Hydrothermal Methods for Preparation of Inorganic and Hybrid Materials

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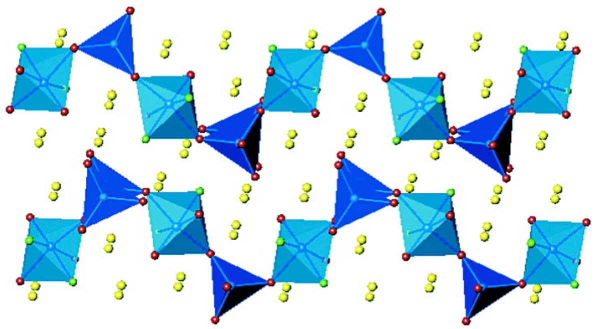
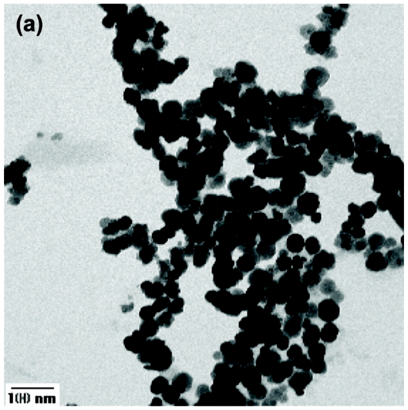
Gypsum ($CaSO_4 \cdot 2H_2O$) single crystals in Naica mine, Chihuahua, Mexico

Hydrothermal Synthesis of New Materials



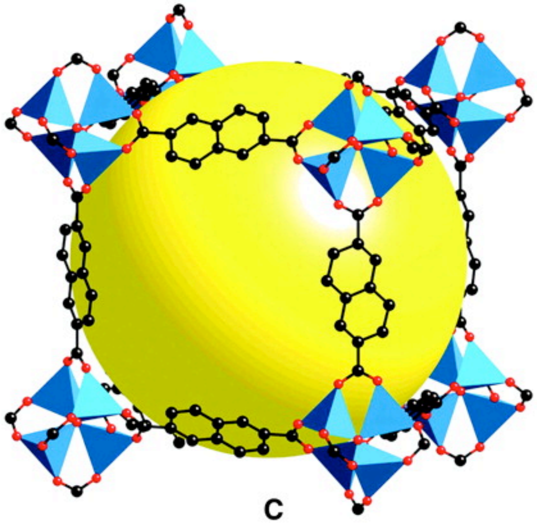
$Ag_4V_2O_6F_2$, a potential Li ion battery cathode

Sorensen, E.M.; Izumi, H.K.; Vaughey, J.T.; Stern, C.L.; Poeppelmeier, K.R. J. Am. Chem. Soc. **2005**, 127, 6347-6352.



Fe_3O_4 nanoparticles

Ge, S.; Shi, X.; Sun, K.; Li, C.; Uher, C.; Baker, J.R.; Banaszak Holl, M.M.; Orr, B.G. *J. Phys. Chem. C* **2009**, *113*, 13593-13599.



IMROF-8, a pourous metal-organic framework

Rosi, N.L.; Eckert, J.; Eddaoudi, M.; Vodak, D.T.; Kim, J.; O'Keefe, M.; Yaghi, O.M. Science **2003**, 300, 1127-1129.

Overview of Topics

Definitions

Why use hydrothermal methods?

Equipment and procedures

Chemistry of metal cations in water

Pourbaix diagrams

Examples: Using speciation data to design oxide syntheses

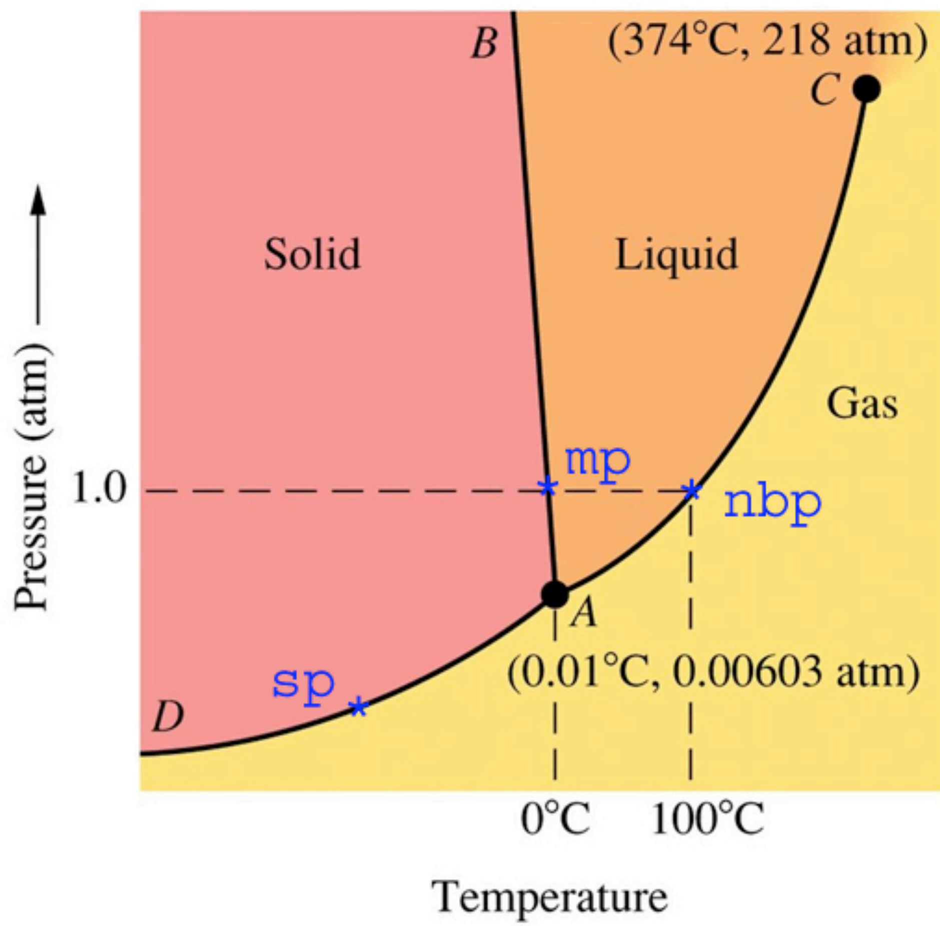
Hydrothermal synthesis of hybrid inorganic-organic compounds

Example: Growing single crystals to characterize corrosion products

Non-aqueous systems

Hydrothermal reaction conditions – sealed container above the normal boiling point of water

Autogenous pressure – developed by the heated reaction mixture, not externally applied



The density, viscosity, and dielectric constant of liquid water decrease as the critical point is approached.

Advantages of Hydrothermal Reaction Conditions

Shorter, lower-temperature reactions compared with traditional solid-state method

Access to metastable phases

No problems with material loss due to volatility of starting materials

Better control of sample homogeneity and particle size

Possibility to include organic components that decompose at high temperatures

Applications in production of battery materials, nanostructured materials, catalysts, porous materials…

Equipment and General Procedure

H_2O,
mineralizer

100-300 ^oC,
hours or days

Reactions of Metal Oxides with Water

Basic oxides dissolve in acid:

$BaO(s) + H_3O^+(aq) \rightleftharpoons Ba^{2+}(aq) + H_2O(l) + OH^-(aq)$

Acidic oxides dissolve to produce acid:

$SeO_2(s) + H_2O(l) \rightleftharpoons H_2SeO_3(aq)$ – a strong acid

$H_2SeO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSeO_3^-(aq)$

Amphoteric oxides react with either acid or base:

$Al_2O_3(s) + 6\ H_3O^+(aq) \rightleftharpoons 2\ Al^{3+}(aq) + 9\ H_2O(l)$

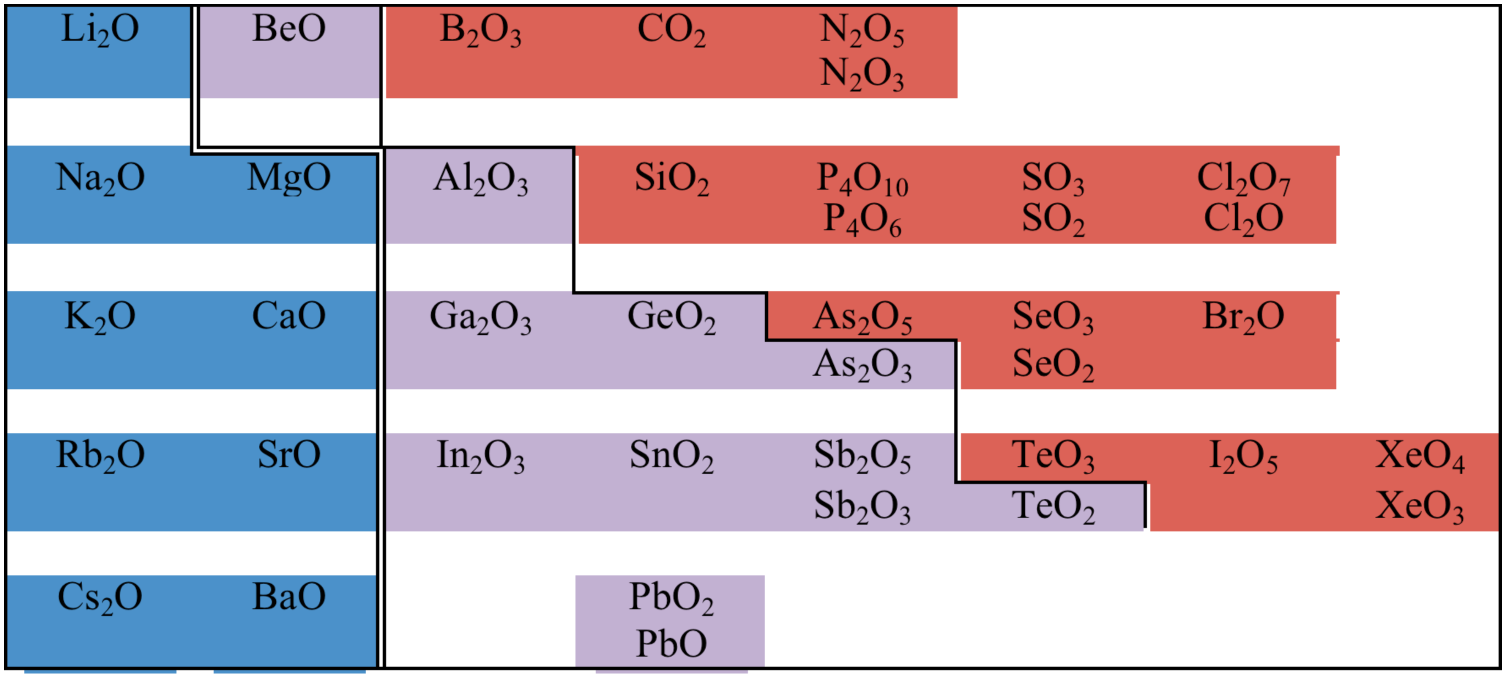
$Al_2O_3(s) + 2\ OH^-(aq) + 3\ H_2O(l) \rightleftharpoons 2\ [Al(OH)_4]^-(aq)$

Many interesting oxides from our point of view are amphoteric!

