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Chemistry of Select Electroceramic Materials: Lead zirconium titanate (PZT), indium tin oxide (ITO) and zinc oxide.

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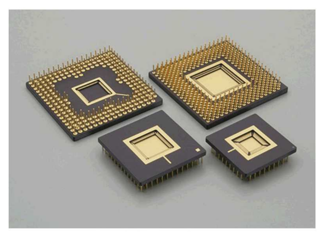
Electroceramic materials



The very broad term of electroceramic materials refers to those ceramics that can perform an electronic function. The application drives the desired properties and the materials range from simple to complex metal oxide species. Some of the most highly applied electroceramic materials would include indium tin oxide (ITO), lead zirconate titanate ($Pb[Zr_xTi_{1-x}]O_3$), and zinc oxide (ZnO),. The various applications these materials are useful for are listed below.

ITO
- photovolatics
- semiconductors
- coatings
  - liquid crystal screens
  - OLEDs
  - Touchscreens
  - sensor wiring
  - plastics
- invisible antennae
- heat reflecting mirrors

PZT
- computer memories
- sensors (flow, level)
- structural inspection
  - automotive
  - aerospace
- ultrasonic cleaners
- sonar devices

ZnO
- additive
  - rubber, plastic, ceramics, glass, cement, lubricant, paint, adhesives…
- refractory applications
- LCD electrodes
- transistors
- LEDs
- transparent
- wide-band gap electrodes

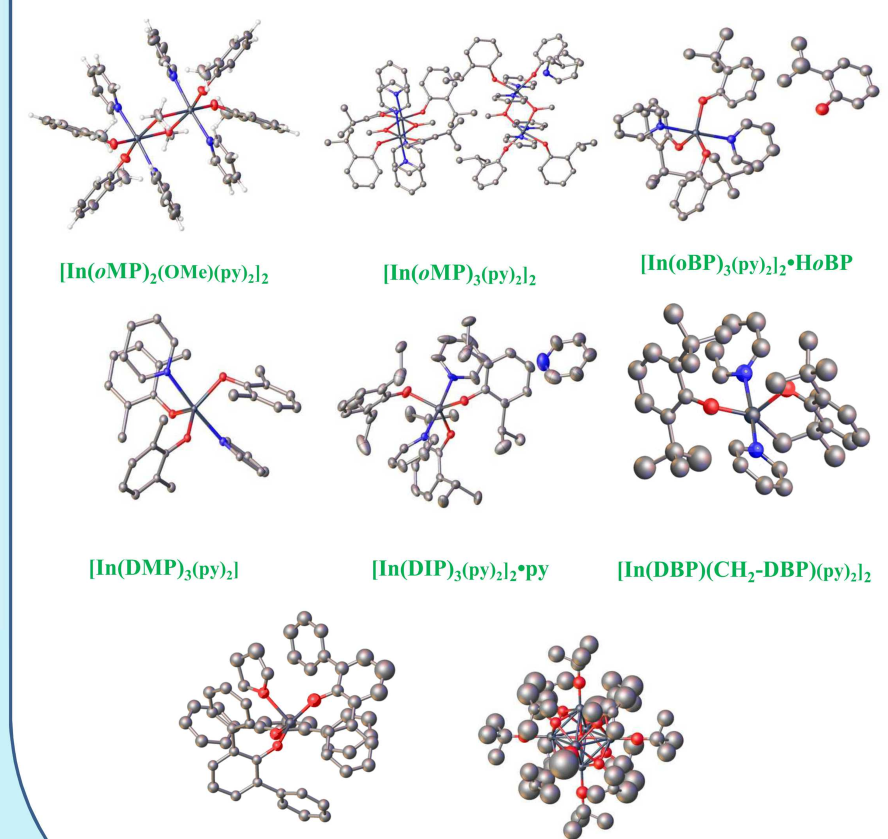
Controlling the physical properties (size, shape, phase) of these ceramics is important to optimize the final electronic behavior. In order to accomplish this, developing new precursors that impart these characteristics is critical.

