PORTFOLIO OF SOLID-STATE MATERIALS CHEMISTRY SYNTHESIS METHODS

- **Direct reactions of solids** – diffusion, nucleation, growth
- **Precursor methods** – single and multiple element sources
- **Co-crystallization techniques** – atomic level mixing
- **Metathesis metal exchange** – rapid solid state synthesis
- **Vapor phase transport** – synthesis as well as purification, crystal growth and doping
- **Ion-exchange methods** - solid, solution and melt approaches
- **Topotactic chemistry** - injection and intercalation – chemical/electrochemical techniques
- **Chimie Douce** – bringing down the heat soft-chemistry methods for synthesis of novel meta-stable materials
RATES OF REACTIONS IN SOLID STATE SYNTHESIS ARE CONTROLLED BY THREE MAIN FACTORS

1. Contact area: surface area of reacting solids related to particle size

2. Rates of diffusion: of ions through various phases, reactants and products

3. Rates of nucleation and growth: of product phase

Let us examine each of the above in turn
SURFACE AREA OF PRECURSORS

• Trivial but a vital consideration in solid state synthesis

• Consider MgO, 1 cm$^3$ cubes, density 3.5 g cm$^{-3}$

• 1 cm cubes: SA 6x10$^{-4}$ m$^2$/g
• 10$^{-3}$ cm cubes: SA 6x10$^{-1}$ m$^2$/g \( (10^9\times6\times10^{-6}/10^4) \)
• 10$^{-6}$ cm cubes: SA 6x10$^2$ m$^2$/g \( (10^{18}\times6\times10^{-12}/10^4) \)

• The latter is equal to a 100 meter running track!!!

• The point is that solid state chemistry reaction rates will be influenced by the contact area of precursors which will depend on the size and packing density of precursor particles and these factors will affect diffusion lengths of the reacting species moving through the growing product layer between particles
MINIMIZING DIFFUSION LENGTHS $<x> \approx (2Dt)^{1/2}$ FOR RAPID AND COMPLETE DIRECT REACTION BETWEEN SOLID STATE MATERIALS AT LOWEST T

Core-corona solid state reactants - made by growth of uniform thickness corona or the core particle

Aimed to increase contact area and decrease reaction diffusion length scale
CORE-CORONA PRECURSOR SYNTHESIS
HOLLOW NANOSPHERES

- \( \text{Co(acac)}_3 + \text{NaBH}_4 + \text{OA} \rightarrow \text{Co}_n(\text{OA})_m \)
- \( \text{S} + \text{OA} + \text{Co}_n(\text{OA})_m \rightarrow \text{S@Co}_n \)
- Co core S corona nanoparticles
- \( \text{S@Co}_n \rightarrow \text{Co}_2\text{S}_3 \) hollow nanospheres
- OA functions as high T solvent, reactant, capping ligand
Oleic Acid $\text{C}_{17}\text{H}_{33}\text{CO}_2\text{H}$

Arrested nucleation and growth of nanocrystals – use of surfactant, ligand, high temperature solvent properties
Co(III) precursor (acetate, acetylacetonate) - NaBH₄ reductant $\rightarrow$ Coₙ

- oleic acid surfactant additive $\rightarrow$ CoₙLₘ
- arrested nucleation and growth of surfactant capped cobalt nanoparticles
- surfactant functions as high T capping ligand and solvent 150-200°C
- surfactant-sulfur injection provides sulfur coat on cobalt nanocluster
- magnetic cobalt sesquisulfide Co₂S₃ product shell layer formed at interface
KIRKENDALL POROSITY

- counter-diffusion of Co(3+)/e(-) and S(2-) across thickening product shell
- **faster diffusion of Co(3+) than S(2-) creates vacancies V[Co] in core**
- size rather than charge effect determines diffusion
- generated vacancies agglomerate in core to form a void
- hollow core created which grows as the product shell thickens
- end result – a hollow nanosphere made of nc cobalt sesqui-sulfide Co$_2$S$_3$
- shell not perfectly sealed - has some porosity between nc comprising shell
- **use - magnetic drug delivery and magnetohyperthermia cancer therapeutics**
THINGS ARE NEVER THAT SIMPLE!!!

Different diffusion processes responsible for the growth of different architecture hollow nanostructures induced by effect of Kirkendall porosity.

Air vacancies white, cobalt orange, $\text{Co}_2\text{S}_3$ product blue.