For transition metals, oxide acidity increases with metal oxidation state:

$MnO < MnO_2 < MnO_3$

Acid-Base Character of Oxides



basic

amphoteric

acidic

Cation Hydrolysis in Water

$$M(H_2O)_x^{n+} + H_2O \rightleftharpoons M(H_2O)_{x-1}(OH)^{(n-1)+} + H_3O^+$$

$$M(H_2O)_{x-1}(OH)^{(n-1)+} + H_2O \rightleftharpoons M(H_2O)_{x-2}(OH)^{(n-2)+} + H_3O^+$$

Further steps can lead to formation of hydroxides (e.g. $Co(OH)_2$, oxoanions (e.g. MnO_4^{2-}), and oxides (e.g. Fe_3O_4)

$$Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+$$

$$Fe(H_2O)_5(OH)^{2+} + H_2O \rightleftharpoons Fe(H_2O)_4(OH)_2^{+} + H_3O^+$$

$$Fe(H_2O)_4(OH)_2^{+} + H_2O \rightleftharpoons Fe(H_2O)_3(OH)_3 + H_3O^+$$

And also

$$2\ Fe(H_2O)_5(OH)^{2+} \rightleftharpoons Fe_2(H_2O)_8(OH)_2^{4+} + 2\ H_2O$$

What Determines the Extent of Cation Hydrolysis?

Multiple hydrolysis steps with favorable equilibrium constants are found for metals with high charge, small radius and high electronegativity.

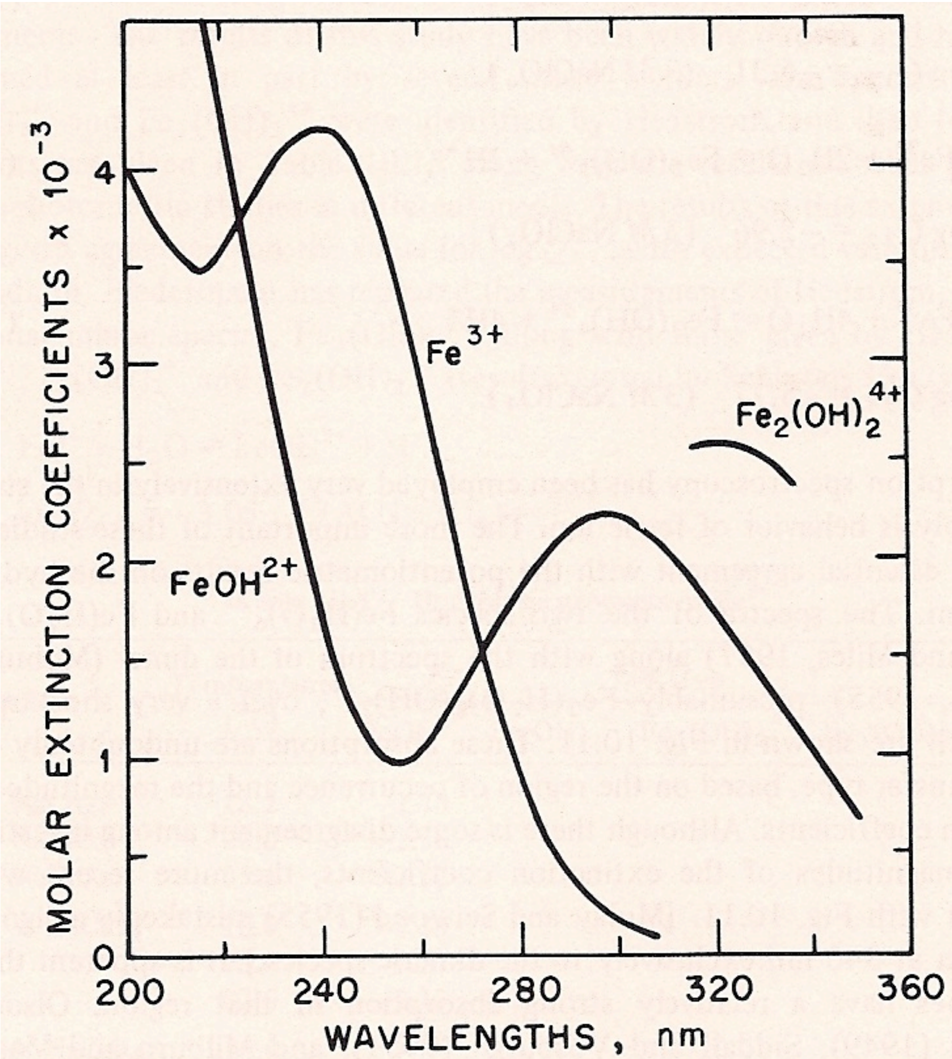
Acidity $\propto Z^2/r$

Note that cations that have high acidity when added to water also form acidic oxides.

Ex) Ti^{4+}, Si^{4+}

Reaction of $TiCl_4$ with water vapor is used in skywriting.

Demonstration: Fe^{3+}(aq) Acidity

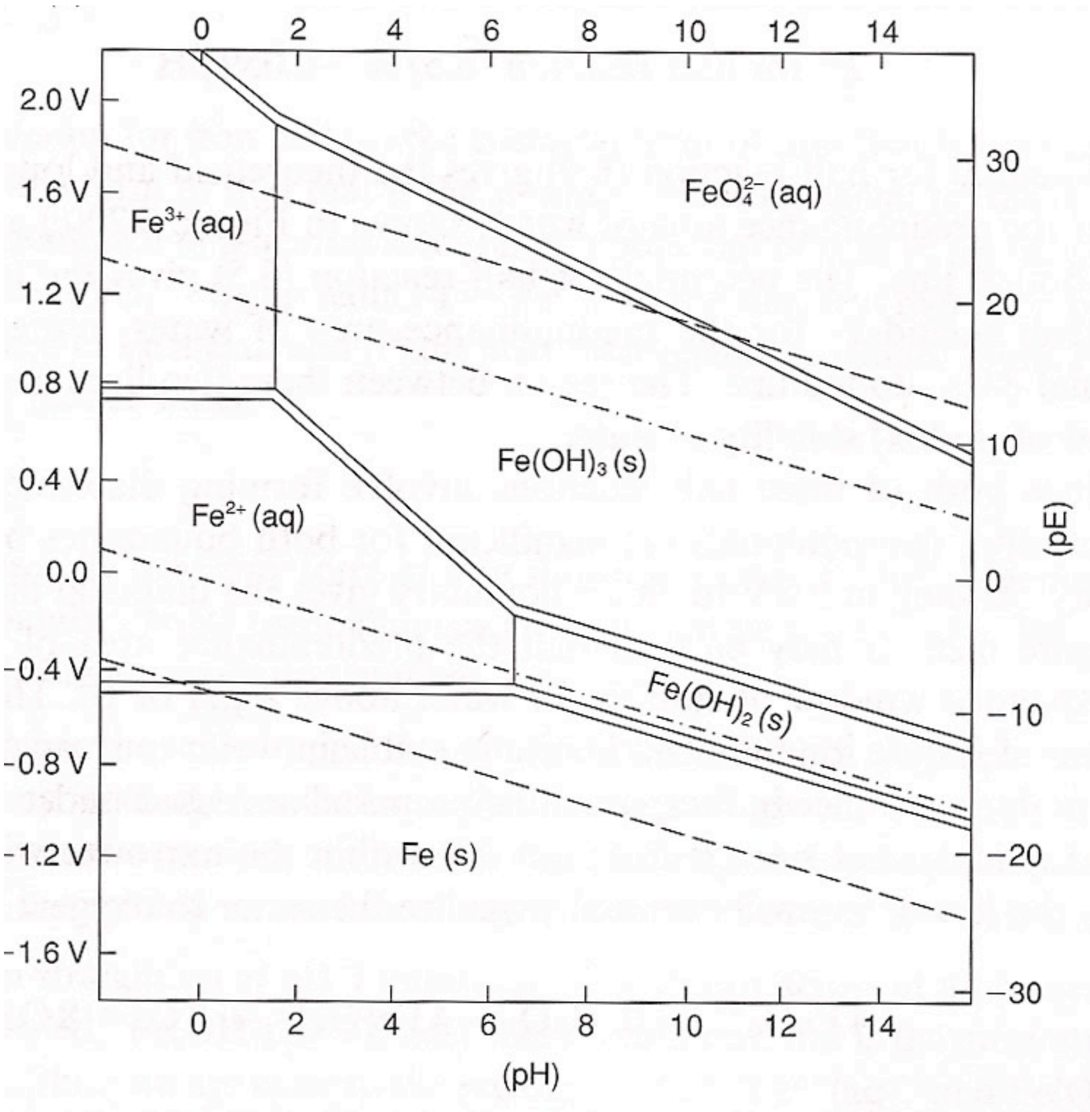


Dissolving an Fe^{3+} salt in water produces an acidic solution

The hexaaquo complex is colorless, while $Fe(H_2O)_5(OH)^{2+}$ has visible absorption and is brownish yellow

Figure from Baes, C.F.; Mesmer, R.E. *The Hydrolysis of Cations*; Wiley-Interscience: New York, 1976.

Pourbaix Diagrams



A visual representation of speciation of a metal as a function of pH and potential

Dashed lines indicate theoretical and practical stability zones for water

Diagram from Wulfsberg, G. *Inorganic Chemistry*; University Science Books: Sausalito, CA, 2000.

