Synthesis and Characterization of Lanthanum halide solvated compounds for use in scintilators, PLnZT and Bio-imaging

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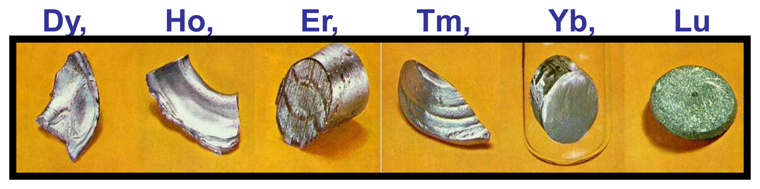
Introduction

Often referred to as the "rare earths", the lanthanide (Ln) elements have gained increased attention over the past few decades. This is due to the development of exciting new fundamental chemistries concerning these Ln cations. The monotonic decrease in the ionic radius resulting from the sequential filling of the *f*-orbitals (the lanthanide contraction) has permitted a systematic probing of the chemistry of these cations. From the rapidly developing families of metalorganic and organometallic complexes, $Ln^{+2/+3}$ alkoxide ($Ln(OR)_x$) complexes have come to the forefront as a unique series of compounds for the production of advanced materials and in molecules that effect useful organic transformations.

Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu



The most widely Ln-precursors used are the halides (LnX_3). In order to understand basic processing variables, a key property that is often overlooked is the shape of the precursors. While both the anhydrous and hydrate precursors are commercially available, it is surprising that these critical precursors have *not* been structurally characterized. This void may be explained by the complex (i.e., expensive) synthetic routes used to generate these materials.

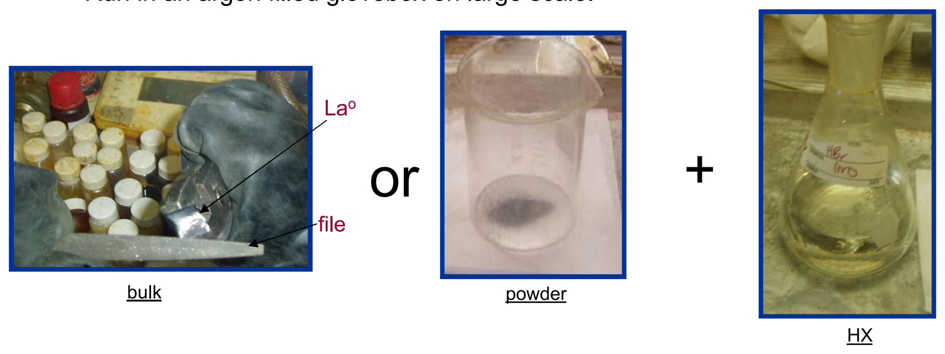
We have developed a simple, novel route to LnX_3 materials through a hydrate precursor - which we have fully characterized for each of the Ln and X precursors. We have also converted the LnX_3 to a series of novel alkoxide precursors ($Ln(OR)_3$) which have also been structurally characterized for the first time. With this family of compounds in hand, we have applied a rational approach to improving existing systems and developing new ones.

Novel Synthesis of Lanthanide Halide Hydrates

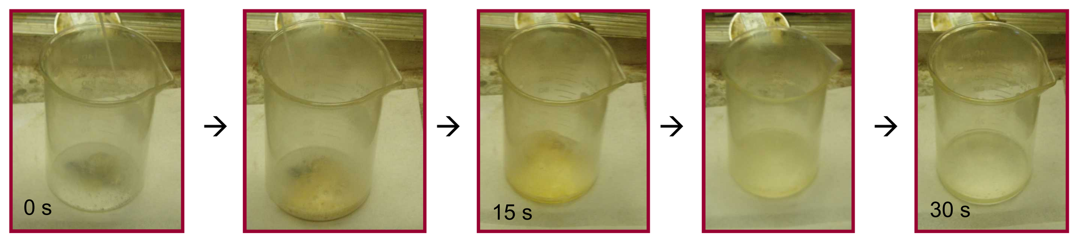
Reaction route: Ln^o + (xs) H-X ⟶ $Ln(H_2O)X_3$

Simple synthesis route to hydrates.