I cannot believe it !!!!
Time evolution of a hollow \( \text{Co}_2\text{S}_3 \) nanocrystal grown from a Co nanocrystal via the nanoscale Kirkendall effect

*Science* 2004, *304*, 711
Time Resolved in situ TEM Study Reveals Bismuth Oxide Hollow Nanoparticle Formation by the Kirkendall Effect

\[ \text{ncBi} + \text{O}_2 \rightarrow \text{ncBi}_2\text{O}_3 \]

*Nano Letters October 2013*
• Kirkendall effect - discovered in 1930’s.

• Occurs during reaction of two solid-state materials and involves the counter diffusion of reactant species, like ions, across product interface usually at different rates.

• Special case of movement of fast-diffusing component cannot be balanced by movement of slow component the net mass flow is accompanied by a net flow of atomic vacancies in the opposite direction.

• Leads to Kirkendall porosity formed through aggregation of vacancies into hollow pores
When starting with perfect building blocks such as monodisperse cobalt nanocrystals a reaction meeting the Kirkendall criteria can lead to agglomeration of vacancies exclusively in the center of the nanocrystal.

General route to hollow nanocrystals of almost any given material and shape – like nanocubes, nanotriangles, nanorods and chains of nanoshells

First proof-of-concept experiment - synthesis of $\text{Co}_2\text{S}_3$ nanoshell starting from Co nanocluster.
Time evolution of a *hollow CoSe$_2$ nanocrystal magnetic dipole chain* grown from a Co nanocrystal and selenium in surfactant capping ligand and solvent via the nanoscale Kirkendall effect – Small September 2007
Scheme of magnetic dipole-dipole coupling of superparamagnetic nanocrystals into magnetic nanocrystal chains

Superparamagnetism – cooperative magnetic coupling of unpaired electron spins in a single Weiss domain ferromagnetic nanocrystal
Magnetotactic bacteria – vesicle templated nucleation and growth of superparamagnetic nanocrystal dipole chain

Communication and cooperative behaviour between bacteria communities – relevant to evolutionary biology ????

I know my magnetic North !!!
Works for Hollow ZnAl$_2$O$_4$ Spinel Nanotubes!!!
Synthesis of ZnO nanowires

ZnO/C 905°C \(\rightarrow\) ZnCO VPT \(\rightarrow\) ZnO VLS NW 880°C
Hollow ZnAl$_2$O$_4$ Spinel Nanotubes

- How does it work – VPT VLS growth (see later)

- ZnO(s) + C(s) $\rightarrow$ ZnCO(g)

- Au$_n$(l) + ZnCO(g) $\rightarrow$ ZnO(NW) + C(s)

- Coat ZnO NW with hydrolysable-polymerizable AlX$_3$ (X = Cl, OR) precursor in solution or vapor phase – sol gel chemistry

- AlX$_3$ + 3H$_2$O $\rightarrow$ Al(OH)$_3$ + 3HCl

- AIOH + HOAl $\rightarrow$ Al-O-Al + H$_2$O

- Thermally treat to make Al$_2$O$_3$ coated ZnO NWs
Hollow ZnAl$_2$O$_4$ Spinel Nanotubes

• Heat further to induce inter-diffusion of core and corona

• Zn$^{2+}$ more mobile than Al$^{3+}$

• Creates Zn$^{2+}$ vacancies in the core ZnO nanowire

• Vacancies agglomerate in core and create Kirkendall porosity

• Final product a ZnAl$_2$O$_4$ hollow Spinel nanotube

• What would you use them for – nanofluidics, ionic nanodiode or transistor, drug storage and delivery vehicle ???
Provide details of the processes that occur when a segmented zinc-copper nanorod is heated in an argon versus oxygen environment.
Three ways to make hollow nanostructures

(a) Kirkendall effect for metal nanoparticles

(b) galvanic exchange with pinhole dissolution

(c) anion exchange with the Kirkendall effect
MINIMIZING DIFFUSION LENGTHS \( <x> \approx (2Dt)^{1/2} \) FOR RAPID AND COMPLETE DIRECT REACTION BETWEEN SOLID STATE MATERIALS AT LOWEST T

- Johnson superlattice precursor
- Deposition of thin film reactants
- Controlled thickness, composition
- Metals, semiconductors, oxides
- Binary, ternary compounds
- Modulated structures
- Solid solutions (statistical reagent mix)
- Diffusion length x control
- Thickness control of reaction rate
- Low T solid state reaction
- Designer element precursor layers
- Coherent directed product nucleation
- Oriented product crystal growth
- LT metastable hetero-structures
- HT thermodynamic product
Metal Dichalcogenides \( \text{MX}_2 \)