Pourbaix Diagrams: Derived from Thermodynamic Data

Vertical boundaries – represent K_{sp} data that depend only pH and not on potential

Ex) $Fe^{3+}(aq) + 3\ OH^{-}(aq) \rightleftharpoons Fe(OH)_3(s)$ $K_{sp} = 4 \times 10^{-38}$

Horizontal boundaries – represent simple redox reactions that depend only on potential

Ex) $Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq)$ $E^{o} = 0.771\ V$

Diagonal boundaries – represent reactions that involve both redox and acid-base chemistry

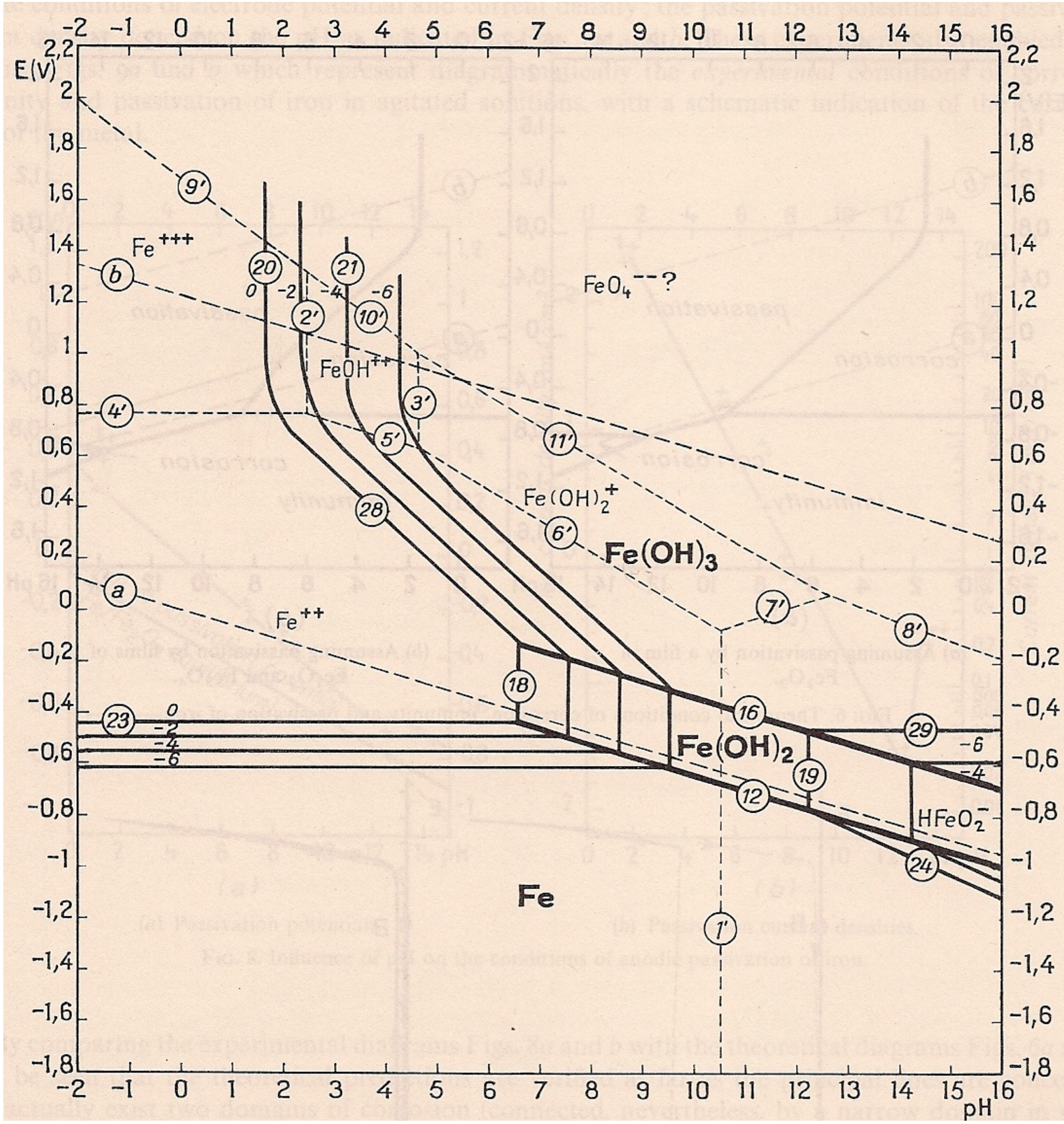
Ex) $FeO_4^{2-}(aq) + 3e^{-} + 8\ H^{+}(aq) \longrightarrow Fe^{3+}(aq) + 4H_2O(l)$ $E^{o} = 2.20\ V$

Use the Nernst equation to find the slope:

$$E = E^{o} - \frac{0.0592}{n} V \cdot mol\, e^{-} \cdot \log Q$$

$$E = 2.20V - \frac{0.0592}{3} V \cdot \log \frac{\left[Fe^{3+}\right]}{\left[FeO_4^{2-}\right]\left[H^{+}\right]^{8}}$$

$$E = 2.20V - \left(0.157 \cdot pH\right)V$$



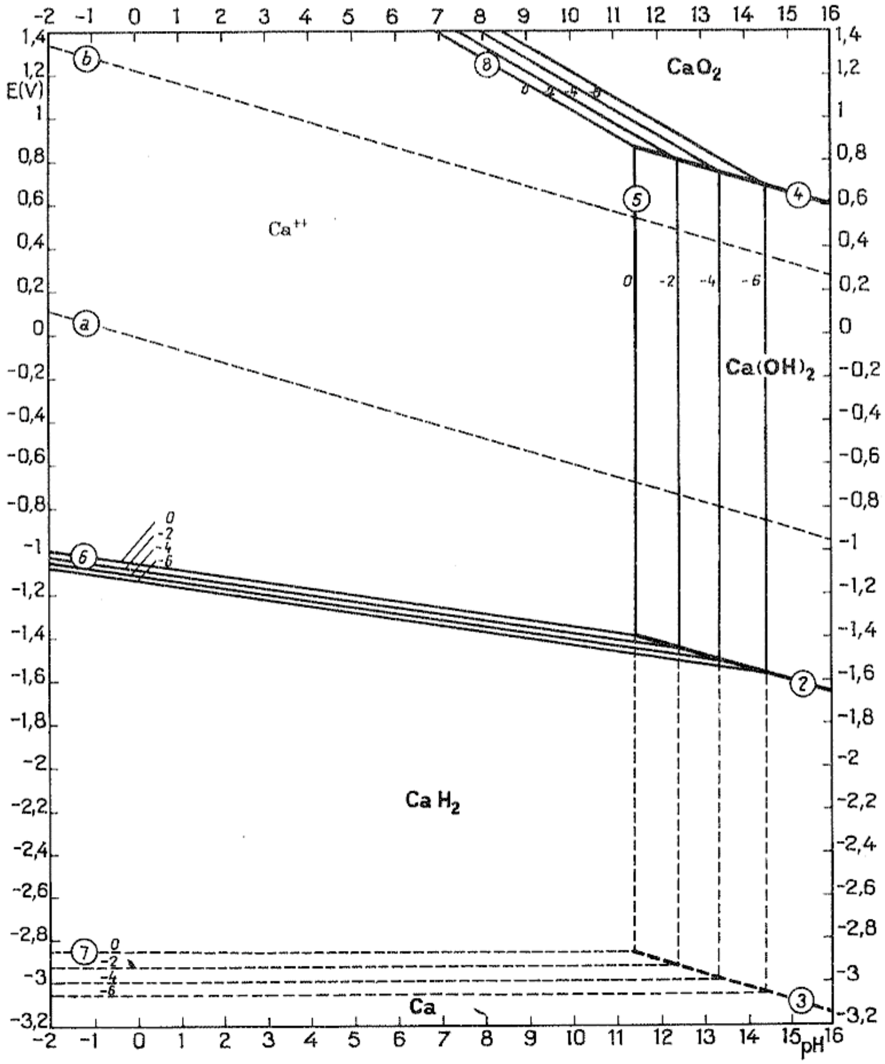
Multiple lines between predominance regions correspond to different total Fe concentrations.

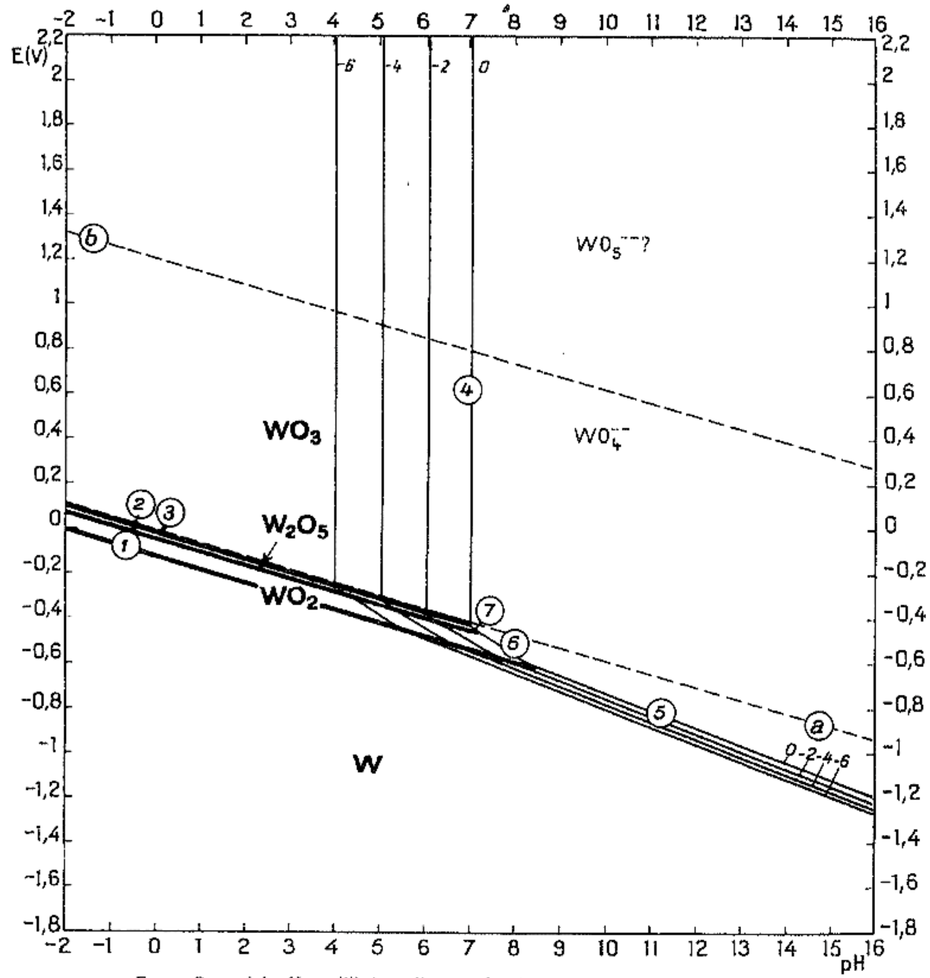
Diagrams can differ in complexity (number of different species considered).