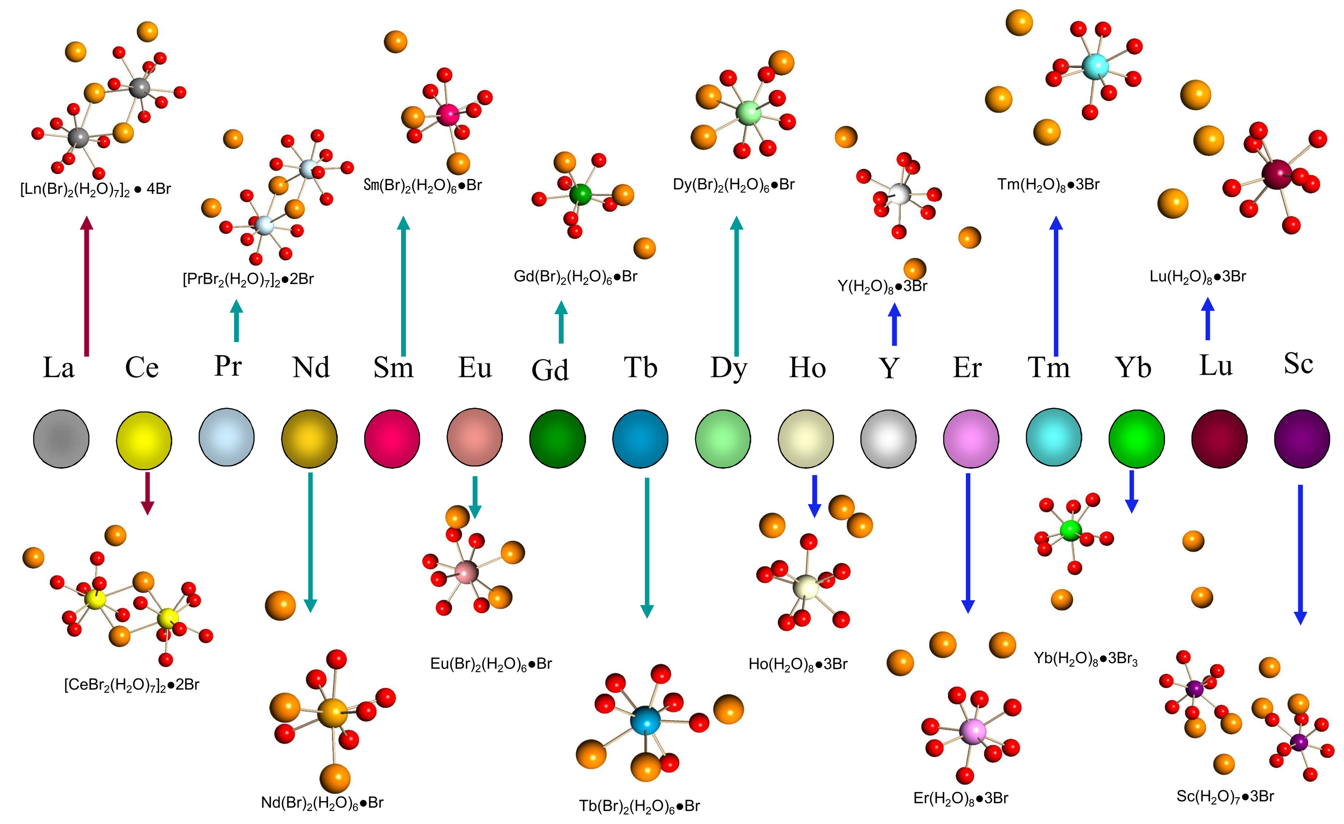
- Synthesis route selected based on simplicity, low cost, and ability to convert to large scale.
- Run in an argon filled glovebox on large scale.