Indium Tin Oxide (ITO)

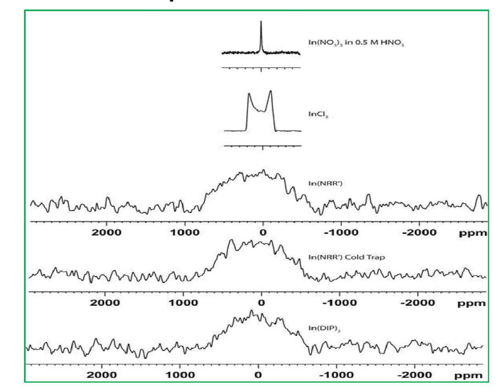
$$InCl_3 + 3LiNMe_2 \rightarrow In(NMe_2)_3 + 3\ LiCl$$

$$In(NMe_2)_3 + 3\ HOAr \rightarrow In(OR)_3 + 3\ HNMe_2$$

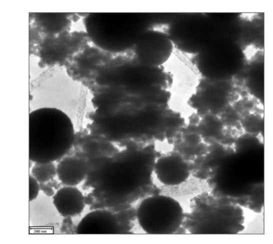
A series of $In(OR)_3$] were synthesized by amide-alcoholysis metathesis. Products ranged from solvated dinuclear to mononuclear complexes.



[113,115]In NMR studies proved to yield very broad peaks.

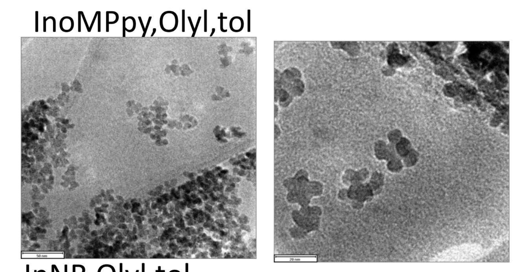


InONepTOl,dyl,tol

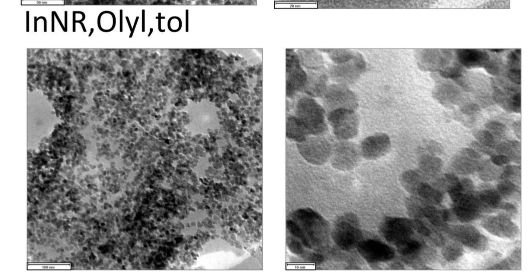


TEM images of SOLVO routes showed NP formed.

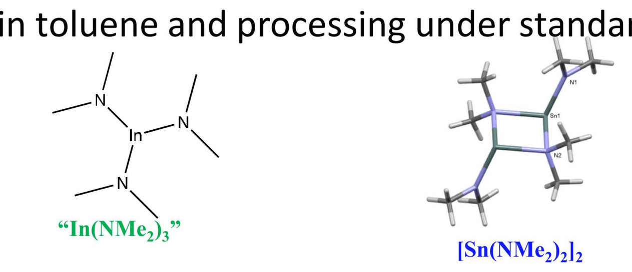
InoMPpy,Olyl,tol



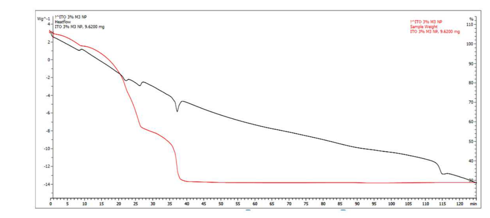
InNR,Olyl,tol

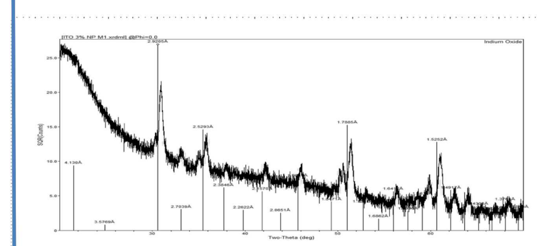


ITO solutions of varied stoichiometries were generated yb mixing the two amide in toluene and processing under standard conditions..

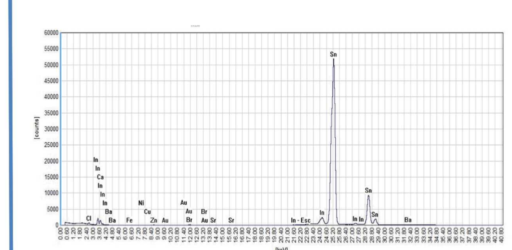


TGA/DSC data revealed decomposition of resulting ITO powder occurred below 250 °C.

