dodecahedral sites**

# 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**

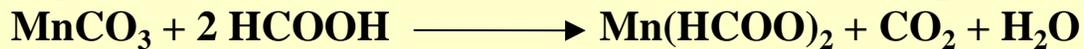
**Low firing temperatures**

# Pechini and Citrate Gel Method

**BaTiO<sub>3</sub>**

by conventional powder method at 1200 °C

**Ba<sup>2+</sup> + Ti(O<sup>i</sup>Pr)<sub>4</sub> + citric acid at 650 °C**



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

**ScMnO<sub>3</sub>**

**without citric acid only mixture of Sc<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>O<sub>3</sub> 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  $\text{NiFe}_2\text{O}_4$  spinel

Good way to make chromite spinels, important tunable magnetic materials

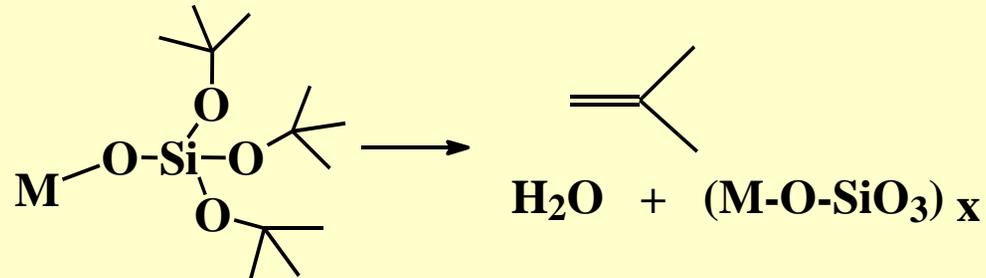
Juggling the electronic-magnetic properties of the  $\text{O}_h$  and  $\text{T}_d$  ions in the spinel lattice

Chromite spinel	Precursor	Ignition T, °C
$\text{MgCr}_2\text{O}_4$	$(\text{NH}_4)_2\text{Mg}(\text{CrO}_4)_2\cdot 6\text{H}_2\text{O}$	1100-1200
$\text{NiCr}_2\text{O}_4$	$(\text{NH}_4)_2\text{Ni}(\text{CrO}_4)_2\cdot 6\text{H}_2\text{O}$	1100
$\text{MnCr}_2\text{O}_4$	$\text{MnCr}_2\text{O}_7\cdot 4\text{C}_5\text{H}_5\text{N}$	1100
$\text{CoCr}_2\text{O}_4$	$\text{CoCr}_2\text{O}_7\cdot 4\text{C}_5\text{H}_5\text{N}$	1200
$\text{CuCr}_2\text{O}_4$	$(\text{NH}_4)_2\text{Cu}(\text{CrO}_4)_2\cdot 2\text{NH}_3$	700-800
$\text{ZnCr}_2\text{O}_4$	$(\text{NH}_4)_2\text{Zn}(\text{CrO}_4)_2\cdot 2\text{NH}_3$	1400
$\text{FeCr}_2\text{O}_4$	$(\text{NH}_4)_2\text{Fe}(\text{CrO}_4)_2$	1150

# Single Source Precursor

Compounds containing desired elements in a proper stoichiometric ratio

Easy chemical pathway for ligand removal



# Vegard's Law

**Vegard law behavior:**

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

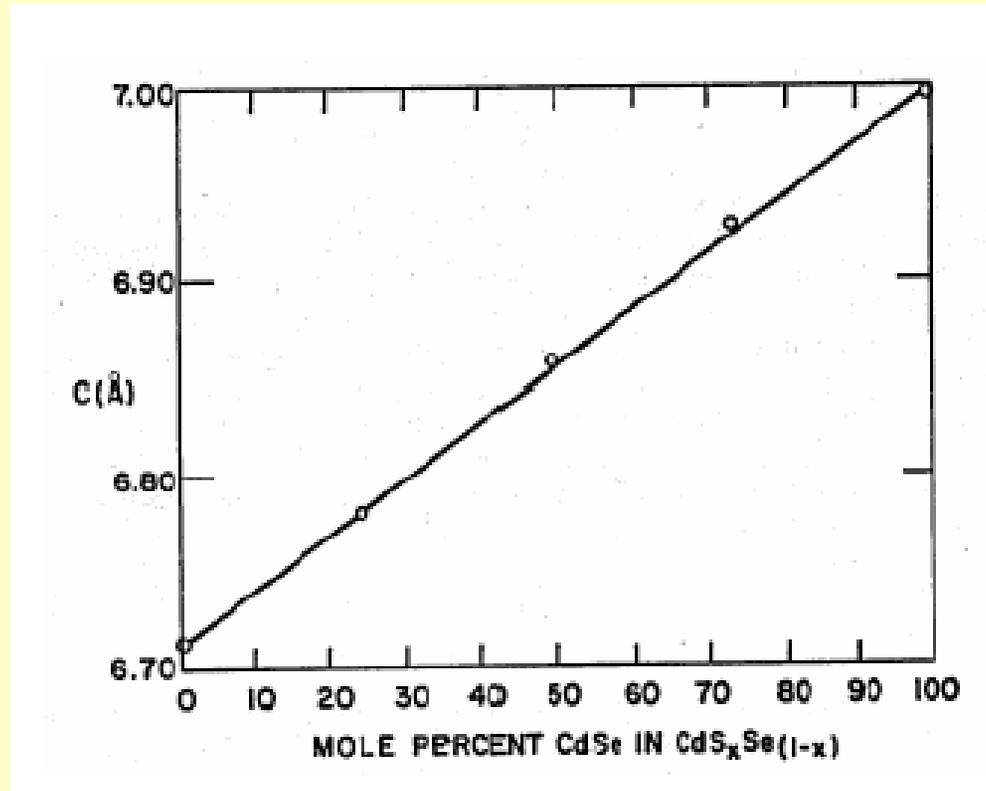
**The composition of the  $A_{1-x}B_x$  alloy can be calculated from Vegard's law**