La^o + (xs) H-Br $\xrightarrow{neat}$ "$LnBr_3(H_2O)_n$"

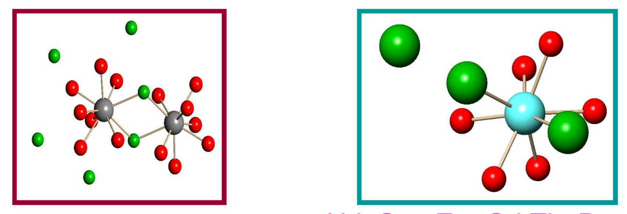


Route applicable to *all* lanthanides and *all* halides!



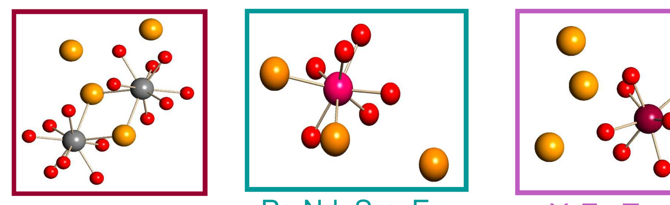
Lanthanide bromide hydrate structures

Lanthanide Chloride Hydrates adopt three types of structures



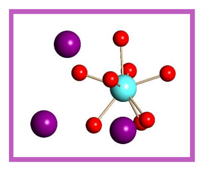
A. dimeric : 2 outer sphere and 1 inner sphere bridging chlorides observed for early Ln cations
B. monomeric : 1 outer sphere and 2 inner sphere chlorides observed for late Ln cations

Lanthanide Bromide Hydrates adopt three types of structures



A. dimeric : 2 outer sphere and 1 inner sphere bridging iodides observed for early Ln cations
B. monomeric : 1 outer sphere and 2 inner sphere iodides observed for middle Ln cations
C. monomeric : 3 outer sphere bromides observed for late cations

Lanthanide Iodide Hydrates adopt one structure type

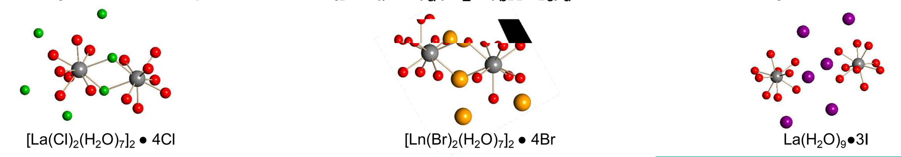


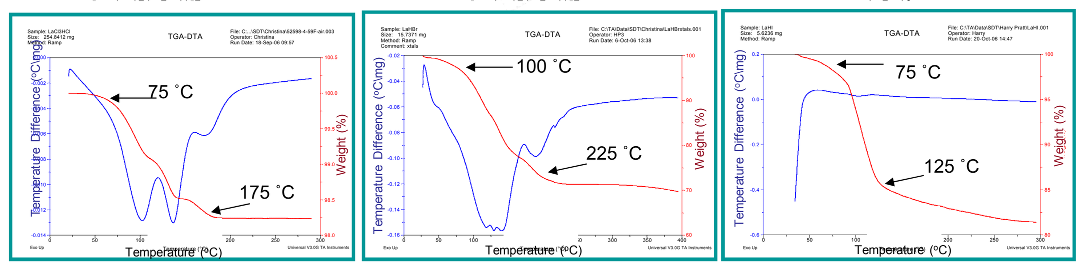
C. monomeric : 3 outer sphere iodides observed for *all* Ln cations

Dehydration of lanthanide halide hydrates

Dehydration yields LaX_3 materials.