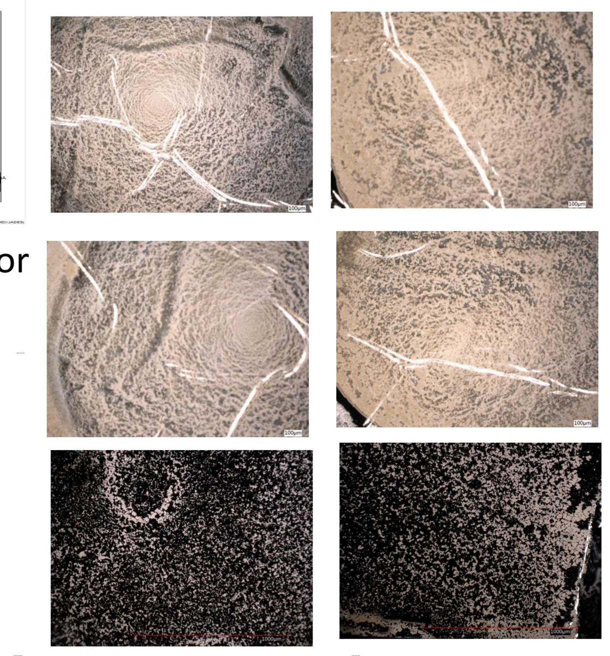




PXRD shows ITO formed for powders and films.



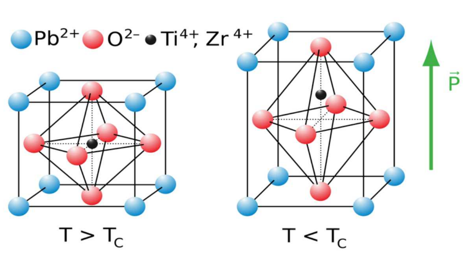
XRF confirms the presence of both cations in the proper stoichiometry.



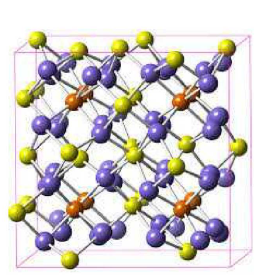
- Warping on substrate present
- "Chalky" residue present after heat treatment
- Films cracked

Materials and structures

PZT: adopts a perovskite structure (ABO_3) with Pb at the A-site and Zr and Ti at the B-site. The ratio of the cations dictates the properties.



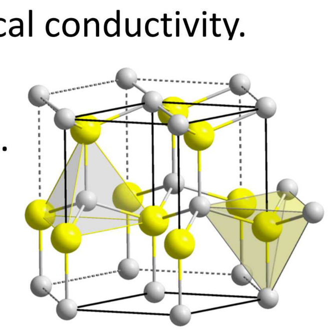
Properties: high dielectric constant; high coupling; high charge sensitivity; high density with a fine grain structure; a high Curie point; and a clean, noise-free frequency response, high piezoelectric charge constant; high mechanical quality reduces mechanical loss, lower operating temperature; low dissipation factor that ensures cooler, more economical operation; high dielectric stability; and low mechanical loss under demanding conditions



ITO: $In_{2-x}Sn_xO_3$ (up to 20% Sn) f is one of the most important transparent, conducting material with In_4Sn moat common formulation.

Properties: melting point is composition dependent (1526–1926 °C), n-type semiconductor (bandgap 4 eV), transparent to visible light; high electrical conductivity.