- \( M = \text{Ti, V, Cr, Zr, Hf, Nb, Ta, Mo, W} \)
- \( X = \text{S, Se, Te} \)
- \( \text{O}_h \) octahedral and \( \text{D}_{3h} \) trigonal pyramidal \( \text{MX}_6 \) building blocks
- Edge sharing trigonal packed \( \text{MX}_{6/3} \) units
- Parallel stacked \( \text{MX}_2 \) layers
- Strong \( M-X \) covalent forces in layers
- Weak VdW forces between layers
- VdW gap between adjacent layers
- Chemistry between the sheets
ELEMENT M + 2X MODULATED SUPERLATTICES - DEPOSITED AND THERMALLY POST TREATED TO GIVE LAYERED METAL DICHALCOGENIDES MX$_2$
MINIMIZING DIFFUSION LENGTHS \(<x> \approx (2D_t)^{1/2}\) FOR RAPID AND COMPLETE DIRECT REACTION BETWEEN SOLID STATE MATERIALS AT LOWEST T

Johnson superlattice reagent design

\[
\{(\text{Ti-2Se})_6(\text{Nb-2Se})_6\}_n
\]

Low T annealing reaction

\[
\{(\text{TiSe}_2)_6(\text{NbSe}_2)_6\}_n
\]

Metastable ternary modulated layered metal dichalcogenide (hcp Se\(^2\)-layers, Ti\(^4+\)/Nb\(^4+\) O\(_h\)/D\(_{3h}\) interlayer sites)
superlattice well defined PXRD

Confirms correlation between precursor heterostructure sequence and superlattice ordering of final product

*Note NbSe\(_2\) is a superconductor !!!*
Superlattice precursor sequence \(6(\text{Ti}-2\text{Se})-6(\text{Nb}-2\text{Se})\) yields ternary modulated superlattice composition \(\{(\text{TiSe}_2)_6(\text{NbSe}_2)_6\}_n\) with 62 well defined PXRD reflections – good exercise – give it a try

Confirms correlation between precursor heterostructure sequence and superlattice ordering of final product
MINIMIZING DIFFUSION LENGTHS $<x> \approx (2Dt)^{1/2}$ FOR RAPID AND COMPLETE DIRECT REACTION BETWEEN SOLID STATE MATERIALS AT LOWEST T.

Johnson superlattice reagent design

$\{(\text{Ti}-2\text{Se})_6(\text{Nb}-2\text{Se})_6\}_n$

High T annealing reaction

$\{(\text{Ti}_{0.5}\text{Nb}_{0.5}\text{Se}_2)\}_n$

Thermodynamic linear Vegard type solid solution ternary metal dichalcogenide “alloy” product with identical layers

**Properties of ternary product** is the atomic fraction weighted average of binary end member components – linear Vegard Law

$P(Ti_x Nb_{(1-x)} Se_2) = xP(Ti Se_2) + (1-x)PNbSe_2$
Several important synthetic parameters and in situ probes

Reactants prepared using standard thin film deposition techniques – more on this later - and consist of nm scale thickness controlled layers of the elements to be reacted.

Elements easily substituted for another

Allows rapid surveys over a class of related reactions and synthesis of iso-structural compounds.
**ELEMENTALLY MODULATED SUPERLATTICES**

- **Diffusion distance** is determined by the multilayer repeat distance which can be continuously varied.

- An important advantage, allowing experimental probe of reaction kinetics and mechanism as a function of inter-diffusion distance and temperature.

- *Multi-layer repeat distances easily verified in prepared reactants and products made under different conditions using low angle XRD.*

- Think about how to make a **BaTiO$_3$-SrTiO$_3$ Perovskite superlattice** or a **MgAl$_2$O$_4$-ZnAl$_2$O$_4$ Spinel superlattice** and then a **BaxSr$_{1-x}$TiO$_3$** and **MgxZn$_{1-x}$Al$_2$O$_4$ solid solution** ??? and why would you do this ???
NANOSCALE PATTERNING OF SHAKE-AND-BAKE SOLID-STATE CHEMISTRY

MINIMIZING DIFFUSION LENGTHS 
\[ \langle x \rangle \approx (2Dt)^{1/2} \] FOR RAPID AND COMPLETE DIRECT REACTION BETWEEN SOLID STATE MATERIALS AT LOWEST \( T \)