Diagram from Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solution*; Pergamon Press: New York, 1966.

basic oxide/hydroxide

acidic oxide





Diagrams from Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solution*; Pergamon Press: New York, 1966.

amphoteric oxide

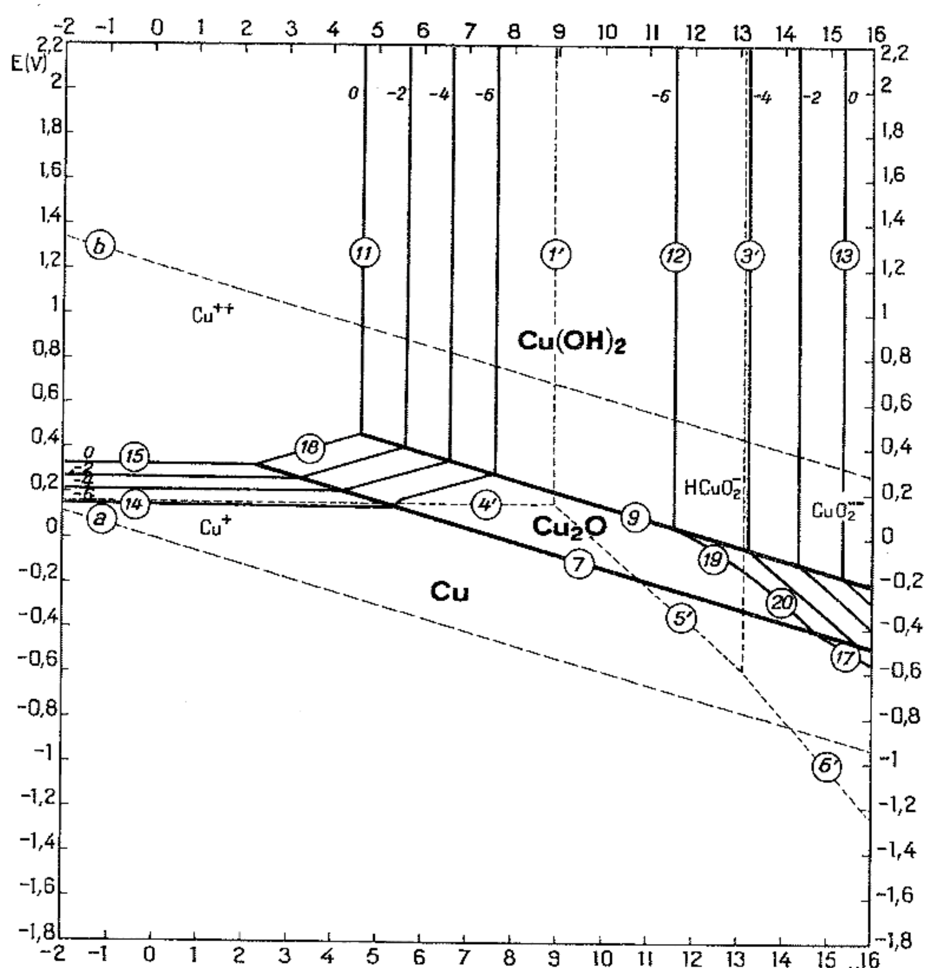
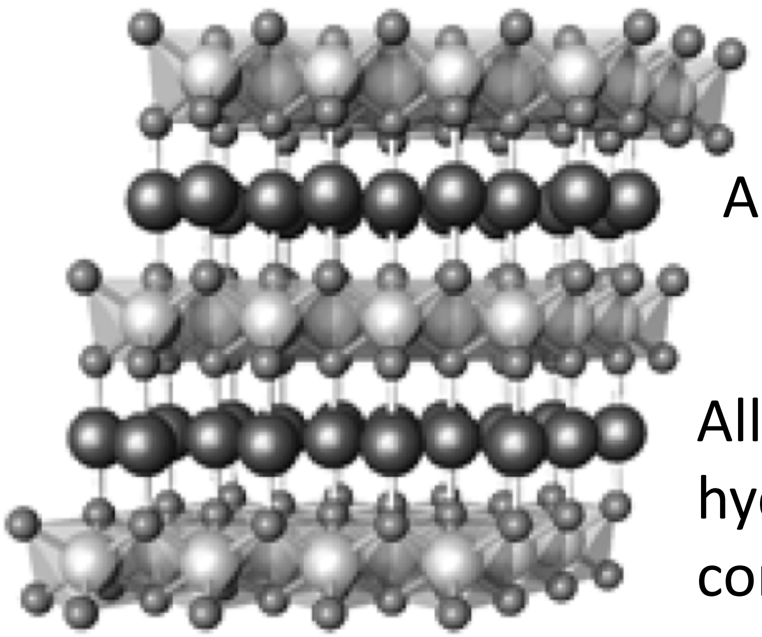


FIG. 2. Potential–pH equilibrium diagram for the system copper–water, at 25°C

Diagram from Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solution*; Pergamon Press: New York, 1966.

Using Acid-Base Character to Design Oxide Syntheses

Synthesis of Delafossite-Type Oxides, ABO_2



Edge-sharing BO_6 octahedra

A cations

All reactions carried out hydrothermally (180-210 °C) in concentrated NaOH solutions.

A = Ag^+, Cu^+ (oxides primarily defined as basic)
B = Sc^{3+}, Co^{3+}, Fe^{3+}, Y^{3+}, La^{3+}, Ga^{3+}, In^{3+}, Al^{3+}…

Sheets, W.C.; Mugnier, E.; Barnabé, A.; Marks, T.J.; Poeppelmeier, K.R. *Chem. Mater.* **2006**, *18*, 7-20.

Accounting for Success and Failure with Acid-Base Character

A-cation source	B-cation source	[NaOH]	products
Cu_2O	Al_2O_3	0.9	$CuAlO_2$
Ag_2O	Al_2O_3	0.9	$AgAlO_2$
Cu_2O	CoOOH	2.0	$CuCoO_2$, Co_3O_4
Ag_2O	CoOOH	2.0	$AgCoO_2$, Co_3O_4
Cu_2O	Sc_2O_3	2.5	$CuScO_2$, ScOOH
Ag_2O	Sc_2O_3	2.5	$AgScO_2$
Cu_2O	La_2O_3	2.5	Cu_2O, $La(OH)_3$
Ag_2O	La_2O_3	2.5	Ag_2O, $La(OH)_3$

Rule of thumb: mimimum solubility required for each reactant oxide is approximately 10^{-4} M

Accounting for Success and Failure with Acid-Base Character

$CuAlO_2$ and $AgAlO_2$ both synthesized at 0.9 M NaOH – Al_2O_3 is the "classic" amphoteric oxide; has solubility on the order of 10^{-1} M at 200 ^oC, 0.5 M NaOH

CoOOH has amphoteric character but requires a larger [NaOH] than Al_2O_3 in order to react

Reactions with Sc_2O_3 illustrate difference in acidity between Cu_2O and Ag_2O; max. solubility for Ag^+ is $10^{-2.5}$ at 200 ^oC, compared with 10^{-4} for Cu^+

Reactions with Y_2O_3, Eu_2O_3, and La_2O_3 returned insoluble hydroxides – these are insufficiently acidic to react in base

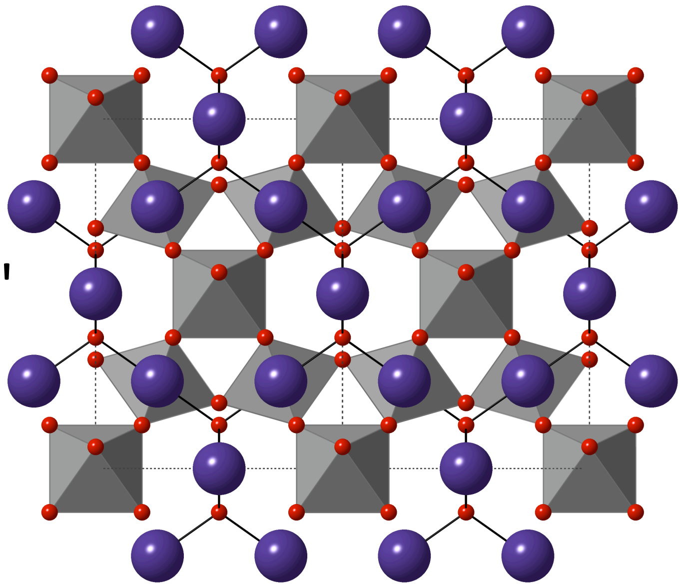
Another Preparative Method Employing Metal Hydrolysis…

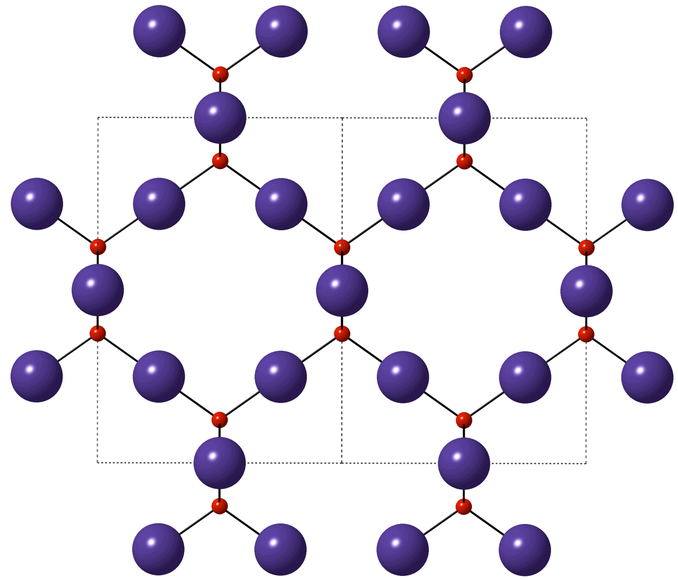
Cookies frequently contain both baking soda ($NaHCO_3$) and baking powder (a mixture of $NaHCO_3$, $CaHPO_4$, and $NaAl(SO_4)_2$)

Baking soda requires an acid to react with the bicarbonate. Baking powder provides its own through hydrolysis of the aluminum cation and reaction of the hydrogen phosphate ion with water.

Example 2: Nb and Ta Pyrochlores

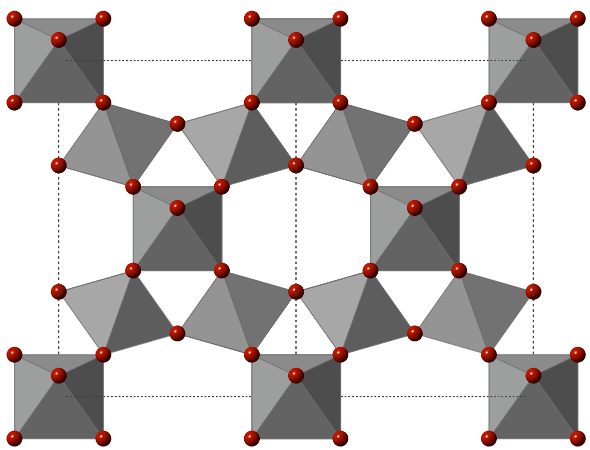
$A_2B_2O_6O'$

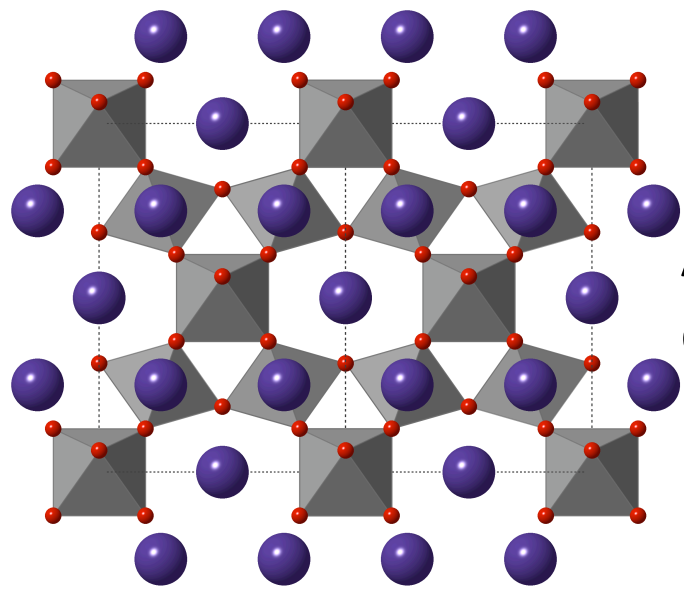




A_2O' network

B_2O_6 network





$A_2B_2O_6$ defect pyrochlore

viewed along [110]