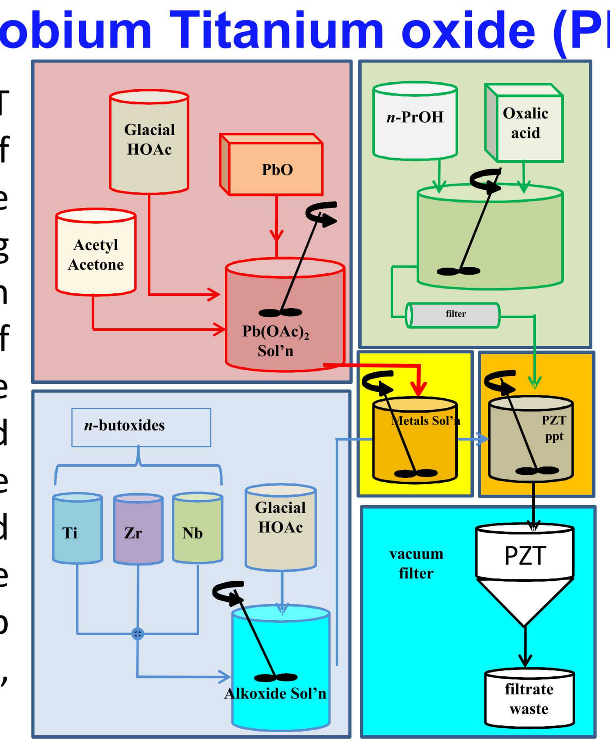
ZnO: zincite adopts the hexagonal ($P6_3mc$) structure.



Properties: wide-bandgap semiconductor, good transparency, room temperature luminescence, wide bandgap.

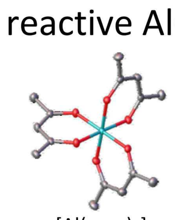
Lead Zirconium Niobium Titanium oxide (PNZT)

The Sandia established route to PXZT materials involve a complex mixture of metal alkoxide, acetate, and reactive species that are precipitated using oxalic acid. PZT materials are often modified through the introduction of additional metal dopants to improve the properties for the desired application. Niobium is one of these modifiers to assist in the electronic and stability properties. A general scheme is shown to the right. Efforts to develop precursors for other dopants (i.e., Sn, Al, La) are detailed.



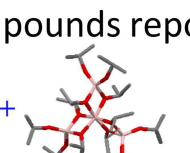
Aluminum (PANZT)

Al precursor alternatives to the very reactive $AlCl_3$ are being developed.



A series of Al-acac derivatives are being developed to improve solubility.

There are a limited number of Al-carboxylate compounds reported

n HOC(O)R +  →

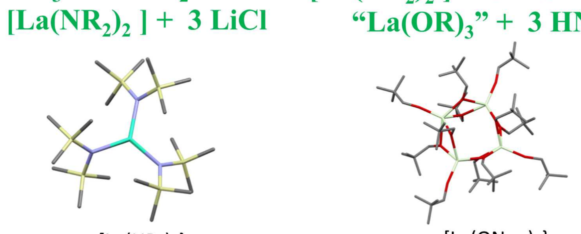
[Al(OPri)3]

Lanthanum (PLNZT)

Commercially available La precursors are not suitable. A series of tailored La- precursors are being developed.

$$LaCl_3 + 3\ KNR_2 \rightarrow [La(NR_2)_2] + 3\ LiCl$$

$$[La(NR_2)_2] + 3\ HOR \rightarrow \text{“}La(OR)_3\text{”} + 3\ HNR_2$$



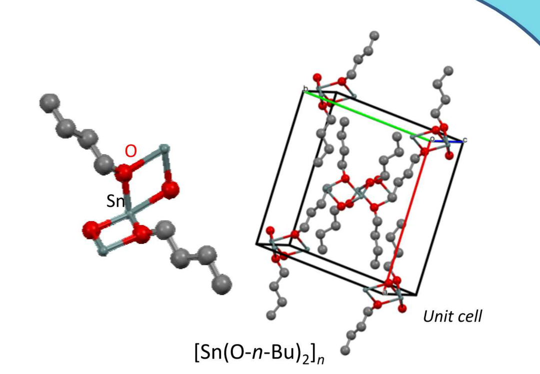
$$\text{“}La(OR)_3\text{”} + n\ HOC(O)R \rightarrow ????$$

Tin (PSNZT)

An amide alcohol metathesis route was followed to generate a wide variety of Sn-alkoxy precursors.