Younan Xia
PDMS MASTER FOR SOFT LITHOGRAPHY

MICROCONTACT PRINTING mCP

Whitesides
Polydimethylsiloxane PDMS

\((H_3C)_3SiO[Si(CH_3)_2O]_nSi(CH_3)_3\)

\[ nSi(CH_3)2Cl2 + nH2O \rightarrow [Si(CH3)2O]x + 2nHCl \]

Condensation polymerization synthesis of PDMS - a very famous polymer – elastomeric and hydrophobic

let’s make a micro-mold and do chemistry
Tutorial - Surface Chemistry of Silica

Silanol reaction:

\[
\text{Si} - \text{Si} + \text{H}_2\text{O} \rightarrow \text{Si} - \text{Si} - \text{Si} - \text{Si}
\]

Silanols:

- Self-assembly
- Colloidal growth
- Hydrophilicity
- Reactivity
- Surface functionalization

Charge and functionalization:

\[
\text{-SiCl} + \text{HOSi}^- = \text{-Si-O-Si}^- + \text{HCl}
\]

Etching:

\[
\text{HF} \rightarrow \text{OH}^+ \rightarrow \text{OH}^- \rightarrow \text{OH}_2^- \rightarrow \text{F}^{-}\text{H}_2\text{O}
\]
PDMS MASTER

- Schematic illustration of the procedure for casting PDMS replicas from a master having relief structures on its surface.
- The master is silanized and made hydrophobic by exposure to \(\text{CF}_3(\text{CF}_2)_6(\text{CH}_2)_2\text{SiCl}_3\) vapor.
- SiCl bind to surface OH groups and anchor perfluoroalkylsilane to surface of silicon master \(\text{CF}_3(\text{CF}_2)_6(\text{CH}_2)_2\text{SiO}_3\) for easy removal of PDMS mold prevents adhesive tearing of mold.
- Each master can be used to fabricate more than 50 PDMS replicas.
- Representative ranges of values for \(h, d,\) and \(l\) are 0.2 - 20, 0.5 - 200, and 0.5 - 200 mm respectively.
NANOSCALE PATTERNING OF SHAKE-AND-BAKE SOLID-STATE CHEMISTRY

Younan Xia

Hydrophobic-hydrophilic micron scale patches with controlled wettability pattern

Microcontact printing with CH₃(CH₂)₇SiCl₃

Withdraw from a nitrate solution in isopropanol

Dry at ~25°C

1) Heat at 600 °C in air
2) Reduce by H₂ at 400 °C

Si with native oxide

Si

CH₃-SAM

Ni(NO₃)₂

Co(NO₃)₂

NiO

α-Fe₂O₃

Co₃O₄

Ni

α-Fe

Fe(NO₃)₃

M(NO₃)₂

MFe₂O₄ (ferrites)

Citric acid

400 °C (2 h)

800 °C (2 h)
NANOSCALE PATTERNING OF SHAKE-AND-BAKE SOLID-STATE CHEMISTRY

(A) Optical micrograph (dark field) of an ordered 2-D array of nanoparticles of Co(NO$_3$)$_2$ that was fabricated on a Si/SiO$_2$ substrate by selective de-wetting from a 0.01 M nitrate solution in 2-propanol. The surface was patterned with an array of hydrophilic Si-SiO$_2$ grids of 5 x 5 mm$^2$ in area and separated by 5 mm.

(B) An SEM image of the patterned array shown in (A), after the nitrate had been decomposed into Co$_3$O$_4$ by heating the sample in air at 600 °C for 3 h. These Co$_3$O$_4$ particles have a hemispherical shape (see the inset for an oblique view) – ferromagnetic or superparamagnetic depending on size.

(C) An AFM image (tapping mode) of the 2-D array shown in (B), after it had been heated in a flow of hydrogen gas at 400 °C for 2 h. These Co particles were on average 460 nm in lateral dimensions and 230 nm in height – ferromagnetic or superparamagnetic.
AFM image of an ordered 2-D array of (A) MgFe$_2$O$_4$ and (B) NiFe$_2$O$_4$ that was fabricated on the surface of a Si/SiO$_2$ substrate by selective dewetting from the 2-propanol solution (0.02 M) that contained a mixture of two nitrates [e.g. 1:2 between Mg(NO$_3$)$_2$ and Fe(NO$_3$)$_3$].

The PDMS stamp contained an array of parallel lines that were 2 mm in width and separated by 2 mm. Twice stamped orthogonally.