**The lattice parameter of a solid solution alloy 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

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

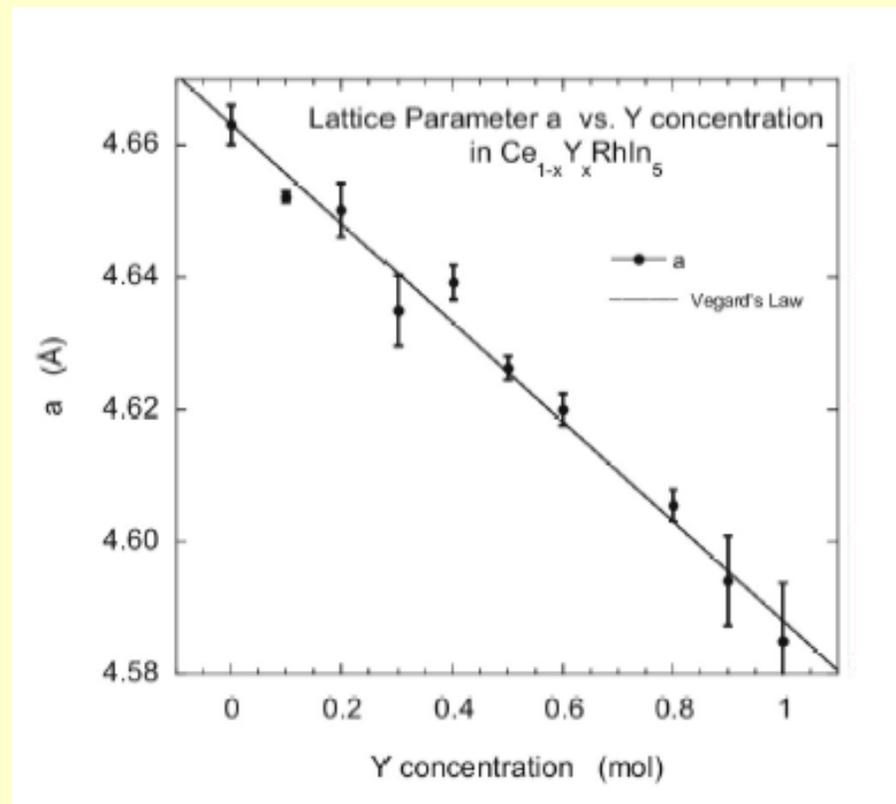


# Vegard's Law

$$P(Y_x Ce_{1-x} RhIn_5) = x P(Y_x Ce_{1-x} RhIn_5) + (1-x) P(Y_x Ce_{1-x} RhIn_5)$$

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

Tetragonal lattice constant  $a$   
as a function of  
Y concentration  $x$   
for the  $Ce_{1-x} Y_x RhIn_5$  system



# Vegard's Law

**A linear relationship exists between the concentration of the substitute element and the size of the lattice parameters**

**The direction of the linear relationship, increasing or decreasing, depends upon the system being analyzed**

**As the concentration of Y is increased, lattice constant  $a$  decreases, implying the cell is contracting along the  $a$  axis**

# Vegard's Law

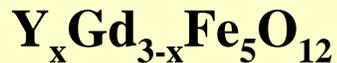
**Vegard law behavior:**

$$\mathbf{P (Y_x Gd_{3-x} Fe_5 O_{12}) = x/3 P (Y_3 Fe_5 O_{12}) + (3-x)/3 P (Gd_3 Fe_5 O_{12})}$$

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

# Vegard's Law

**Tunable magnetic properties by tuning the x value in the binary garnet**



**3  $T_d$   $Fe^{3+}$  sites, 5 UPEs**

**2  $O_h$   $Fe^{3+}$  sites, 5 UPEs**

**Ferrimagnetically coupled material, oppositely aligned electron spins on the  $T_d$  and  $O_h$   $Fe^{3+}$  magnetic sublattices**

**Counting spins  $Y_3Fe_5O_{12}$  ferrimagnetic at low T:  $3 \times 5 - 2 \times 5 = 5$  UPEs**

**Counting spins  $Gd_3Fe_5O_{12}$  ferrimagnetic at low T:  $3 \times 7 - 3 \times 5 + 2 \times 5 = 16$  UPEs**

**$Y_xGd_{3-x}Fe_5O_{12}$  creates a tunable magnetic garnet that is strongly temperature and composition dependent,**

**applications in permanent magnets, magnetic recording media, magnetic bubble memories and so forth, similar concepts apply to magnetic spinels**

