SAND2011-6125C

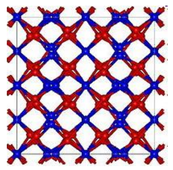
Synthesis and Characterization of a Novel Family of Yttrium Alkoxides for Production of Luminescent Nanomaterials

Sarah M. Hoppe, Timothy J. Boyle, Leigh Anna M. Steele, Daniel T. Yonemoto

Sandia National Laboratories, Advanced Materials Laboratory
1001 University Boulevard SE, Albuquerque, New Mexico 87106
Ph: (505)272-7638; Fax: (505)272-7336; e-mail:shoppe@sandia.gov

Introduction

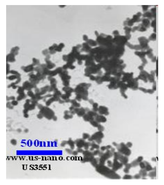
Yttria doped with lanthanide cations (Y_2O_3:Ln) ceramic materials have become of interest for applications in lasers, bioimaging probes, and scintillators. In these materials, Y_2O_3 is often used as a support or stable matrix for the luminescent emitter Ln dopants. These materials are being investigated as potential replacements for the highly toxic cadmium based (CdE) quantum dots.

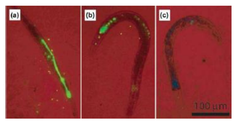


Crystal structure of Y_2O_3

Y_2O_3:Ln have been of recent interest since they are reportedly non-toxic, have long fluorescence lifetimes with sharp, strong fluorescent emission, are neuroprotective, monochromatic, have high luminescent efficiency, and are chemically and physically stable. In addition, the upconversion properties of the Ln dopants results in a different luminescence and can therefore be easily distinguished from spontaneous background fluorescence in biological samples.

In addition to their biological uses, Y_2O_3:Ln materials also promise to yield improved scintillator materials. In particular, their high light yield, fast decay times, and excellent energy resolution make them ideal candidates for these detectors. These materials can differentiate various types of radiation, such as gamma rays and neutrons, by fluorescing different colors and intensities. It has been shown that lanthanide luminescence appears more intense when used in dopant quantities. This makes Y_2O_3 a vital part of the system, but submicrometer sized particles (like those shown at right) are difficult to disperse in aqueous solvents. It is necessary to synthesize nanometer sized yttria that is easily reproducible, scalable, dispersable, and amenable to dopants.





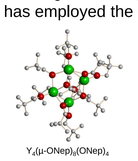
Previously, our group has shown that the precursor used to generate nanomaterials has a significant impact on the final size, shape, and morphology of the materials generated. Y_2O_3 particles are typically made from commercially available precursors. Alkoxide precursors have been understudied.

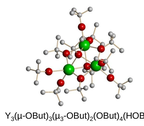
This project aims to synthesize a novel family of yttrium alkoxides ($Y(OR)_3$) and decompose them into nanomaterials of different sizes and shapes. The steric bulk of the ligand and the structure of the $Y(OR)_3$ used should have varying effects. Two nanoparticle synthesis methods were investigated since they are easily scalable and have easily managed variables to tailor the final nanomaterials generated. After optimization, these Y_2O_3 nanomaterials will be doped with other Ln cations and their luminescence properties evaluated for use in bioimaging and scintillator applications.

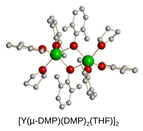
Shen, J. et. al. *Dalton Trans.* **2008**. 42, 5687. Hilderbrand, S. et. al. *Chem Comm.* **2009**. 4188.

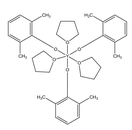
Previously Characterized $Y(OR)_3$

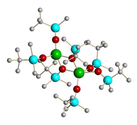
Several yttrium alkoxides can be found in the literature. The earliest structures were synthesized using YCl_3 or by forming $Y_5(OPr^i)_{13}O$ from $(NH_4)_3Y(NO_3)_6$ and reacting with the appropriate alcohol. More recent work by our group and others has employed the easier aminolysis route presented in this work.

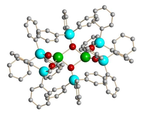

$Y_4(\mu\text{-ONep})_8(ONep)_4$

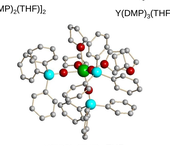

$Y_3(\mu\text{-OBut})_3(\mu_3\text{-OBut})_2(OBut)_4(HOBut)_2$


$[Y(\mu\text{-DMP})(DMP)_2(THF)]_2$


$Y(DMP)_3(THF)_3$


$[Y(DMBS)_3]_2(HDMBS)$

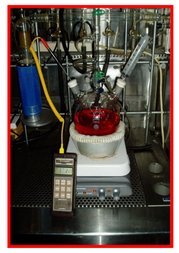

$[Y(\mu\text{-TPS})(TPS)_2]_2$


$Y(TPS)_3(THF)_3$•THF

Boyle, T.J., et. al. *Inorg. Chem.* **2007**, 49, 3705.
Gradeff, P.S., et. al. *Inorg. Chem.* **1990**, 29, 420. Evans, W.J., et. al. *Inorg. Chem.* **1989**, 28, 4308.
Coan, P.S., et. al. *Inorg. Chem.* **1991**, 30, 3570. Veith, M., et. al. *J. Mater. Chem.* **1999**, 9, 3069.