Citric acid HOC(CH$_2$CO$_2$H)$_3$ forms atomically mixed Mg(II)/Fe(III) multidentate complex - added to reduce the reaction temperature between these two nitrate solids in forming a homogeneous ferrite product.

Ferrite nanoparticles ~300 nm in lateral dimensions and ~100 nm in height.
DOING ‘REAL’ SOLID STATE SYNTHESIS IN THE LAB

DIRECT REACTION OF SOLIDS - “SHAKE-AND-BAKE” SOLID STATE SYNTHESIS

• Although this approach may seem to be *ad hoc* and a little irrational at times, the technique has served solid state chemistry for well over the past 50 years

• It has given birth to the majority of high technology devices and products that we take for granted every day of our lives

• Thus it behooves us to look critically and carefully at the methods used in the lab if one is to move beyond trial-and-error methods to the new solid state chemistry and a rational and systematic approach to synthesis of materials
THINKING ABOUT **MIXING** SOLID REAGENTS

- Drying reagents MgO/Al\(_2\)O\(_3\) 200-800°C, max SA

- *In situ* decomposition of precursors at 600-800°C
  \[ \text{MgCO}_3/\text{Al(OH)}_3 \rightarrow \text{MgO/Al}_2\text{O}_3 \rightarrow \text{MgAl}_2\text{O}_4 \]

- Intimate mixing of precursor reagents – enhancing contact area !!!

- Homogenization of solid reactants using organic solvents, grinding, **ball milling**, ultra-sonification
THINKING ABOUT CONTAINER MATERIALS

• Chemically inert crucibles, boats

• Noble metals Nb, Ta, Au, Pt, Ni, Rh, Ir

• Refractories: alumina, zirconia, silica, boron nitride, graphite

• Reactivity with containers at high temperatures needs to be carefully evaluated for each system – know your solid state chemistry
THINKING ABOUT SOLID STATE SYNTHESIS

HEATING PROGRAM

- Furnaces, RF, microwave, lasers, ion and electron beams
- Prior reactions and frequent cooling, grinding and regrinding - boost SA of reacting grains
- Overcoming sintering, grain growth, brings up SA, fresh surfaces, enhanced contact area
- Pellet and hot press reagents – densification and porosity reduction, higher surface contact area, enhances rate, extent of reaction
- Care with unwanted preferential component volatilization if T too high, composition dependent
- Need INERT atmosphere for unstable oxidation states
**PRECURSOR** SOLID STATE SYNTHESIS METHOD

- **Co-precipitation** - high degree of homogenization, high reaction rate - applicable to nitrates, acetates, citrates, carboxylates, oxalates, alkoxides, b-diketonates, glycolates

- **Concept**: precursors to magnetic Spinels – tunable magnetic recording media

  - Zn\((\text{CO}_2)_2\)/Fe\(_2\)[(\text{CO}_2)_2]\(_3\)/H\(_2\)O 1 : 1 solution phase mixing

  - H\(_2\)O evaporation, salts *co-precipitated – solid solution* mixing on atomic/molecular scale, filter, calcine in air

  - Zn\((\text{CO}_2)_2\) + Fe\(_2\)[(\text{CO}_2)_2]\(_3\) → ZnFe\(_2\)O\(_4\) + 4CO + 4CO\(_2\)

- **High degree of homogenization, smaller diffusion lengths, fast rate at lower reaction temperature**
PROBLEMS WITH CO-PRECIPITATION METHOD

- Co-precipitation requirements:
  - Similar salt solubility's
  - Similar precipitation rates
  - Avoid super-saturation as poor control of co-precipitation
  - Useful for synthesizing complex oxides like Spinels, Perovskites

- Disadvantage: often difficult to prepare high purity, accurate stoichiometric phases
DOUBLE SALT PRECURSORS

• Precisely known stoichiometry double salts have controlled element stoichiometry:

• $\text{Ni}_3\text{Fe}_6(\text{CH}_3\text{CO}_2)_{17}\text{O}_3(\text{OH}).12\text{Py}$

• Basic double acetate pyridinate

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

• Product highly crystalline phase pure $\text{NiFe}_2\text{O}_4$ spinel
**DOUBLE SALT PRECURSORS**