## **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)**

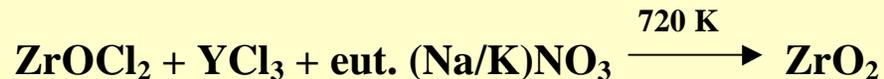
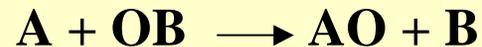
# Flux Method

**Lux-Flood formalism**

**oxide = strong base**

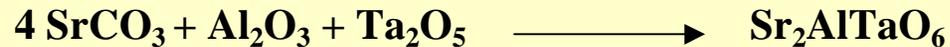
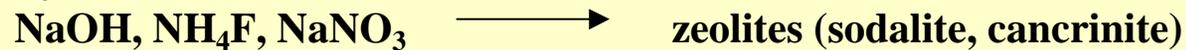
**acid = oxide acceptor**

**base = oxide donor**



# Flux Method

**fly ash (aluminosilicates)**



**900 °C in SrCl<sub>2</sub> flux**

**1400 °C required for a direct reaction**



# Flux Method

**Electrolysis in molten salts**

**Reduction of  $\text{TiO}_2$  pellets to Ti sponge in a  $\text{CaCl}_2$  melt at  $950\text{ }^\circ\text{C}$**

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

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

**graphite anode**

**anodic oxidation**



**cathode  $\text{TiO}_2$  pellet**

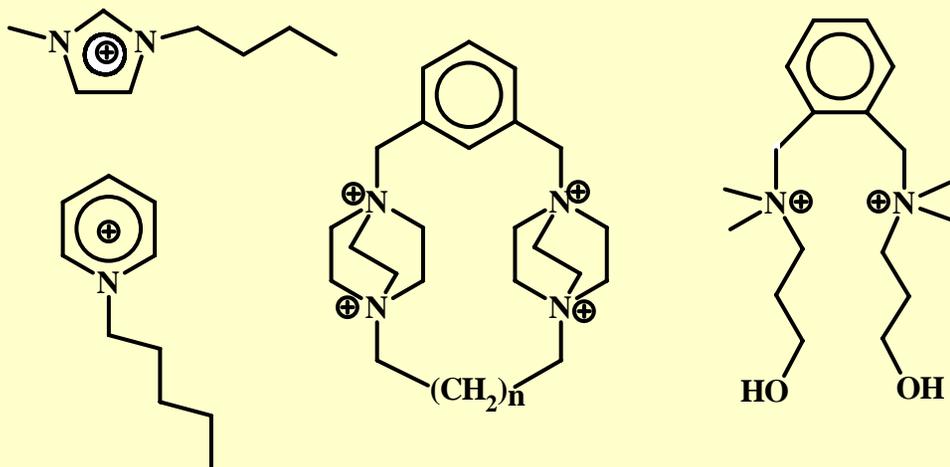
**cathodic reduction**



# Ionic Liquids

**Organic cations (containing N, P)**

**Inorganic anions:  $\text{Cl}^-$ ,  $\text{AlCl}_4^-$ ,  $\text{Al}_2\text{Cl}_7^-$ ,  $\text{Al}_3\text{Cl}_{10}^-$ ,  $\text{PF}_6^-$ ,  $\text{SnCl}_3^-$ ,  $\text{BCl}_3^-$ ,  $\text{BF}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{OSO}_2\text{CF}_3^-$  (triflate),  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ ,  $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ ,  $\text{PO}_4^{3-}$**

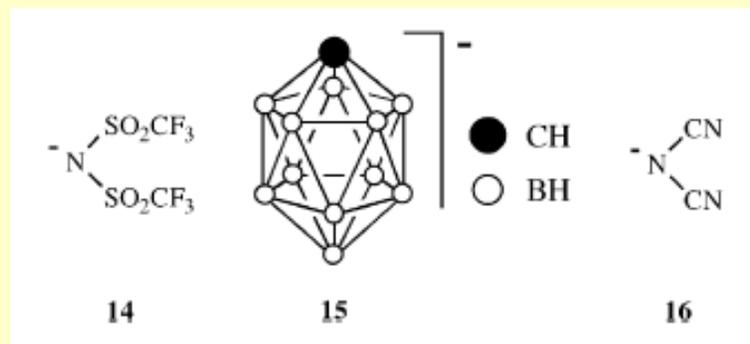
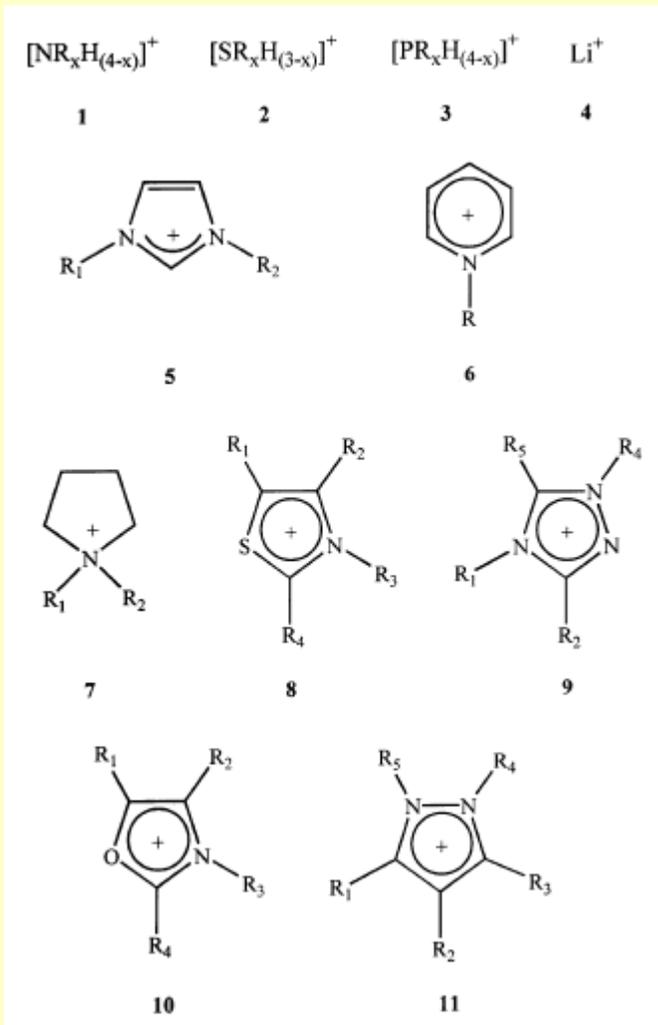