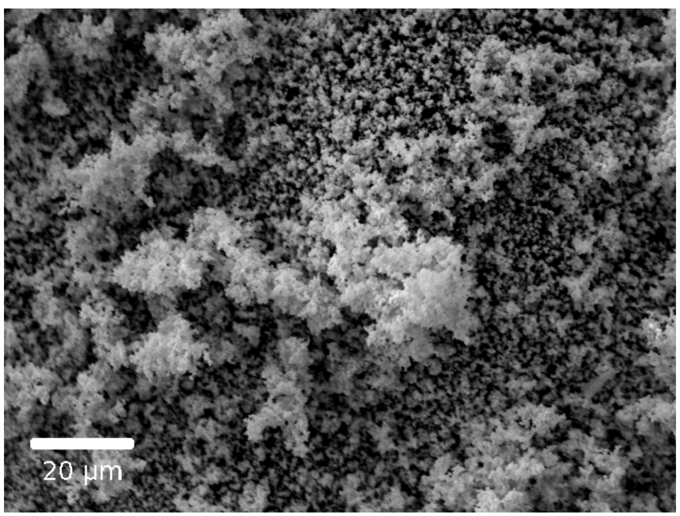
Hydrothermal Synthesis

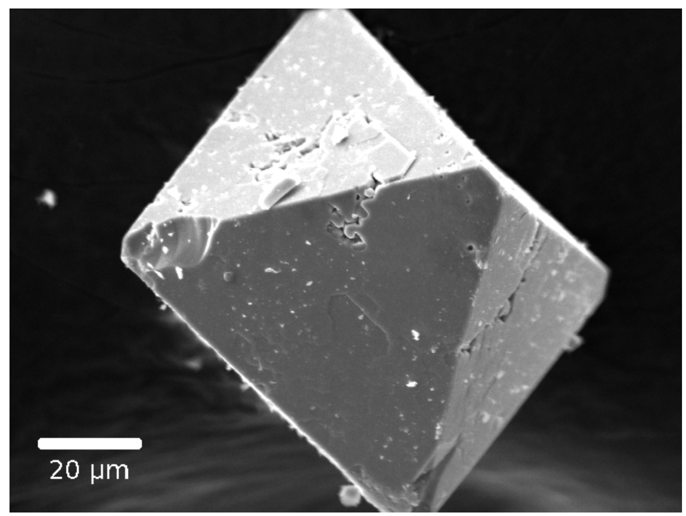
$$M_2O_5(s) + 2\ KOH(aq) \xrightarrow[250\ ^{o}C,\ 3\text{-}5\ days]{H_2O,\ 1.2\ M\ KOH} K_{2-x}M_2(O,OH)_6 \cdot nH_2O(s) + H_2O(l)$$

M = Nb, Ta*

x = 0.74, n = 1.3 for Ta
x = 0.73, n = 1.2 for Nb

Ta

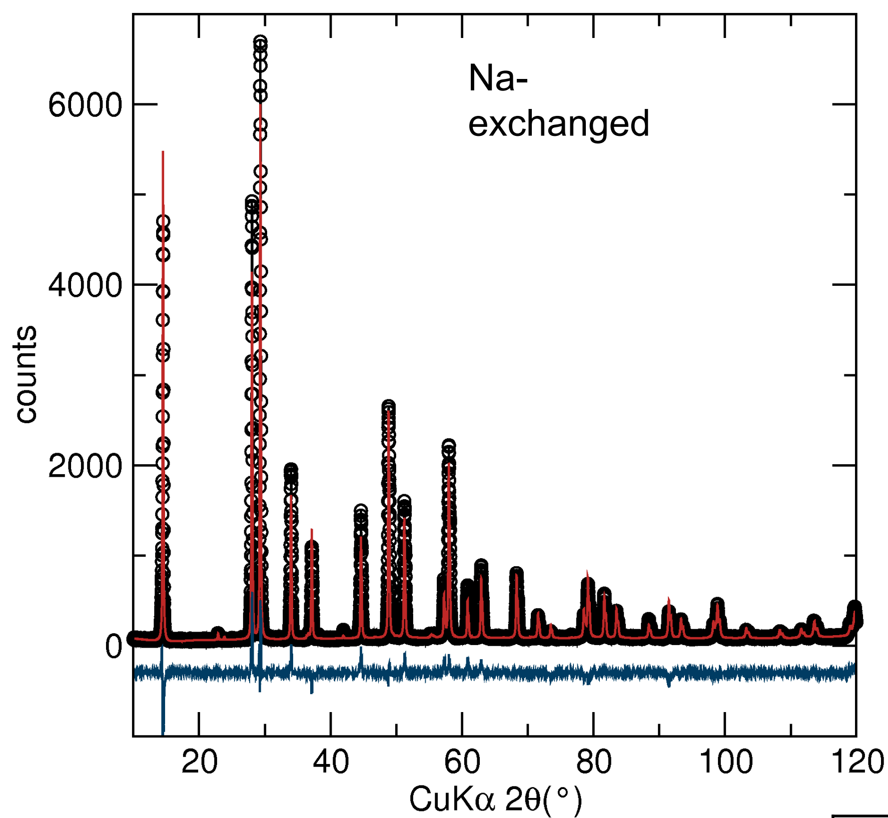




Nb

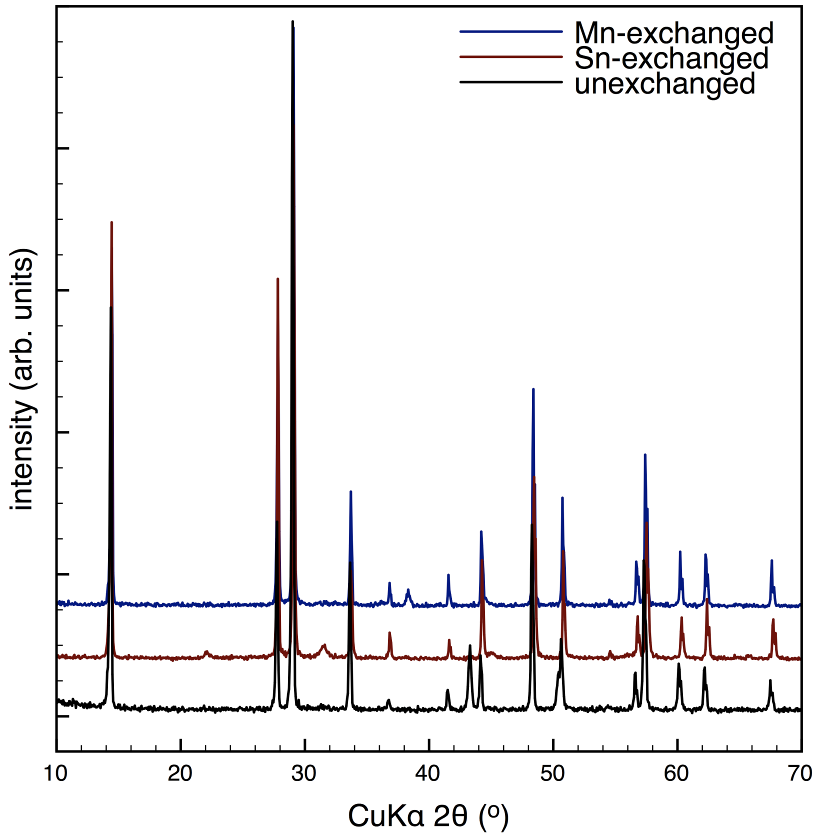
* Duan, N.; Tian, Z.-R.; Willis, W.S.; Suib, S.L.; Newsam, J.M.; Levine, S.M. *Inorg. Chem.* **1998**, *37*, 4697-4701.
Goh, G.K.L.; Haile, S.M.; Levi, C.G.; Lange, F.F. *J. Mater. Res.* **2002**, *17*, 3168-3176.

Ion-Exchange Reactions



Exchanged cation	Ionic radius (Å) (coord. # = 8)	Refined lattice parameter (Å)	Metal ratio (EDS)
K^+ (un-exchanged)	1.65	10.621	1.25 K: 2 Ta
Na^+	1.32	10.533	0.89 Na: 2 Ta

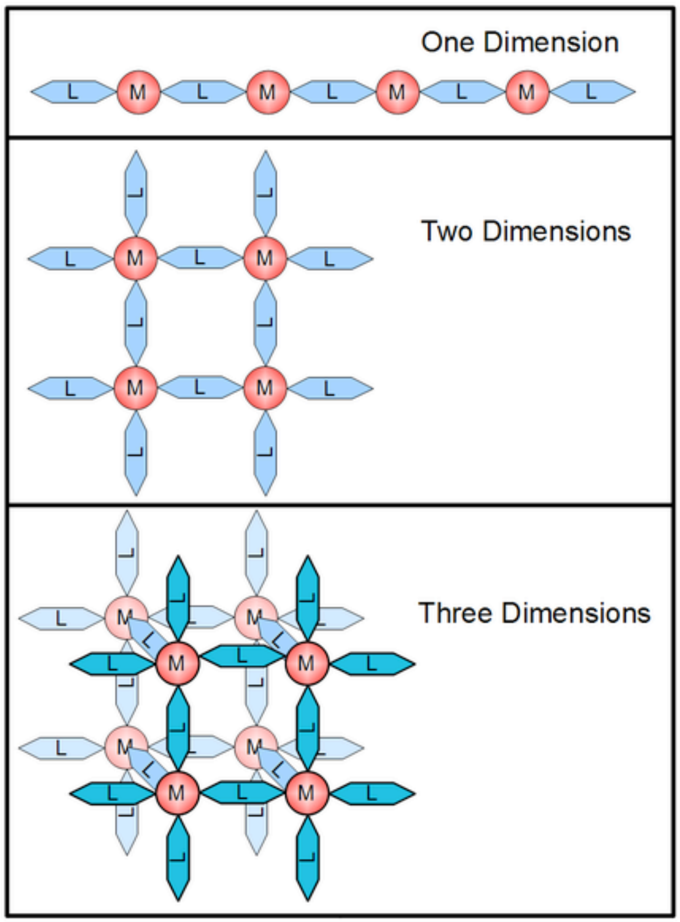
Ion-Exchange Reactions



Exchanged cation	Ionic radius (Å) (coord. # = 8)	Refined lattice parameter (Å)	Metal ratio (EDS)
K^+ (un-exchanged)	1.65	10.653	1.14 K: 2 Nb
Mn^{2+}	1.10	10.640	0.68 K: 0.30 Mn: 2 Nb
Sn^{2+}	1.36	10.615	0.23 K: 0.16 Sn: 2 Nb