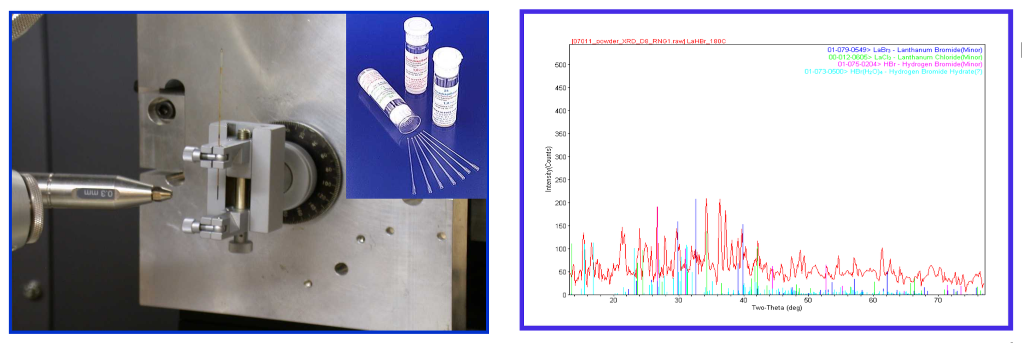
- The dehydration temperature for $\{[La(\mu\text{-}X)_a(H_2O)_b][X]_c\}_d$ was determined by TGA/DTA:





TGA/DTA provided the temperature at which dehydration of these materials occur. To perform that dehydrate the Ln material solution was heated in an oil bath set at 200°C under vacuum for 2 hours. The resulting white powder was then loaded into the beryllium dome for XRD analysis. Upon pure LnX_3 conversion into amide followed by alkoxide could be carried out.

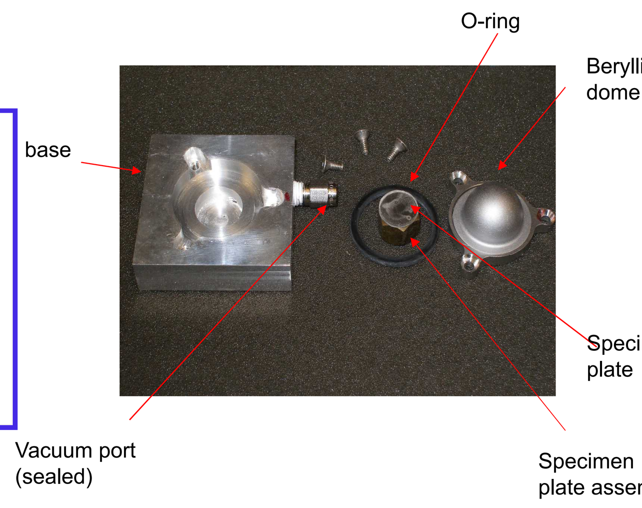
Micro XRD initially used shows phase purity but difficult to unequivocally ID the material

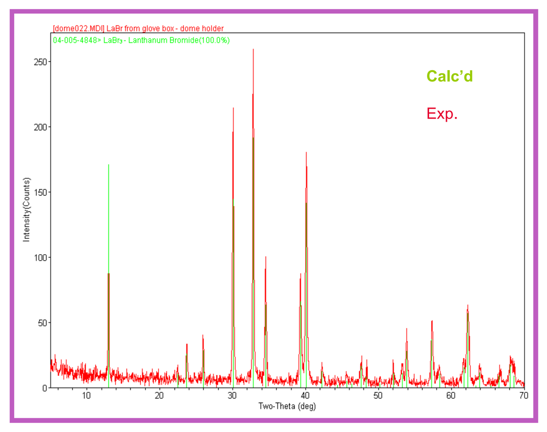


Micro XRD is used to analyze small areas, typically 30 to 500mm in diameter. An XYZ stage with an attached fiber/film holder is used to mount the air-sensitive samples.

Beryllium Dome (BeD) XRD sample holder for reactive specimens yields improved characterization of LaX_3.