<table>
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<th>Chromite Spinel Precursor compound</th>
<th>Ignition T, °C</th>
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<tr>
<td>MgCr$_2$O$_4$ (NH$_4$)$_2$Mg(CrO$_4$)$_2$.6H$_2$O</td>
<td>1100-1200</td>
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<tr>
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<tr>
<td>MnCr$_2$O$_4$ MnCr$_2$O$_7$.4C$_5$H$_5$N</td>
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<tr>
<td>CoCr$_2$O$_4$ CoCr$_2$O$_7$.4C$_5$H$_5$N</td>
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</tr>
<tr>
<td>CuCr$_2$O$_4$ (NH$_4$)$_2$Cu(CrO$_4$)$_2$.2NH$_3$</td>
<td>700-800</td>
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<tr>
<td>ZnCr$_2$O$_4$ (NH$_4$)$_2$Zn(CrO$_4$)$_2$.2NH$_3$</td>
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</tr>
<tr>
<td>FeCr$_2$O$_4$ (NH$_4$)$_2$Fe(CrO$_4$)$_2$</td>
<td>1150</td>
</tr>
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</table>

Good way to make chromite Spinels, important tunable magnetic materials

*juggling electronic-magnetic properties of the A O$_h$ and B T$_d$ ions in the Spinel lattice*
Solid State Synthesis

Some Case Histories
PEROVSKITE FERROELECTRICS
BARIUM TITANATE

• Control of grain size determines ferroelectric properties, important for capacitors, microelectronics

• Direct heating of solid state precursors is of **limited** value in this respect

• *Lack of stoichiometry, size and morphology control*

• \( \text{BaCO}_3(s) + \text{TiO}_2(s) \rightarrow \text{BaTiO}_3(s) \)

• Sol-gel reagents useful to create **single source** barium titanate precursor with well-defined and correct stoichiometry
Single Source Precursor

$\text{Ba}[\text{TiO(O}_2\text{C}_4\text{O}_4)_2]$
SINGLE SOURCE PRECURSOR SYNTHESIS OF BARIUM TITANATE

- $\text{Ti(OBu)}_4\text{(aq)} + 4\text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4\text{(s)} + 4\text{BuOH(aq)}$
- $\text{Ti(OH)}_4\text{(s)} + \text{C}_2\text{O}_4^{2-}\text{(aq)} \rightarrow \text{TiO(C}_2\text{O}_4\text{)(aq)} + 2\text{OH}^-\text{(aq)} + \text{H}_2\text{O}$
- $\text{Ba}^{2+}\text{(aq)} + \text{C}_2\text{O}_4^{2-}\text{(aq)} + \text{TiO(C}_2\text{O}_4\text{)(aq)} \rightarrow \text{Ba[TiO(C}_2\text{O}_4\text{)]}_2\text{(s)}$

- Precipitate contains barium and titanium in correct ratio and at 920 °C decomposes to barium titanate according to:

  - $\text{Ba[TiO(C}_2\text{O}_4\text{)]}_2\text{(s)} \rightarrow \text{BaTiO}_3\text{(s)} + 2\text{CO}\\uparrow\text{(g)} + 2\text{CO}_2\\uparrow\text{(g)}$

- Grain size important for control of ferroelectric properties !!!

- Used to grow single crystals hydrothermally – see later – synthesis in high T high P aqueous environment
Why is $\text{BaTiO}_3$ a Ferroelectric?

- $\text{Ba}^{2+}$ is larger than the vacancy in the octahedral network tolerance factor $> 1$.
- This expands the octahedron, which leads to a shift of $\text{Ti}^{4+}$ toward one of the corners of the octahedron.
- The direction of the shift can be altered through application of an electric field.

\[
a = \sqrt{2}(r_A + r_0) = 2(r_B + r_0) \quad t = \frac{r_A + r_0}{\sqrt{2}(r_B + r_0)}
\]
Perovskite – paraelectric - ferroelectric – antiferroelectric – superparaelectric states
Above $T_c \sim 120 \, ^\circ C$ - Cubic perovskite – in absence of E-field no permanent electric dipoles – equivalent O-Ti-O bonds in $\text{BaTiO}_3$ - behaves as paraelectric in E-field with non-interacting induced E-dipoles

Below $T_c$ Tetragonal perovskite long-short axial O-Ti—O bonds – domains of aligned cooperatively interacting induced permanent E-dipoles in absence of E-field in $\text{BaTiO}_3$ which interact and align in E-field to give ferroelectric properties

BASICS: FERROELECTRIC $\text{BaTiO}_3$

Paraelectric $a = 4.018\, \text{Å}$

Displacive Transition

Ferroelectric $a = 3.997\, \text{Å}$, $c = 4.031\, \text{Å}$

Ti moves off center
Above $T_c$ – cubic paraelectric - random, induced, non-interacting E-dipoles in E-field