$$SnCl_2 + 2\ LiNMe_2 \rightarrow Sn(NMe_2)_2 + 2\ LiCl$$

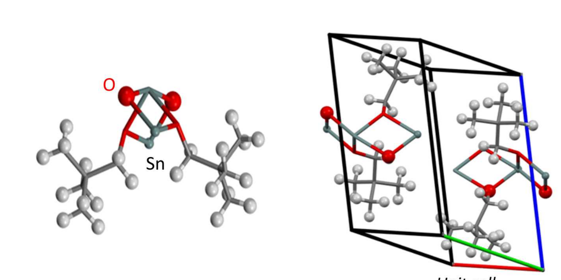
$$Sn(NMe_2)_2 + 2\ HOAr \rightarrow Sn(OR)_2 + 2\ HNMe_2$$



[Sn(O-n-Bu)2]∞

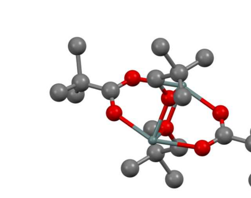
T.Zoller, L.Iovkova-Berends, C.Dietz, T.Berends, K.Jurkschat Chem.-Eur.J. (2011) 2361.

The n-butanol (HO-n-Bu) and the neo-pentanol (H-ONep) derivatives were of interest as they match the alkoxy ligands used in the PNZT mixture shown above.



[Sn(ONep)2]∞

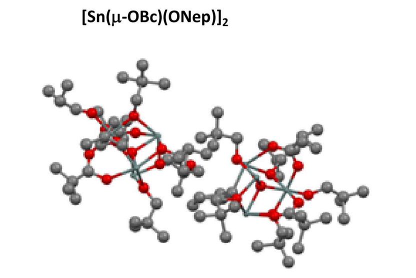
Modification of the $Sn(OR)_2$ occurs in the preparation with HOAc. Therefore, the reaction of these precursors with a series of sterically varied carboxylic acids were examined.



[Sn(μ-OBc)(ONep)]2

$$Sn(OR)_2 + HO_2CR \rightarrow Sn(OR)(ORc) + HOR$$

The products are mixed oxidation state "Sn(O)(OR)(ORc)" species. The oxide and re-dox is believed to occur by esterification generated water.

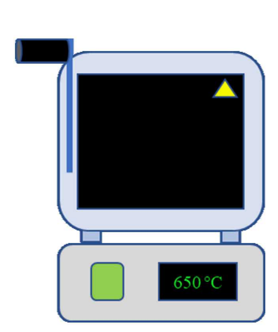


[$Sn_6(\mu_4$-O)(μ_3-ONep)$_3$(ONep)(OBc)$_3$]

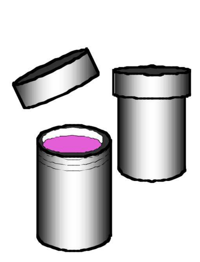
Routes to the various materials

A wide variety of routes are used to produce materials from the different tailored precursors. These can involve circumjacent, protective, or reactive gas atmospheres.

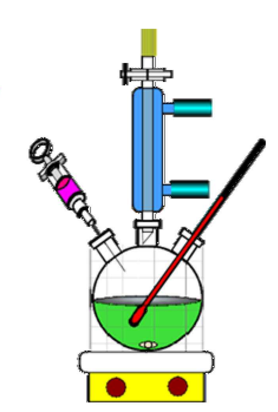
Nanomaterials



Bulk Powders
Thermal treatment at TGA determined temperatures in a box/tube furnace.

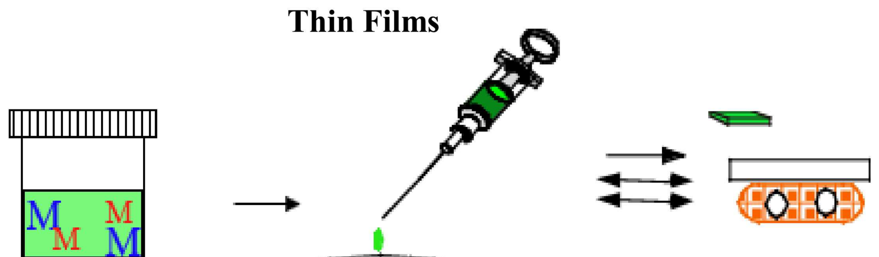


Solvo-Thermal Synthesis
180 °C for 24 h.