# Ionic Liquids

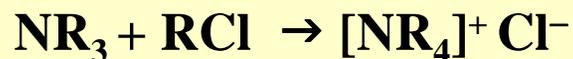
**Oldest known (1914) : EtNH<sub>3</sub><sup>+</sup>NO<sub>3</sub><sup>-</sup> mp 12 °C**

- 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**

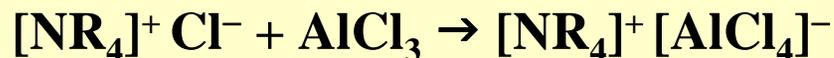
# Ionic Liquids



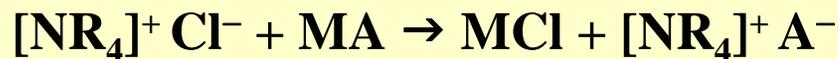
# Synthesis of Ionic Liquids



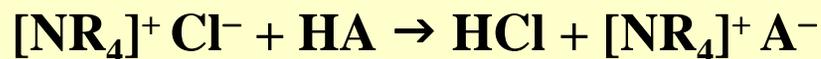
## Aluminates



## Metal halide elimination



## Reaction with an acid



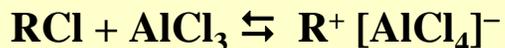
## Ion exchange



# Halogenoaluminate(III) Ionic Liquids

The most widely studied class of IL

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



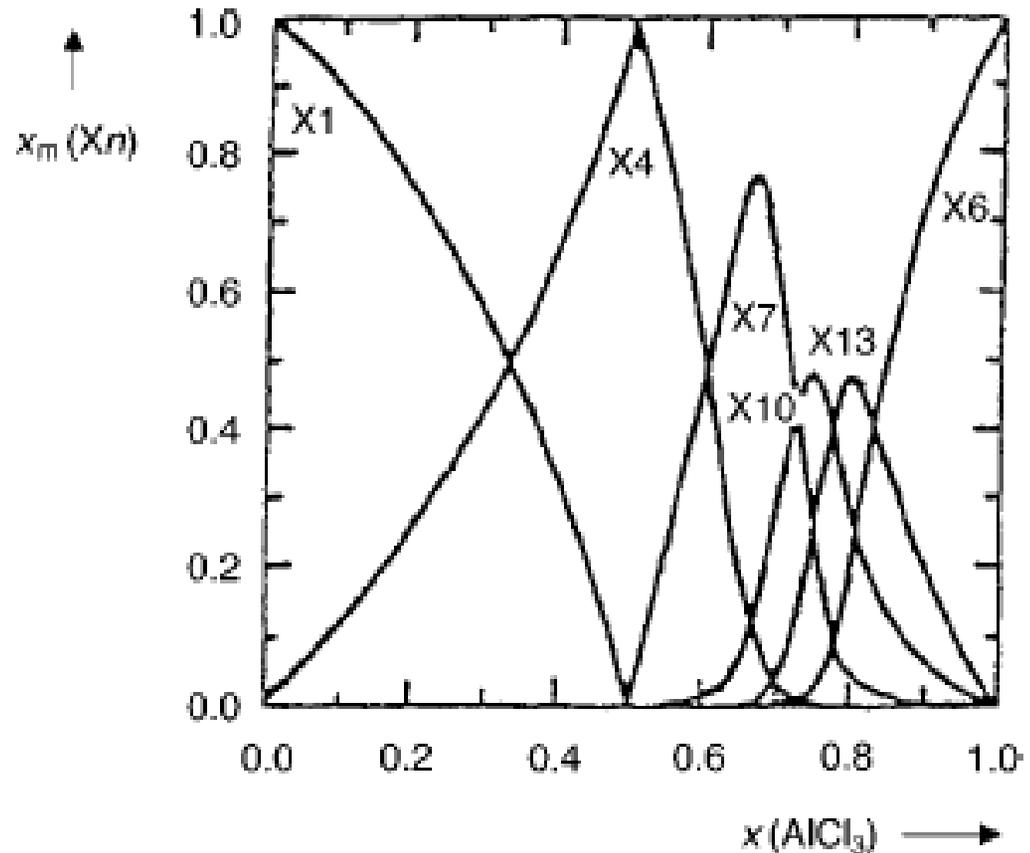
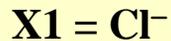
Acidic: excess of  $AlCl_3$  as  $[Al_2Cl_7]^-$        $x(AlCl_3) > 0.5$