$LaBr_3$
Hexagonal
Space group: $P6_3/m$
a = 7.969(6) Å
c = 4.508(2) Å
volume = 247.9 Å³





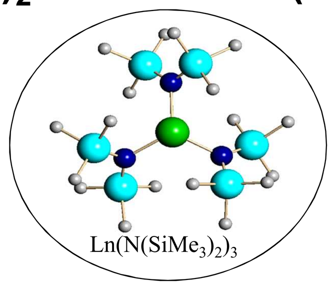
BeD (beryllium dome) XRD of the dried material was phase pure $LaBr_3$.

Conversion of LnX_3 (X=Cl, Br, I) into Ln alkoxides

Metal alkoxides ($M(OR)_x$) have been shown to be excellent sol-gel precursors but there are very few structurally characterized $Ln(OR)_3$ readily available in the literature. Using an amide-alcohol exchange synthesis route, we generated a library of soluble precursors and investigate which of these will generate the high quality PLnZT films through sol-gel routes.

$$LnX_3 + 3\ KN(SiMe_3)_2 \longrightarrow Ln(N(SiMe_3)_2)_3 + 3\ KX$$

Having pure $Ln(NR_2)_3$ is critical to successful synthesis of the $Ln(OR)_3$.

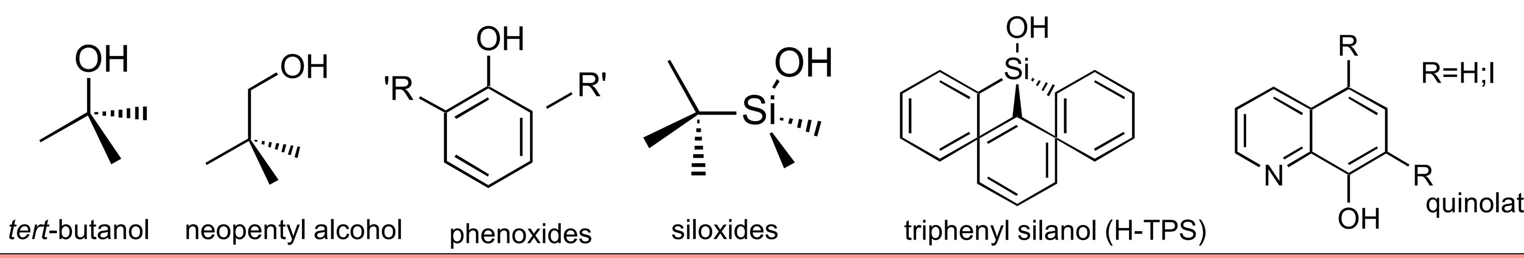


$Ln(N(SiMe_3)_2)_3$

We have developed several select protocols and detection schemes for the purification of these compounds.

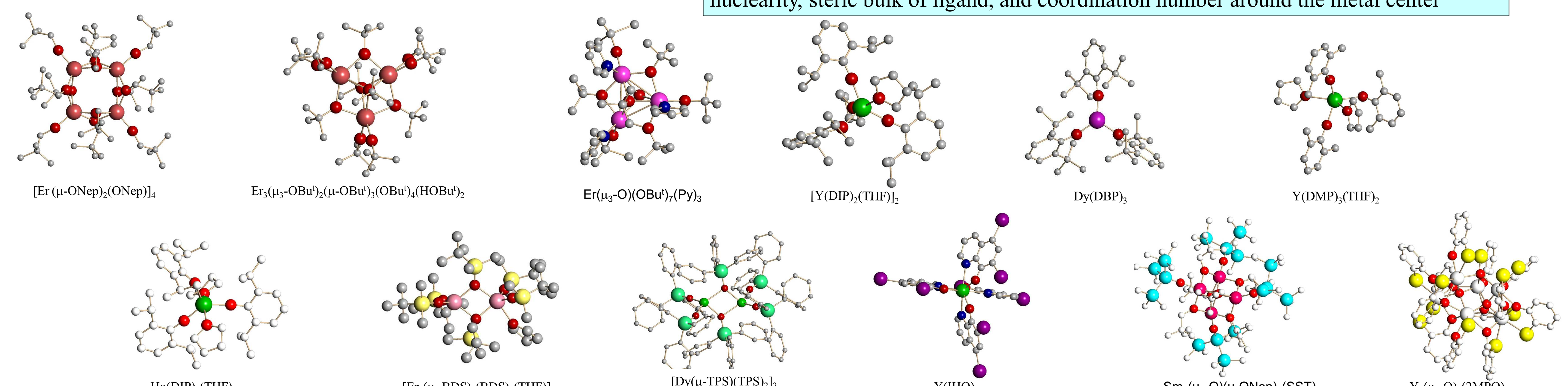
$$Ln(N(SiMe_3)_2)_3 + 3\ HOR \longrightarrow Ln(OR)_3 + 3\ HNR_2$$