Solution Precipitate
Room temperature precursor solution introduced to a high boiling solvent.

Thin Films



Step 1.
- Dissolution of precursor in a 'wetting' solvent

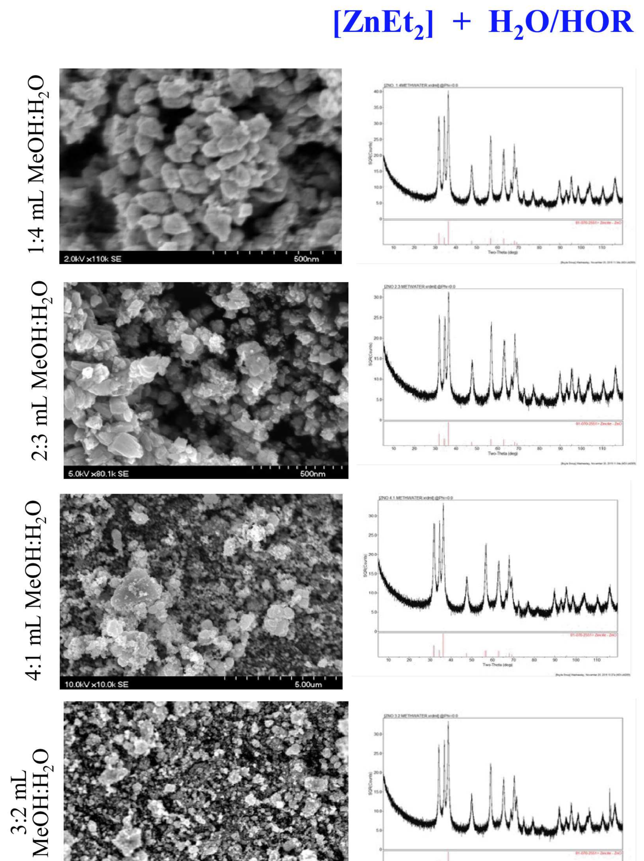
Step 2.
- Drop casting of the precursor solution onto a support.

Step 3.
- Coated support is heat treated on hot-plate. Can be done in multiple steps.

Zinc oxide

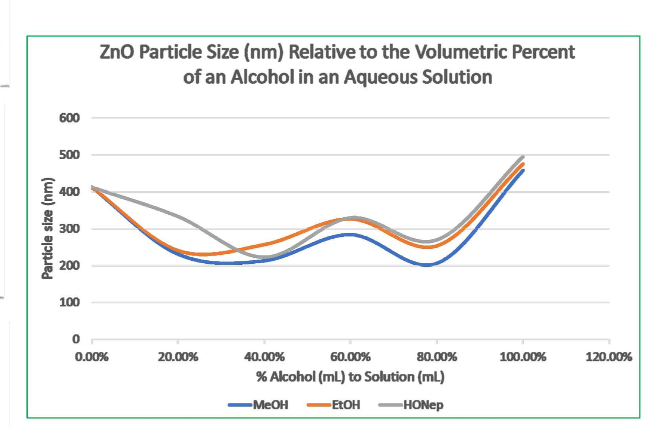
Controlling the morphology and size of zincite (ZnO) materials is of importance for reproducible material properties. A study concerning the precipitation of $ZnEt_2$ with water in alcohol was investigated

$$[ZnEt_2] + H_2O/HOR \rightarrow ZnO + H\text{-}Et$$



TEM images | PXRD pattern

PXRD patterns verify the zincite phase had formed for each sample. TEM and DLS analyses indicated that the size of the particles could be controlled by the ratio of water and alcohol.



A plot of the size versus the concentration of alcohol show the tunability of the final ZnO.

Summary and Conclusions

A series of electroceramic material precursors have been developed for a wide range of applications.

- **ITO materials**
  - a family of In(OR)3 species isolated and found to produce nano-ITO.
  - thin film work shows cracking and flaking.
- **PXNZT materials**
  - Al carboxylate species being developed
  - La amide, alkoxide, and carboxylate are under investigation
  - set of tin alkoxide and their subsequent carboxylate modifiers have been identified.
- **ZnO materials**
  - Control over the final morphology and size have been demonstrated by altering the ppt solvent system

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