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

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

# Equilibria in Halogenoaluminate(III) IL

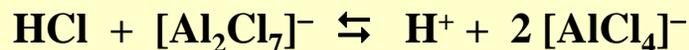
## Equilibria in IL



# Halogenoaluminate(III) Ionic Liquids



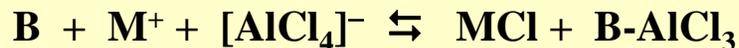
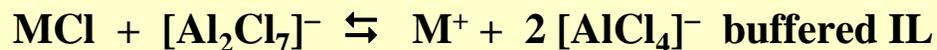
**Acidic IL with an excess of  $\text{AlCl}_3$**



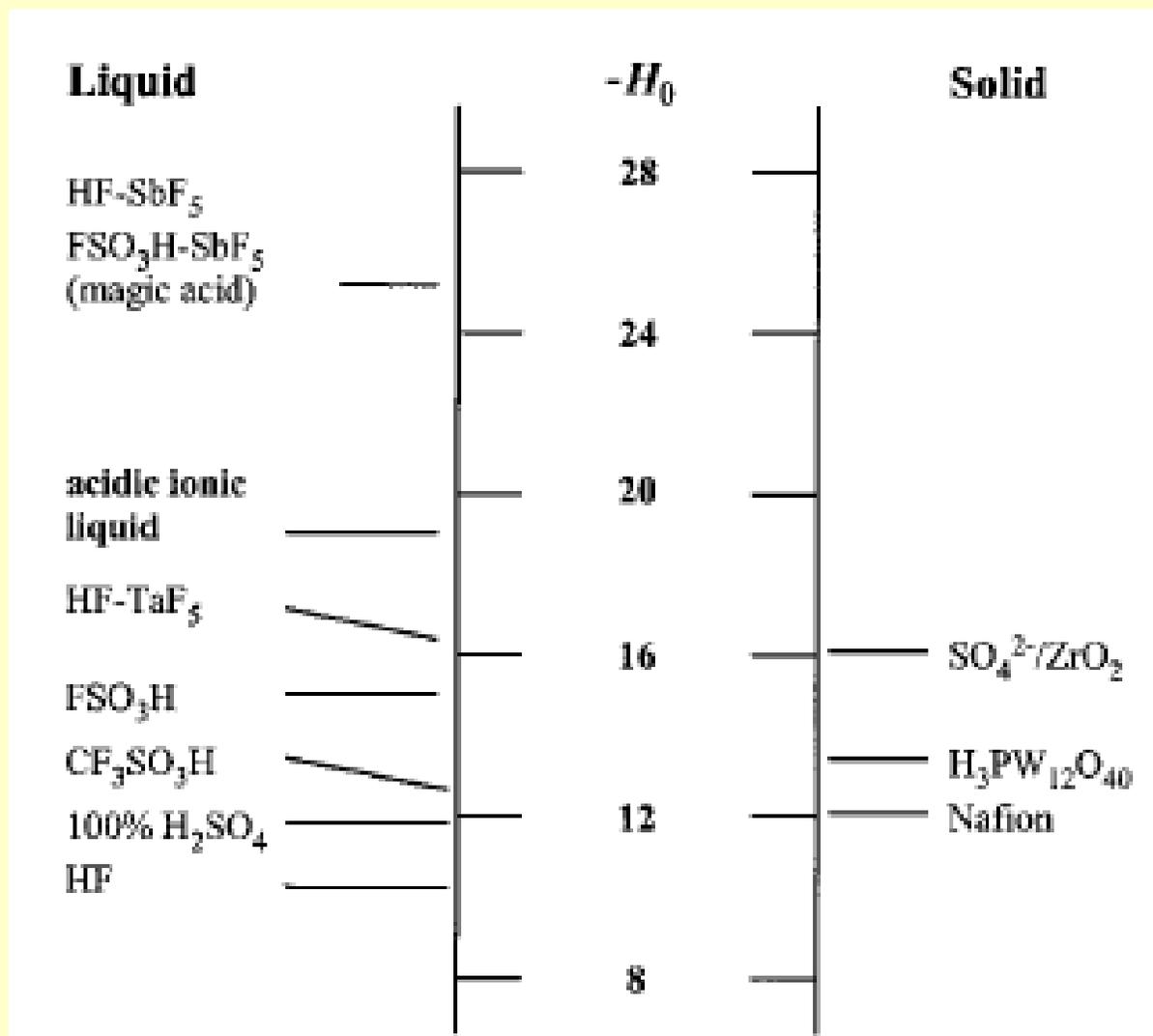
**Proton extremely poorly solvated = high reactivity**