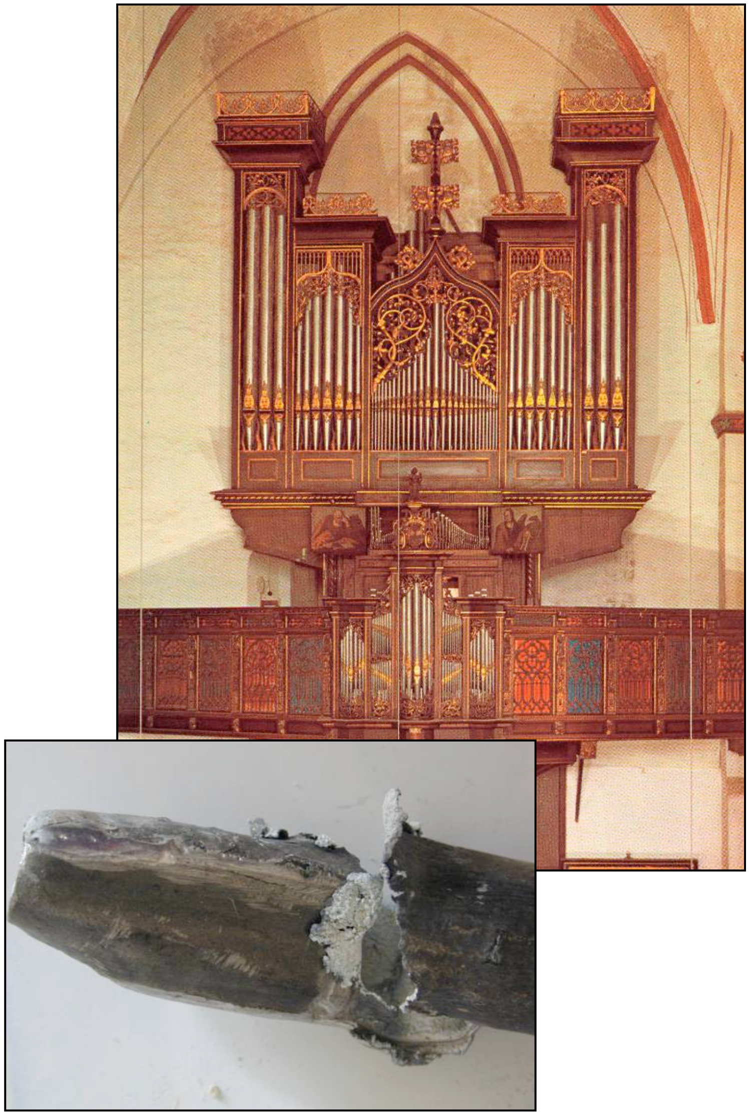
Hydrothermal Synthesis of Inorganic-Organic Hybrid Networks

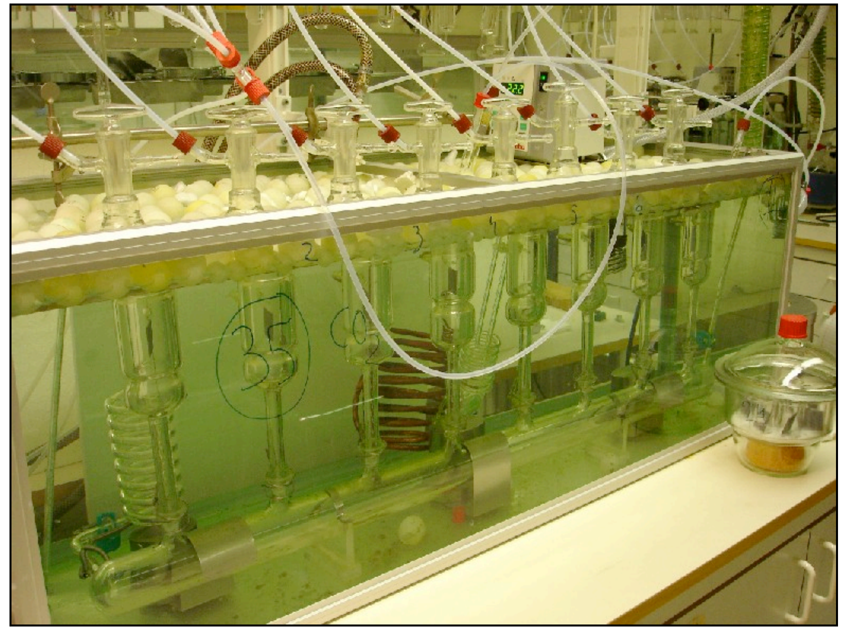
Thousands of synthesized compounds can be described as coordination polymers, hybrid inorganic-organic networks, metal-organic frameworks…



Extensive linkages limit solubility under ambient conditions, and organic component requires mild reaction conditions.

Growing Single Crystals to Characterize Corrosion Products





Laboratory and field studies show that organic acid exposure is a major cause of corrosion in lead-tin alloy organ pipes.

Photos courtesy of Ibo Ortgies, Göteborg Organ Art Center

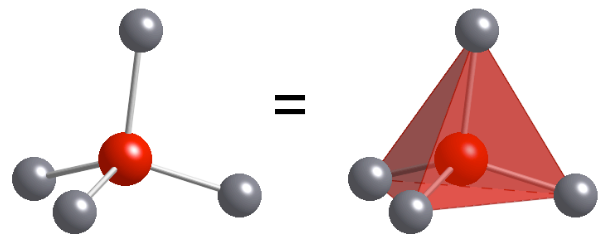
Basic lead formate:

$$2PbO + 2HCOOH \xrightarrow[17\ hrs]{H_2O,\ 120\ ^{o}C} Pb_2O(CHOO)_2$$

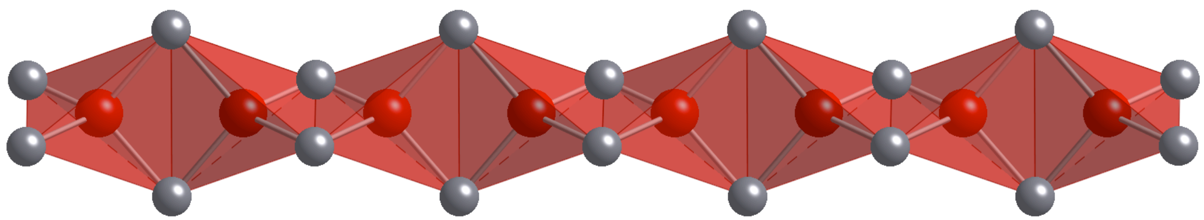
Basic lead acetate:

$$Pb(CH_3COO)_2 \cdot 3H_2O + 2PbO \xrightarrow[10\ hrs]{H_2O,\ 120\ ^{o}C} Pb_3O_2(CH_3COO)_2 \cdot (0.5)H_2O$$