Below $T_c$ multi-domain tetragonal ferroelectric - cooperative E-dipole interactions in each domain – aligned in domain but randomly oriented between domains

Multidomain ferroelectric dipoles align in E field below $T_c$

Go Nano - Single domain giant paraelectric superparaelectric

Note - small grains - tetragonal to cubic surface gradients - ferroelectricity is particle size dependent and can be lost
HYSTERESIS OF POLARIZATION - HALLMARK OF FERROELECTRIC IN APPLIED FIELD E

Random domain paraelectric

Ps saturation polarization
Pr remnant polarization
Ec coercive field

Aligned domain ferroelectric

Single domain superparaelectric

Polarization Hysteresis Behavior $P$ vs $E$
Diagnostic of Ferroelectric – used as capacitor, NLO and memory devices
Dielectric Constant

If you apply an electric field, $E$, across a material the charges in the material will respond in such a way as to reduce (shield) the field experienced within the material, $D$ (electric displacement)

$$D = \varepsilon E = \varepsilon_0 E + P = \varepsilon_0 E + \varepsilon_0 \chi_e E = \varepsilon_0 (1 + \chi_e) E$$

where $\varepsilon_0$ is the dielectric permittivity of free space ($8.85 \times 10^{12} \text{ C}^2/\text{N-m}^2$), $P$ is the polarization of the material, and $\chi_e$ is the electric susceptibility. The relative permittivity or dielectric constant of a material is defined as:

$$\varepsilon_r = \varepsilon / \varepsilon_0 = 1 + \chi_e$$

When evaluating the dielectric properties of materials it is this quantity we will use to quantify the response of a material to an applied electric field.
Dielectric, Paraelectric and Ferroelectric Polarization

Interaction of E-field with electrons of an atom or ion give electronic and ionic polarization of charge

dielectric
Paraelectric no hysteresis
Ferroelectric hysteresis
Distortion Reduces Cubic to Tetragonal Symmetry, VB More Bonding, CB More Anti-Bonding and Enhances $E_g$
Symmetry Constraints and Dielectric Properties

Dielectric properties can only be found with certain crystal symmetries

Piezoelectric
  Do not possess an inversion center (noncentrosymmetric)

Ferroelectric/Pyroelectric
  Do not possess an inversion center (noncentrosymmetric)
  Posses a Unique Polar Axis
High-sensitivity accelerometer composed of ultra-long vertically aligned ferroelectric-piezoelectric BaTiO$_3$ nanowire arrays

Nature Communications November 2013
Synthesis of Ultra-long BaTiO₃ NWs

- Ti (film) + O₂ → Ti-TiO₂

- 750°C Air Oxidation

- Ti-TiO₂ + NaOH + H₂O → Ti-NaTiO₃ NWs

- Hydrothermal (aqueous/pressure) synthesis 210°C

- Ti-NaTiO₃ NWs + Ba(OH)₂ + H₂O → Ti-BaTiO₃ NWs

- Hydrothermal topotactic ion exchange 150-250°C
(a) Schematic diagram of sensor device using BaTiO3 NW arrays. (b) Schematic of piezoelectric voltage generation from NWs. Polarization direction (P) represents the alignment direction of the dipoles. Application of dynamic stress $\sigma(t)$ on NW arrays produces voltage $V(t)$ generation (c) frequency dependent sensitivity test of sensor
Synthesis of a Ferroelectric Random Access Memory (FeRAM) 0.5 Tbit/in²

Polarization Switching by Changing Direction of Applied Electric Field


DPN Synthesis Precursor Sol-Gel thermal treatment:

\[ \text{Pb(OR)}_2 + \text{Ti(OR)}_4 \rightarrow \text{PbTiO}_3 \]
DPN Synthesis of PbTiO$_3$ (PTO)

- Schematic drawings illustrating the dip-pen nanolithography (DPN) of ferroelectric PbTiO$_3$ (PTO) nanodots.
  - (a) Patterns of PTO nanodots formed by DPN.
  - (b) Formation of a nanopattern using a PTO precursor sol on the surface of epitaxially matched conducting Nb-doped Nb:SrTiO$_3$ by DPN.
  - (c) To obtain highly crystallized PTO nanodots, an annealing process is carried out after the lithography of the PTO nanopattern is performed.