**Superacid  $[\text{EMIM}]\text{Cl}/\text{AlCl}_3/\text{HCl}$   $H_0 = -19$  (HSO<sub>3</sub>F:  $H_0 = -15$ )**

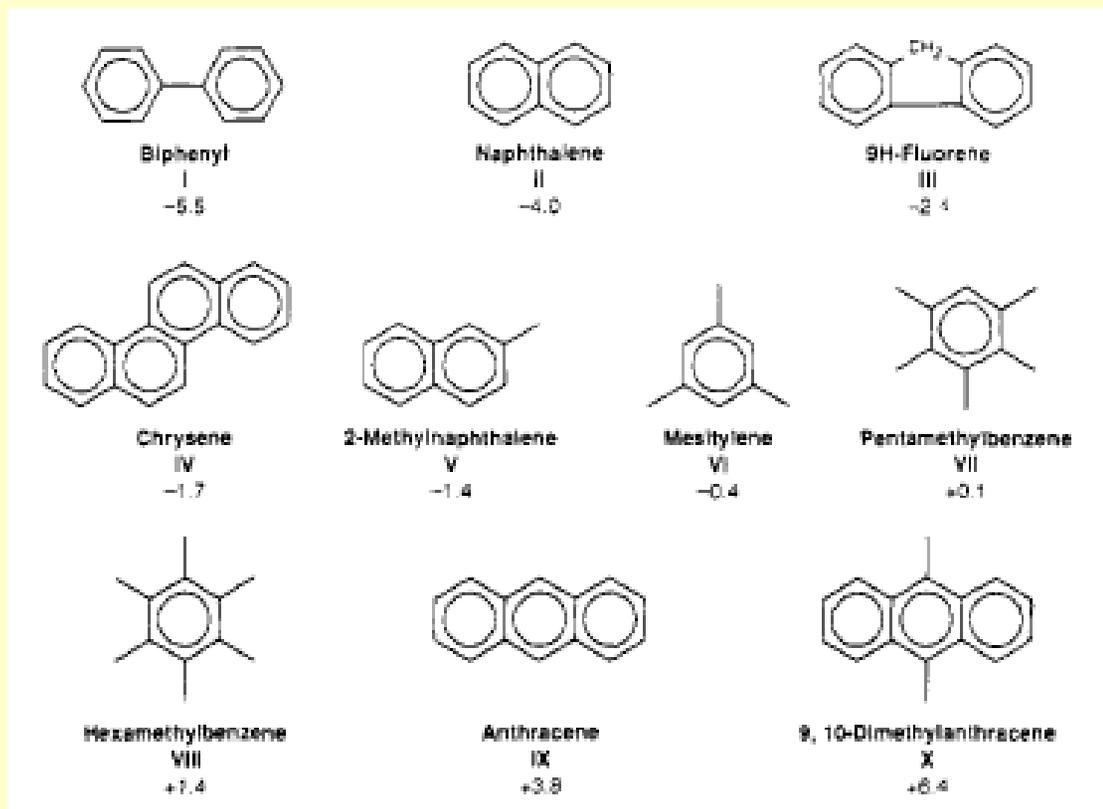
**Latent acidity**



# Superacidity



# Superacidic [EMIM]Cl/AlCl<sub>3</sub>/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<sub>b</sub> 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		