HOR =



tert-butanol, neopentyl alcohol, phenoxides, siloxides, triphenyl silanol (H-TPS), quinolates

Synthesized and fully characterized over 60 novel lanthanide alkoxides that differ in nuclearity, steric bulk of ligand, and coordination number around the metal center



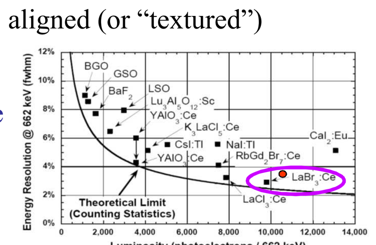
$[Er(\mu\text{-ONep})_2(ONep)]_4$, $Er_3(\mu_3\text{-OBu}^t)_2(\mu\text{-OBu}^t)_3(OBu^t)_4(HOBu^t)_2$, $Er(\mu_3\text{-O})(OBu^t)_3(Py)_3$, $[Y(DIP)_3(THF)]_2$, $Dy(DBP)_3$, $Y(DMP)_3(THF)_2$, $Ho(DIP)_3(THF)_2$, $[Er_2(\mu\text{-BDS})_2(BDS)_4(THF)]$, $[Dy(\mu\text{-TPS})(TPS)_2]_2$, $Y(IHQ)_3$, $Sm_4(\mu_4\text{-O})(\mu\text{-ONep})_8(SST)_4$, $Y_8(\mu_3\text{-O})_3(2MPO)_{12}$

Applications

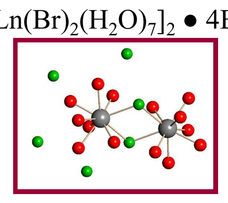
Scintilators

Opportunity: Lanthanum halide ($LaBr_3$:Ce^{+3} and $CeBr_3$) scintillators show superior performance for γ-ray detection over most materials
Problem: Lanthanum halide crystals are fragile and expensive

Approach: Make crystallographically aligned (or "textured") lanthanum halide ceramics to
- Reduce light scattering
- Enhance mechanical performance
- Increase production yield and reduce cost.