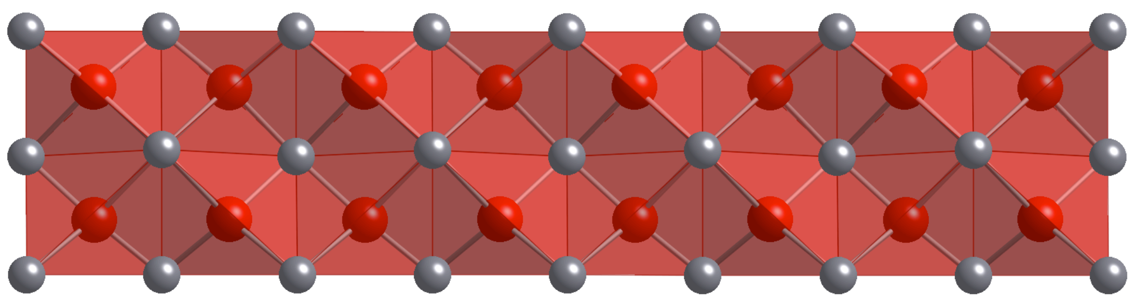
Pb_4O tetrahedron



Pb_2O^{2+} chain

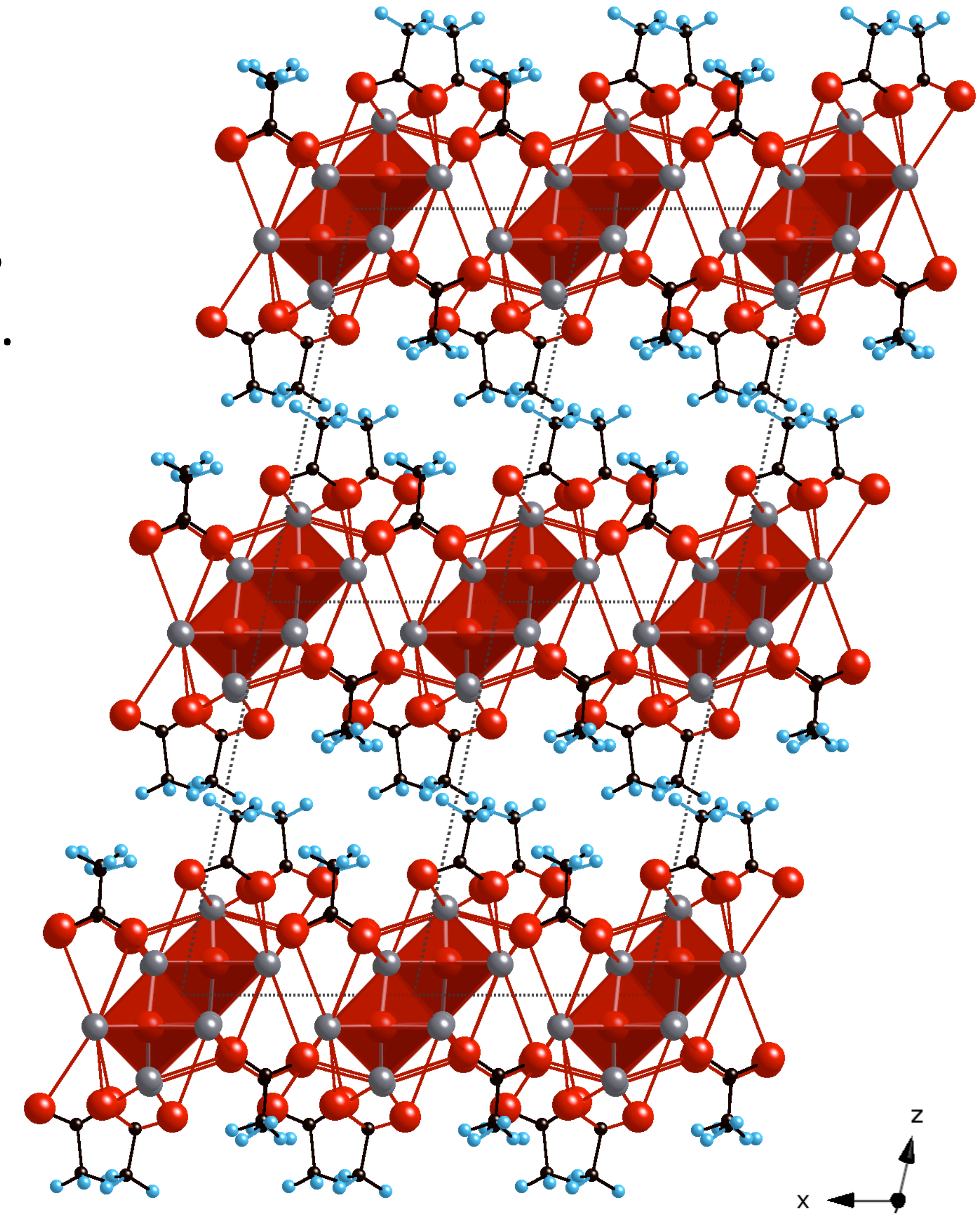


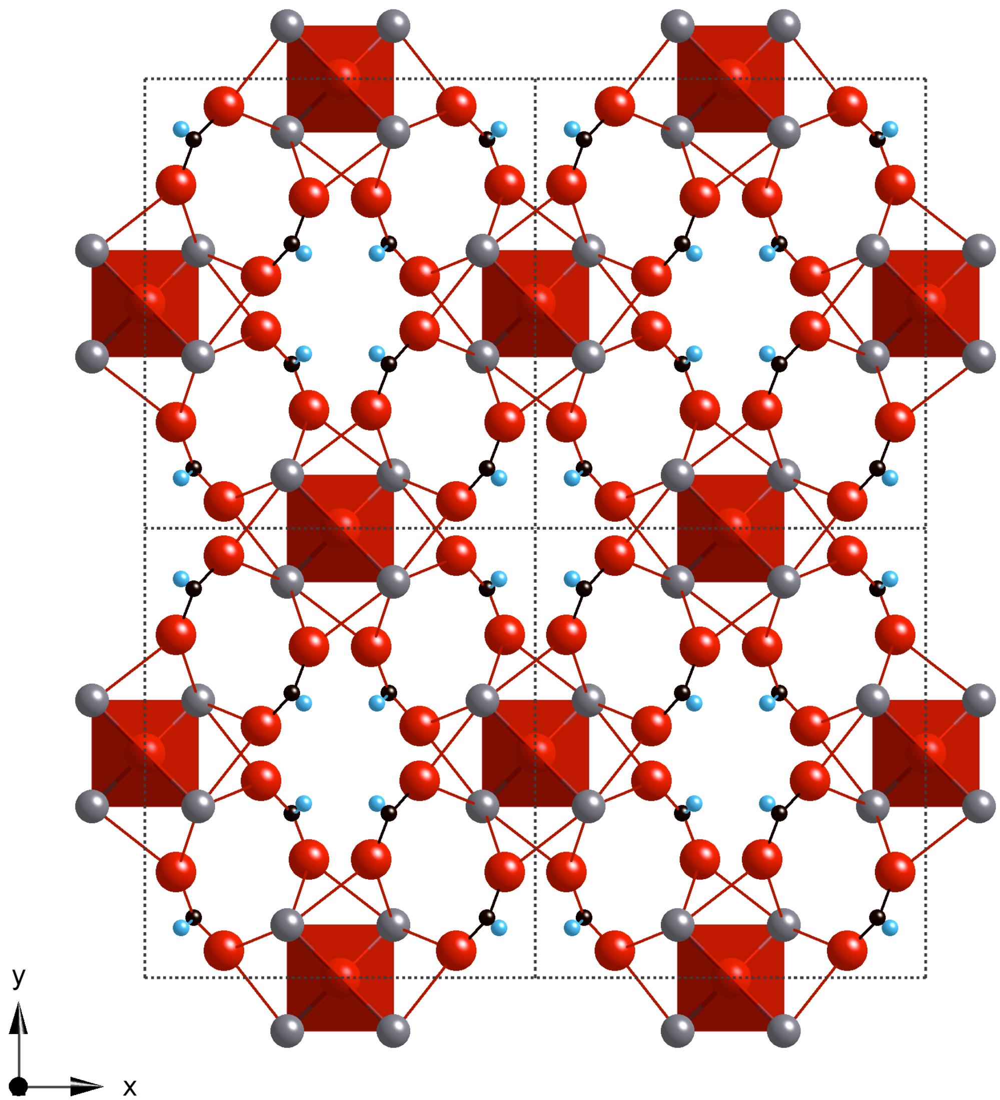
$Pb_3O_2^{2+}$ chain



Basic lead acetate:

Acetate ions link $Pb_3O_2^{2+}$ chains to form two-dimensional layers.



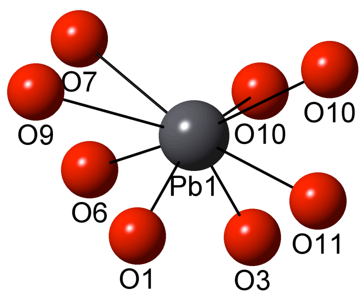


Basic lead formate:

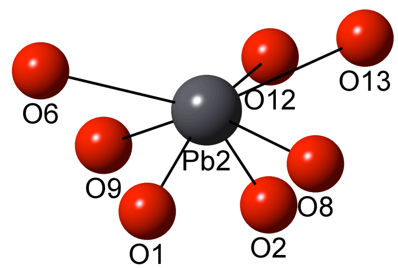
Formate ions link Pb_2O^{2+} chains into a three-dimensional network.

Analysis of Lead Coordination Environments

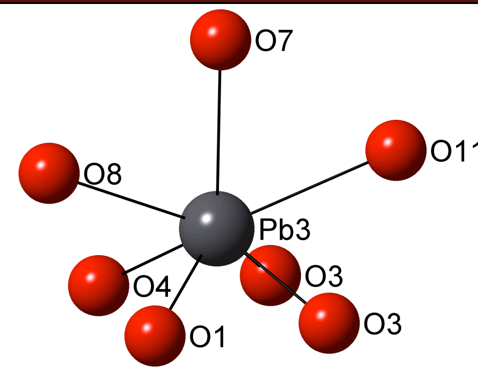
Basic lead acetate:



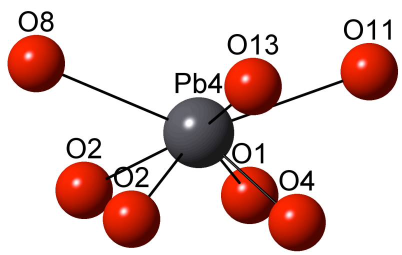
BVS = 2.05



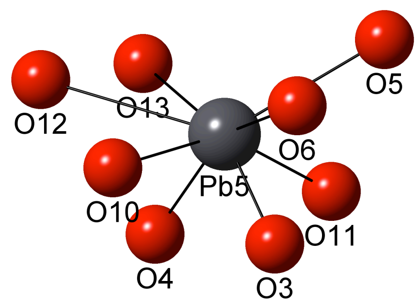
BVS = 2.00



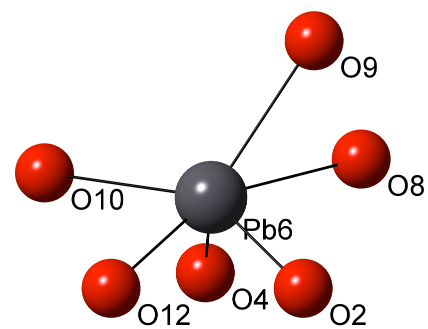
BVS = 1.99



BVS = 1.99

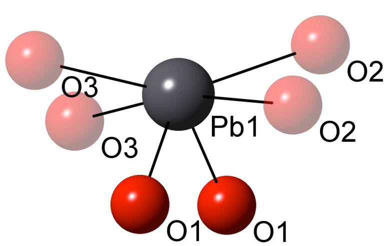


BVS = 1.98



BVS = 2.02

Basic lead formate:



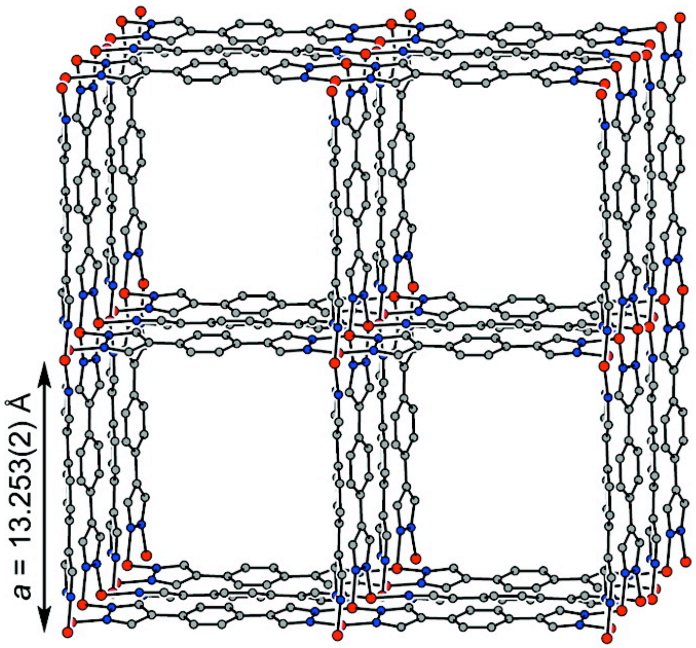
BVS = 1.94

Pb^{2+}: [Xe] $4f^{14}5d^{10}6s^{2}$

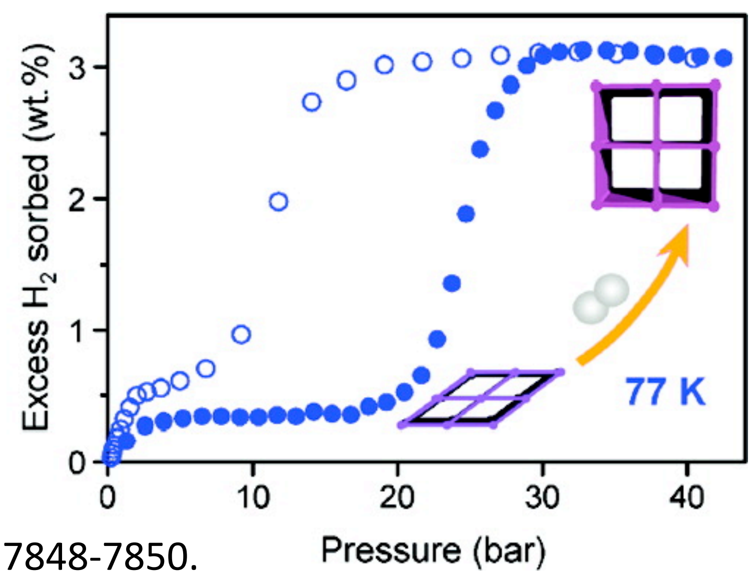
Ideal bond valence sum (BVS) = 2

Non-Aqueous Systems: Growth of MOFs and ZIFs

MOF: Metal-Organic Framework



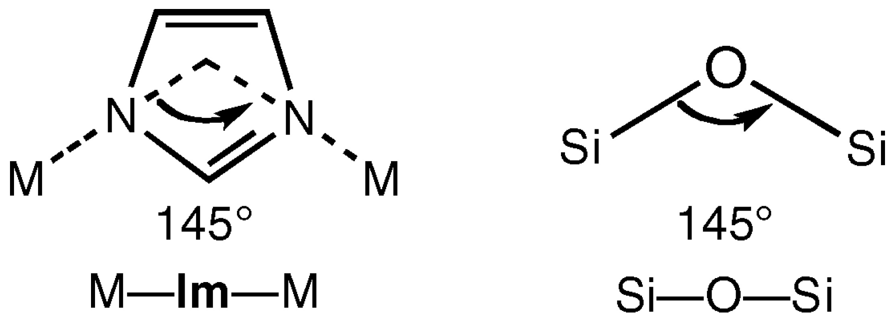
Synthesized from $Co(CF_3SO_3)_2$ and 1,4-benzenedi(4'pyrazoyl) in diethylformamide (DEF) at 130 ^oC. DEF decomposes to form amines that deprotonate the ligand.