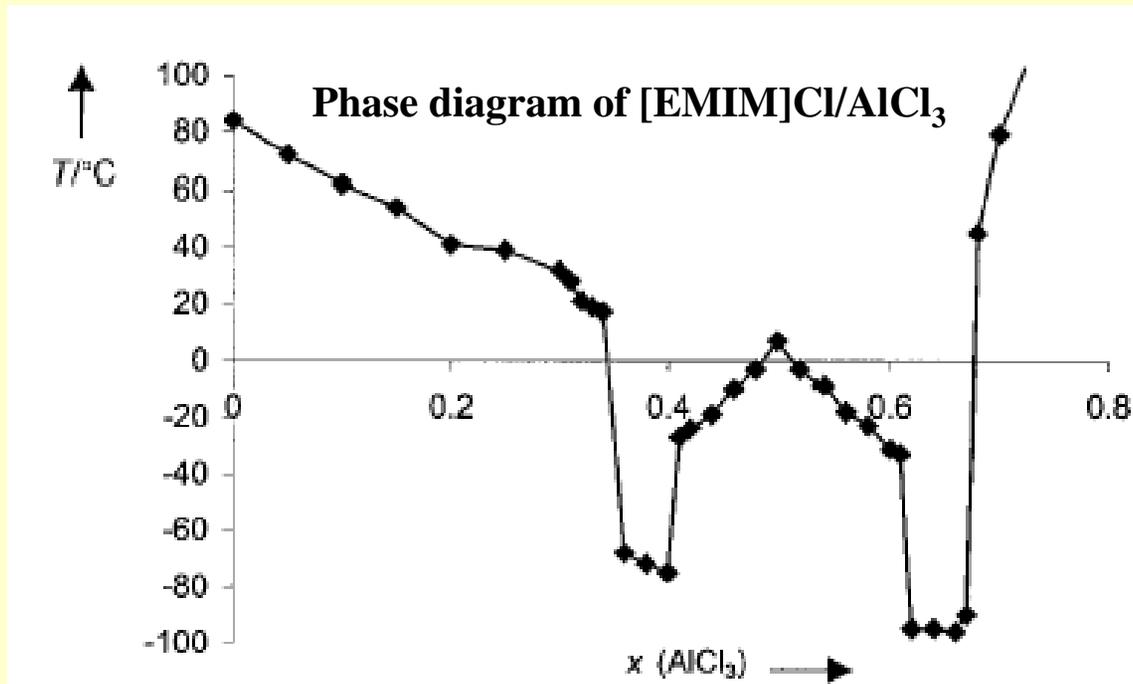
# Melting Point of Ionic Liquids

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



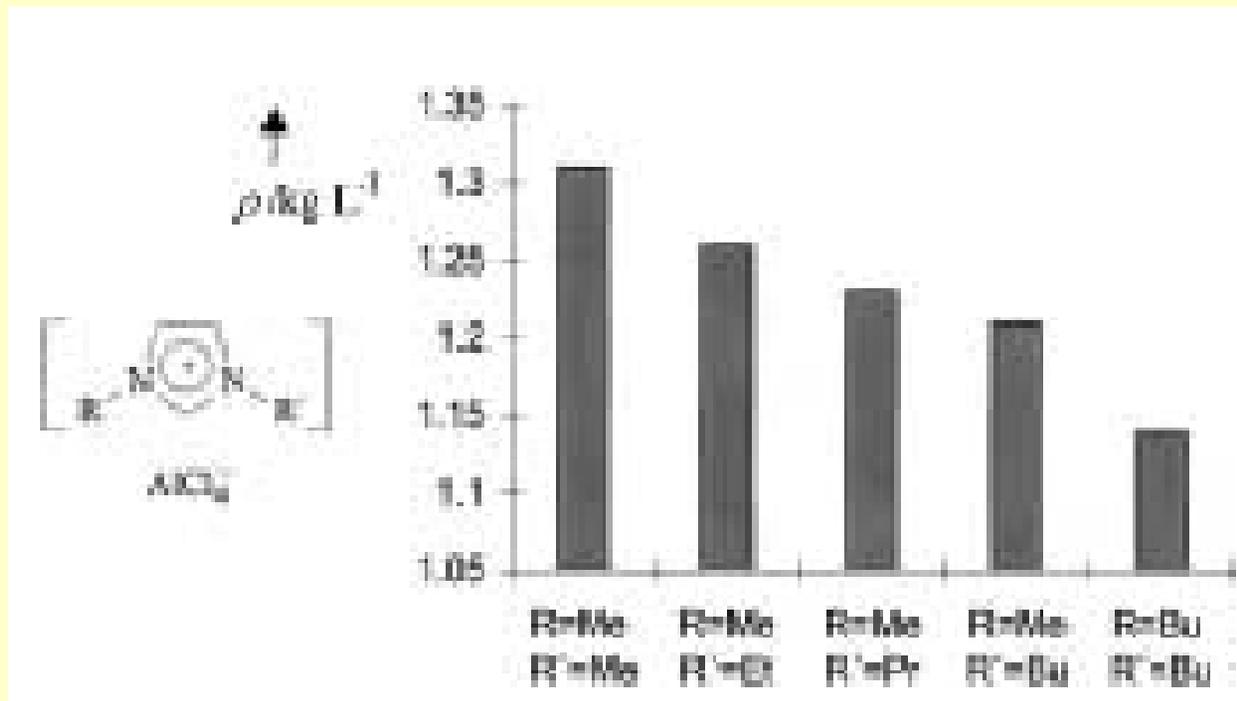
# Melting Point of Ionic Liquids



R	X	mp/ <sup>o</sup> C
Me	Cl	125
Et	Cl	87
n-Bu	Cl	65
Et	NO <sub>3</sub>	38
Et	AlCl <sub>4</sub>	7
Et	BF <sub>4</sub>	6
Et	CF <sub>3</sub> SO <sub>3</sub>	-9
Et	(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub> N	-3
Et	CF <sub>3</sub> CO <sub>2</sub>	-14
n-Bu	CF <sub>3</sub> SO <sub>3</sub>	16

# Density of Ionic Liquids

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

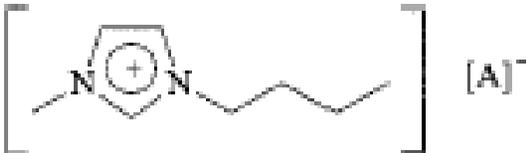


# Viscosity of Ionic Liquids

The viscosity of IL depends on:

van der Waals interactions

H-bonding

	Anion $[A]^-$	$\eta$ [cP]
	$CF_3SO_3^-$	90
	$n-C_4F_9SO_3^-$	373
	$CF_3COO^-$	73
	$n-C_3F_7COO^-$	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**