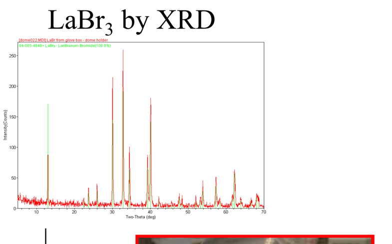


$[Ln(Br)_2(H_2O)_7]_2$ • 4Br



Remove H_2O

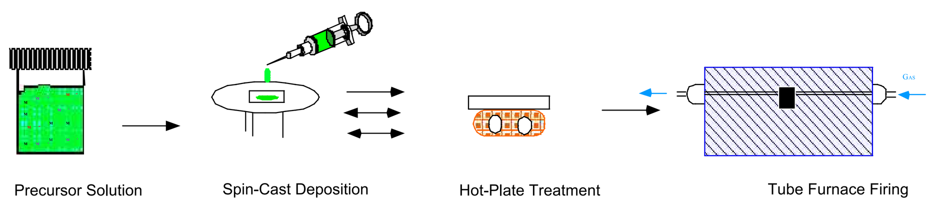
$LaBr_3$ by XRD

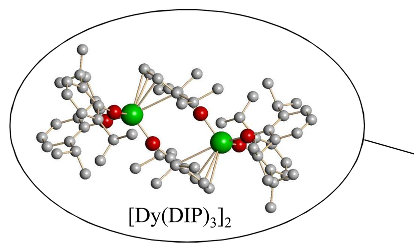


Hot Press to get Transparent crystal of $LaBr_3$

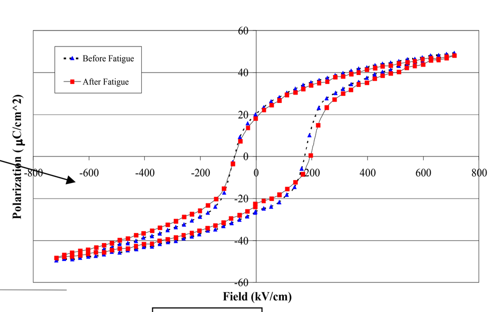
PLnZT

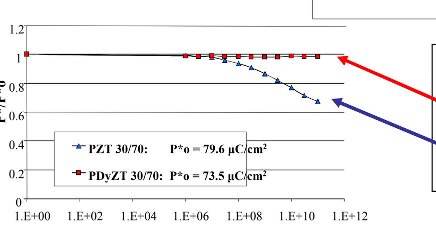
Following the patented "Basic Route to PZT" (BRP) we systematically introduced the Ln family with NO_3 ligands. Due to their disruptive nature on thin films, we substituted the novel alkoxides that we developed.





$[Dy(DIP)_3]_2$

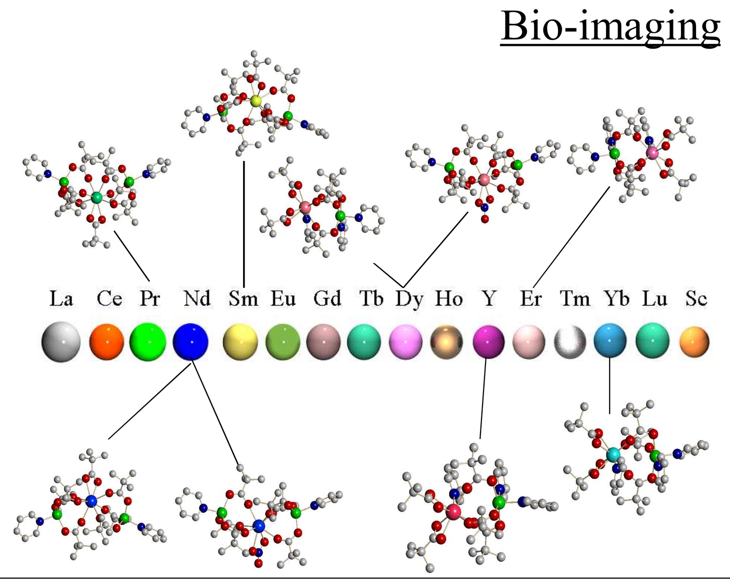




Fatigue testing of PDyZT and PZT thin films

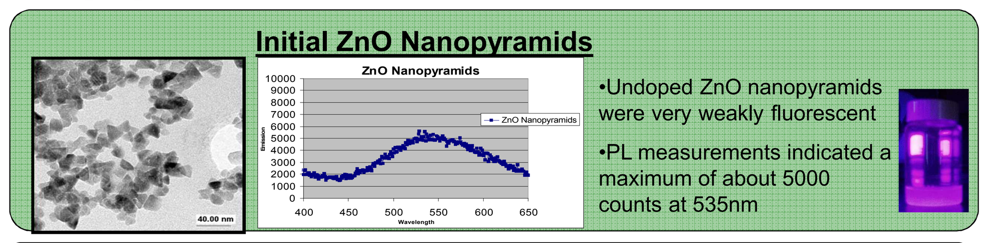
Boyle *et al. Inorg. Chem.* 2005.