Choi, H.J.; Dincă, M.; Long, J.R. J. Am. Chem. Soc. **2008**, *130,* 7848-7850.

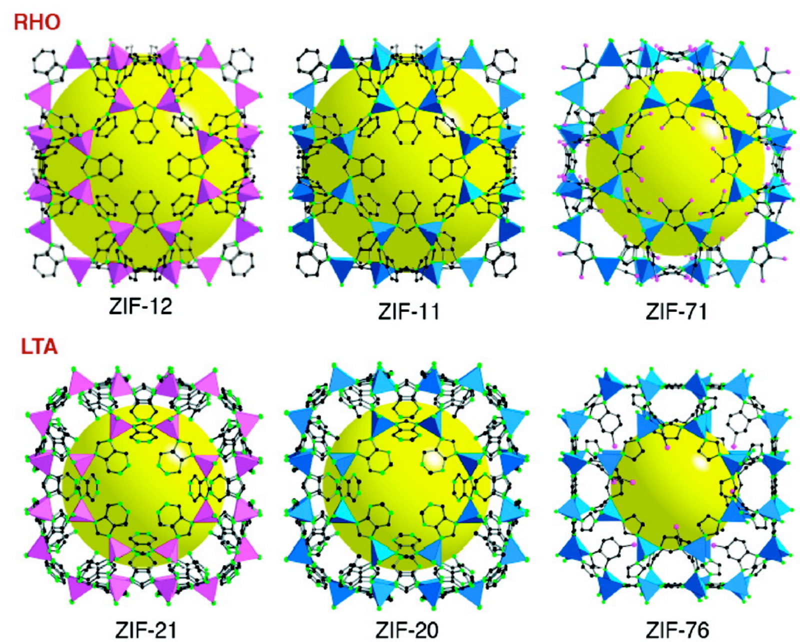
Non-Aqueous Systems: Growth of MOFs and ZIFs

ZIF: Zeolitic Imidazolate Framework



Three-dimensional networks with tetrahedral topologies

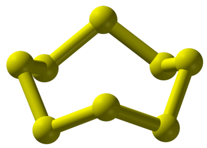
Synthesized from hydrated metal salts, protonated imidazole ligands (HIm) and amide solvents at 85-150 ^{o}C



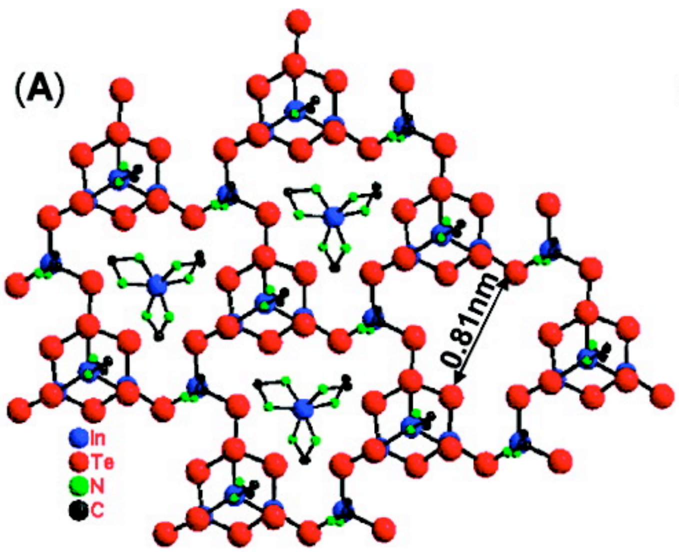
Phan, A.; Doonan, C.J.; Uribe-Romo, F.J.; Knobler, C.B.; O'Keefe, M.; Yaghi, O.M. *Acc. Chem. Res.* **2010**, *43,* 58-67.

Non-Aqueous Systems: Chalcogenide Synthesis

Use of amine-based synthesis prevents unwanted metal hydrolysis, and amine can serve as a reactant as well as a solvent.



S_8 ring can be activated by ring-opening nucleophilic attack by an amine – may also be true for other elemental chalcogenides.



$[In(en)_3][In_5Te_9(en)_2]\cdot 0.5en$
Synthesized from KIn_2, Te, and ethylenediamine (en) at 190 ^oC

Zhang, Q.; Chung, I.; Jang, J.I.; Ketterson, J.B.; Kanatzidis, M.G. *Chem. Mater.* **2009**, *21*, 12-14.

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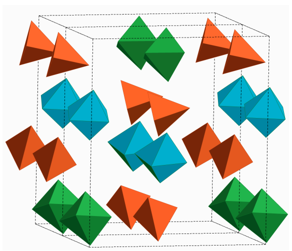
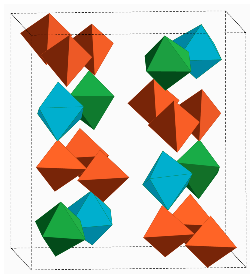
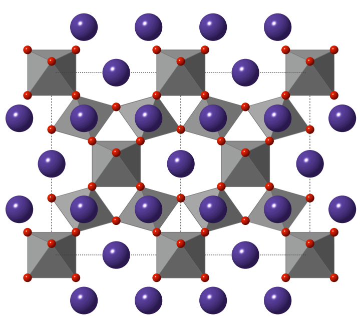
Solvothermal Synthesis of Polymorphs of M(ethylenediamine)$_3$MoS$_4$ (M = Ni, Co, Mn)



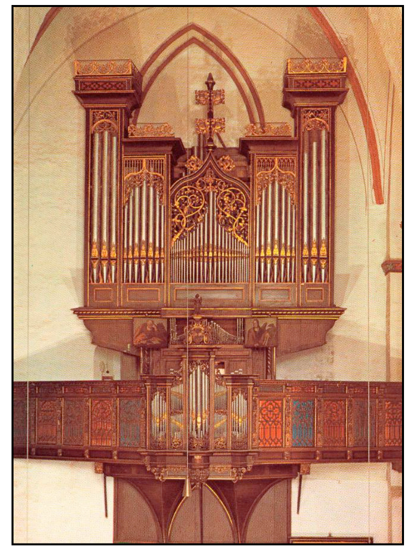


Tian, H.; Iliff, H.A.; Moore, L.J.; Oertel, C.M.
Cryst. Growth Des. **2010**, *10*, 669-675.

Hydrothermal and Ion-Exchange Syntheses of Nb and Ta Defect Pyrochlores



Corrosion of Lead-Tin Alloy Organ Pipes and Crystal Chemistry of Basic Lead Carboxylates



Oertel, C.M.; Baker, S.P.; Niklasson, A.; Johansson, L.-G.; Svensson, J.-E.
J. Electrochem. Soc. **2009**, *156*, C414-C421.

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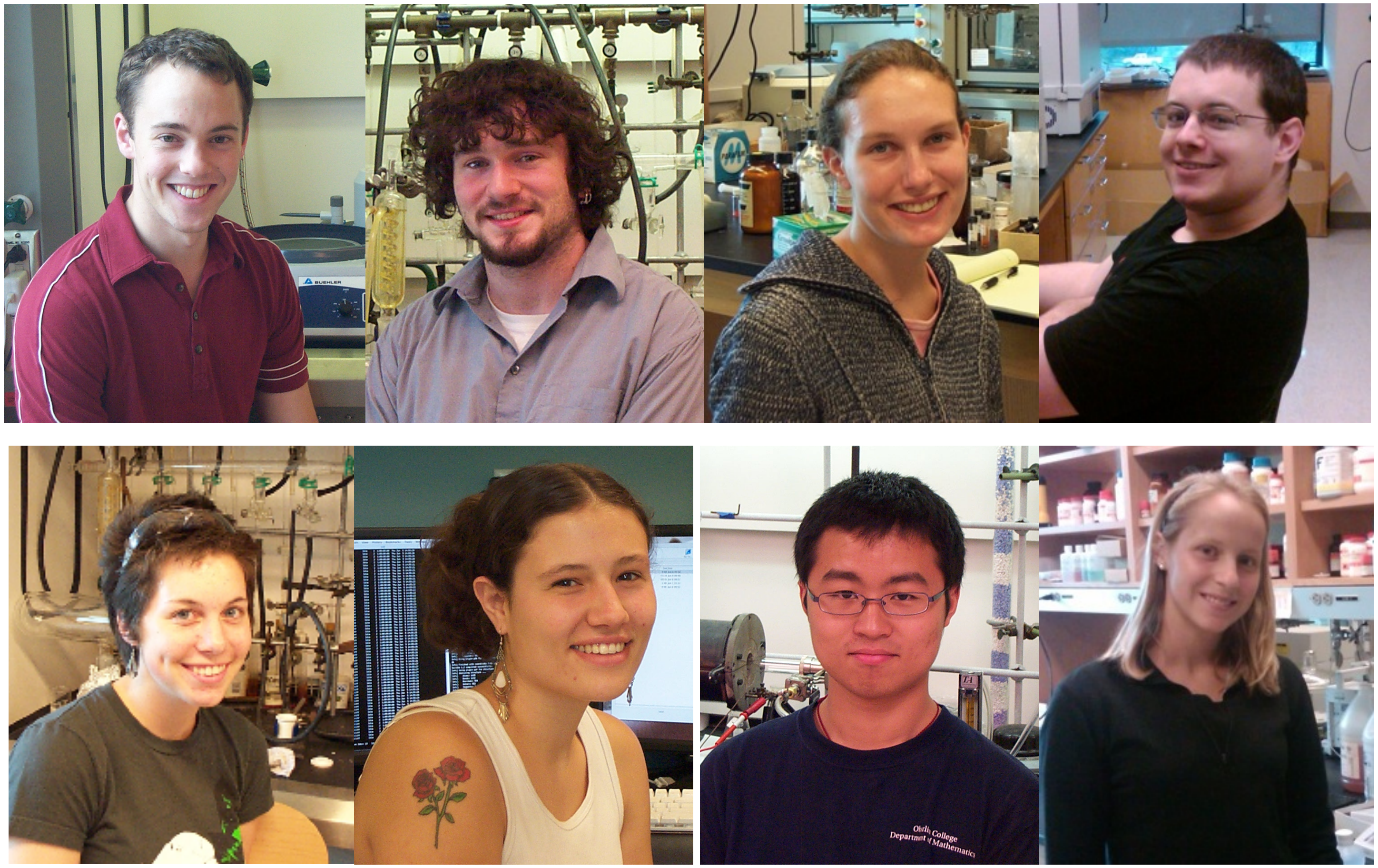

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