**water-soluble [BMIM] Br, CF<sub>3</sub>COO, CF<sub>3</sub>SO<sub>3</sub>**

**Water-immiscible [BMIM] PF<sub>6</sub> (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N**

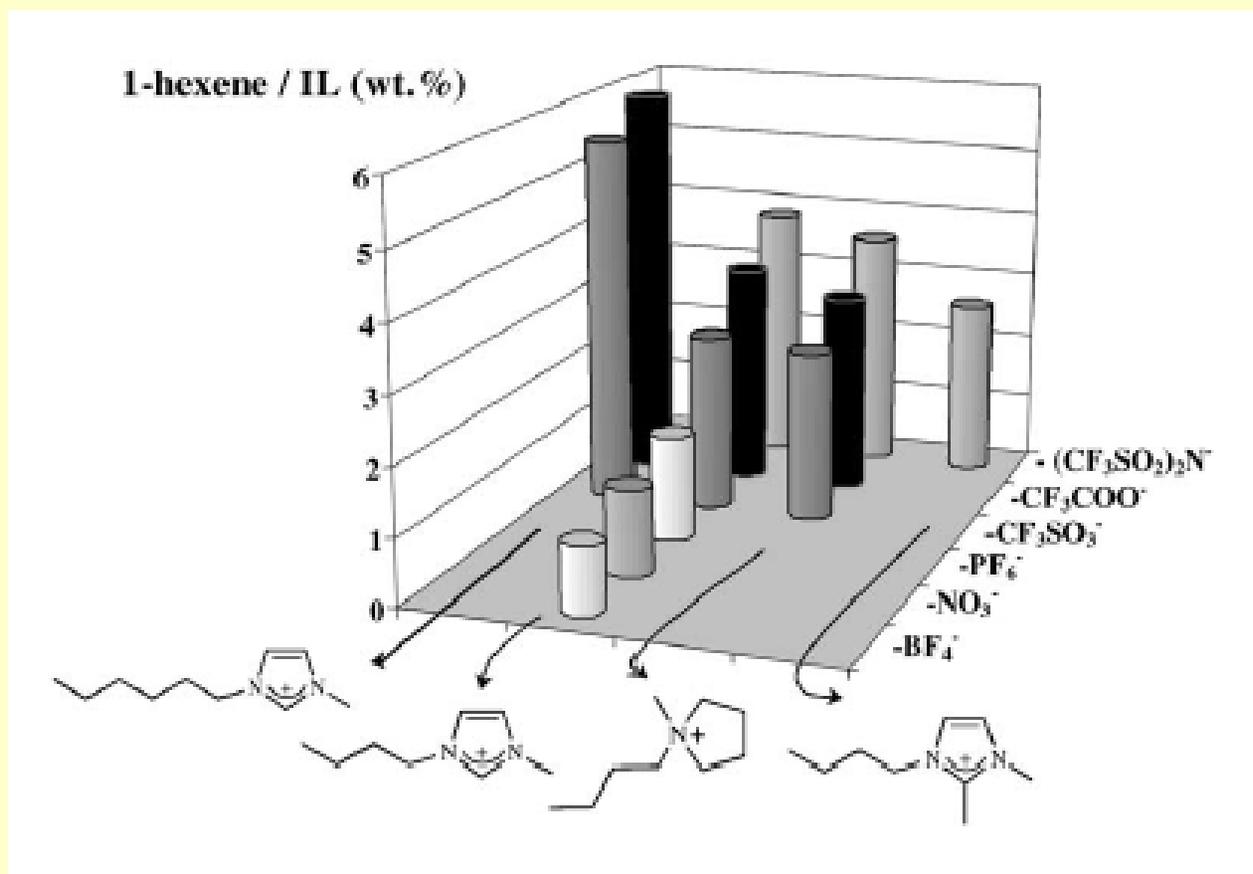
**IL miscible with organic solvent IF their dielectric constant is above a certain limit given by the cation/anion combination**

**Polarity by E<sub>(T)</sub>(30) scale**

**[EtNH<sub>3</sub>][NO<sub>3</sub>] 0.95 between CF<sub>3</sub>CH<sub>2</sub>OH and water**

**[BMIM] PF<sub>6</sub> as methanol**

# Solubility in/of Ionic Liquids



# Applications of Ionic Liquids

**Electrodeposition of metals and alloys (also nanoscopic)**

**Al, CoAl<sub>x</sub>, CuAl<sub>x</sub>, FeAl<sub>x</sub>, AlTi<sub>x</sub>**

**Semiconductors Si, Ge, GaAs, InSb, CdTe**

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

**Melt of MeEtImCl at 120 °C**

**BiCl<sub>3</sub>, SrCl<sub>2</sub>, CaCl<sub>2</sub>, CuCl<sub>2</sub> dissolve well**

<b>Constituent</b>	<b>BiCl<sub>3</sub></b>	<b>SrCl<sub>2</sub></b>	<b>CaCl<sub>2</sub></b>	<b>CuCl<sub>2</sub></b>
<b>Concentration</b> <b>(mol kg<sup>-1</sup> MeEtImCl)</b>	<b>0.068</b>	<b>0.50</b>	<b>0.18</b>	<b>0.050</b>

**Substrate Al**

**-1.72 V vs the Ag/Ag<sup>+</sup> reference electrode**

# Applications of Ionic Liquids

**Biphasic solvent systems**

**Preparation of aerogels**



**Natural gas sweetening (H<sub>2</sub>S, CO<sub>2</sub> removal)**

**Electrolytes in batteries or solar cells**

**Dissolving spent nuclear fuel (U<sup>4+</sup> oxidized to U<sup>6+</sup>)**

**Extraction**

**Enzyme activity**

# Applications of Ionic Liquids

## Olefin polymerization

Ethene +  $\text{TiCl}_4$  +  $\text{AlEtCl}_2$  in acidic IL

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



## Olefin hydrogenation

Cyclohexene +  $\text{H}_2$  +  $[\text{RhCl}(\text{PPh}_3)_3]$  (Wilkinson's catalyst)