Bio-imaging



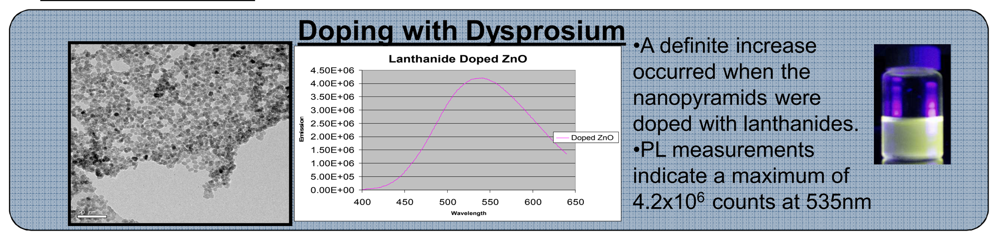
$ZnOAc_2 \cdot 2H_2O$ + TMAOH(tetramethyl ammonium hydroxide) $\xrightarrow{Butanediol}$ ZnO Nanopyramids

Initial ZnO Nanopyramids



- Undoped ZnO nanopyramids were very weakly fluorescent
- PL measurements indicated a maximum of about 5000 counts at 535nm

Doping with Dysprosium

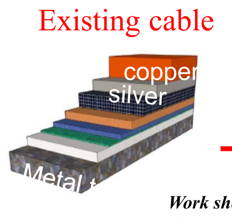


- A definite increase occurred when the nanopyramids were doped with lanthanides.
- PL measurements indicate a maximum of 4.2×10^6 counts at 535nm

YBCO

Due to the increase need for energy transport Sandia invested in developing a cost effective route to superconducting cable. The exciting cables are multi-layer and contain several expensive components. One idea is to simplify the structure by replacing several layers with a superconducting material called YBCO. One route to making the YBCO (yttrium, barium, copper oxide) precursor is to mix Ba, Y and Cu acetates in trifluoroacetic acid (TFA). To improve properties different yttrium alkoxides can me use in place of the acetate.

Existing cable



Simplify the architecture
Find multifunctional buffer layers
Reduce the number of layers

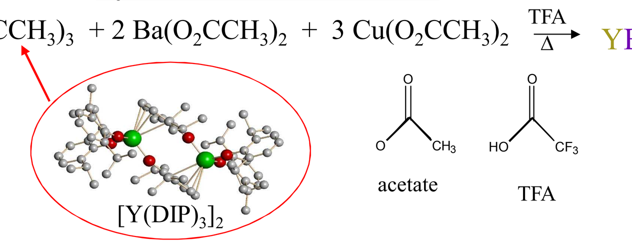
Sandia's cost effective cable

Superconductor YBCO
epitaxial buffer layer $SrTiO_3$
metal tape

Work shop on superconductivity may8-11 2006 George Crabtree, Argonne

Synthesis of YBCO solution

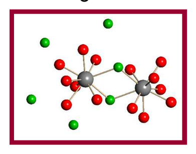
$$Y(O_2CCH_3)_3 + 2\ Ba(O_2CCH_3)_2 + 3\ Cu(O_2CCH_3)_2 \xrightarrow[\Delta]{TFA} YBa_2Cu_3O_9$$



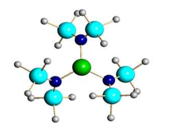
$[Y(DIP)_3]_2$, acetate, TFA

Conclusion

Developed a novel synthetic route to LnX_3
Optimization of the $LaBr_3$ is underway for use as scintilators



Converted LnX_3 into amides and then alkoxides

 + 3HOR ⟶ $Ln(OR)_3$

Novel alkoxides used for a variety of applications such as:
-Improve fatigue of PLnZT

-Mixed metal Zn/Ln carboxylates to improve luminescence

-To improve characteristics of YBCO by replacing the yttrium component with novel yttrium alkoxides

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