**Conducting AFM tip and substrate enable PFM and EFM ferroelectricity measurements on individual dots**
Figure 2. AFM images of PTO nanodots formed by DPN. (a) Array of PTO nanodots formed by DPN using various dip-pen deposition times. (b) Plot of the lateral dimension of the PTO dot as a function of the dip-pen deposition time. (c) Plot of the thickness of the PTO nanodot as a function of the dip-pen deposition time.
Figure 3. Minimum-sized PTO nanodot with a lateral dimension of 37 nm. (a) AFM image of the minimum-sized PTO nanodot. (b) Three-dimensional AFM image of the minimum-sized PTO nanodot. The thickness of this minimum-sized nanodot is ~22 nm. (c) HR-TEM image of the minimum-sized PTO nanodot. The $c/a$ ratio (i.e., tetragonality) was estimated to be 1.08.
Figure 4. PFM and EFM measurements of a PTO nanodot formed by DPN. (a) Electrical contact of a PTO nanodot with an AFM tip for PFM and EFM measurements. (b) Image of the PTO nanodot obtained by AFM with a Pt-coated Si$_3$N$_4$ cantilever. (c) PFM image of the PTO nanodot. (d) Value of $d_{33}$ for the minimum-sized PTO nanodot plotted as a function of the applied voltage. (e) EFM image of the PTO nanodot after switching with a bias of −0.5 V. (f) EFM image of the PTO nanodot after switching with a bias of +0.5 V.
INDIUM TIN OXIDE ITO – CHANGED THE WORLD!

• Indium sesquioxide $\text{In}_2\text{O}_3$ - wide electronic bandgap $\text{E}_g$ semiconductor

• Electrical conductivity enhanced by n-doping with (10%) $\text{Sn}^{(4+)}$

• **ITO is $\text{Sn}_n\text{In}_{2-n}\text{O}_3$**

• ITO is optically transparent - electrically conducting - thin films vital as electrode material for solar cells, electrochromic windows/mirrors, LEDs, OLEDs, LC displays, electronic ink, photonic crystal ink
INDIUM TIN OXIDE – CHANGED THE WORLD!

• Precursors - EtOH solution - 
  \((2-n)\text{In(OBu)}_3/n\text{Sn(OBu)}_4\)

• Hydrolytic poly-condensation to form gel, spin coat gel onto glass substrate to make thin film: 
  \(\text{InOH} + \text{HOSn} \rightarrow \text{InOSn}\)

• Dry gel at 50-100°C, heat at 350°C in air to produce high conductivity \(\text{Sn}_n\text{In}_{2-n}\text{O}_3\)

• Check electrical conductivity and optical transparency
Doping Basics on TCOs – The Big Four

- **ITO**: Sn doped In2O3 - 1: 9 solid solution
  - n-doped with Sn(IV) isomorphously replacing In(III)

- **ATO**: Sb doped SnO2 – *how would you make it?*
  - n-doped with Sb(V) isomorphously replacing Sn(IV)

- **FTO**: F doped SnO2 – *how would you make it?*
  - n-doped with F(-I) isomorphously replacing O(-II)

- **AZO**: Al doped ZnO – *how would you make it?*
  - n-doped with Al(III) isomorphously replacing Zn(II)

- *How would you make p-doped versions?*
TCO Materials are **NOT** that Simple

- $\text{In}_2\text{O}_3$ is **Bixbyite** structure (3/4 oxygen’s present in a $\text{CaF}_2$ lattice) – called C-type rare earth sesquioxide lattice
- **Objective** is to optimize optical transparency and electrical conductivity
- **ITO Sn : In = 1 : 9 solid solution** – Linear Vegard Law and Mossbauer proves Sn(IV)
- Sn(IV) isomorphously replace some In(III) sites
- Note - **high Sn(IV) doping** in ITO creates some extra O interstitials in $\text{In}_2\text{O}_3$ lattice formed during synthesis in air
- Highly doped ITO is **non-stoichiometric**
TCO Materials are *NOT* that Simple

- Highly doped ITO is **non-stoichiometric**

- $\text{In}_{2-x}\text{Sn}_x\text{O}_{3+x/2}$

- Replacing $x\text{In}(\text{III})$ with $x\text{Sn}(\text{IV})$ requires charge balance by $x/2[\text{O}(-\text{II})]$

- Challenge - **optimizing electrical conductivity of ITO by post synthetic reduction** to remove some interstitial oxygen’s and activate some Sn(IV) donors to give a maximum of 1 conduction electron per Sn(IV) in lattice

- $\text{In}_{2-x}\text{Sn}_x\text{O}_3$