Nanomaterial Synthesis

Of the many routes used to generate nanomaterials, our laboratory employs two: (I) solution precipitation (SPPT) which involves injecting the precursor dissolved in a solvent into a hot solution of solvent and surfactant; (II) solvothermal (SOLVO) which involves adding the sample to a Parr™ acid digestion bomb, adding the desired solvent, and "pressure cooking" at a set temperature for a predetermined length of time.



solution precipitation (SPPT)

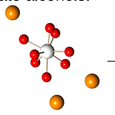
Parr™ acid digestion bomb (SOLVO)

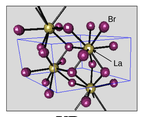
A variety of solvent systems are available for the production of nanomaterials. The SPPT route generally produces nanodots; whereas the SOLVO route tends to produce more complex shapes.

Yttrium Alkoxide Synthesis

The synthesis of novel $Y(OR)_3$ started with yttrium metal which was reacted with HBr or HCl to generate the corresponding yttrium halide hydrate [YX_3*n(H_2O)]. The hydrate was dried multiple times to leave the anhydrous YX_3 that was reacted with potassium bis(trimethylsilyl)amide to form yttrium amide ($Y(N(SiMe_3)_2)_3$). The amide was purified by filtration and sublimation and reacted with the appropriate alcohols.

$Y^o + (xs)\ HBr \longrightarrow \xrightarrow{\triangle} YBr_3$

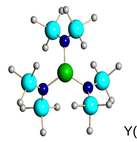

$Y(H_2O)_8$•3Br



YBr_3

$YBr_3 + 3\ KN(SiMe_3)_2 \longrightarrow Y(N(SiMe_3)_2)_3 + 3\ KBr$

Having pure $Y(N(SiMe_3)_2)_3$ is critical to successful synthesis of the $Y(OR)_3$


$Y(N(SiMe_3)_2)_3$

A systematic study of $Y(OR)_3$ started with the six aryl alcohols (shown at right). These alcohols are commercially available and increase in steric bulk from left to right and from top to bottom. The trends seen in the nuclearity, geometry, and coordination of the resultant alkoxides can then be studied in terms of the steric bulk of the alcohols. Three solvents were used (below) because they increase in polarity and can also change the structure of the alkoxides. The solvated yttrium di-*tert*-butylphenoxides ($Y(DBP)_3$solv) showed a bridging OH (blue box at right) that was not seen in the other structures and is under investigation.

Solvents:


tol toluene


THF tetrahydrofuran

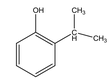

py pyridine

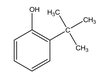
Yttrium Aryloxides

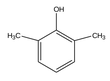
$Y(N(SiMe_3)_2)_3 + 3\ H\text{-}OR \longrightarrow Y(OR)_3 + 3\ HN(SiMe_3)_2$

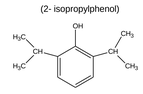
Aryl alcohols:

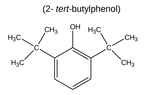

H-*o*MP (2- methylphenol)

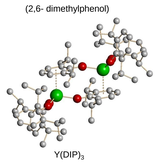

H-*o*PP (2- isopropylphenol)

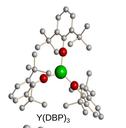

H-oBP (2- *tert*-butylphenol)

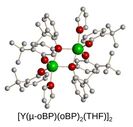

H-DMP (2,6- dimethylphenol)

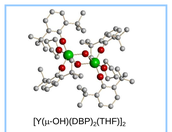

H-DIP (2,6- diisopropylphenol)

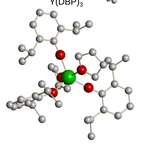

H-DBP (2,6- di-*tert*-butylphenol)

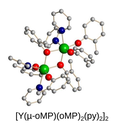

$Y(DIP)_3$

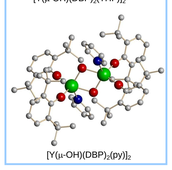

$Y(DBP)_3$

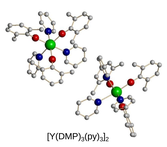

$[Y(\mu\text{-oBP})(oBP)_2(THF)]_2$

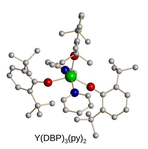

$[Y(\mu\text{-OH})(DBP)_2(THF)]_2$


$Y(DIP)_3(THF)_2$


$[Y(\mu\text{-oMP})(oMP)_2(py)_2]_2$


$[Y(\mu\text{-OH})(DBP)_2(py)]_2$

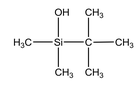

$[Y(DMP)_3(py)]_2$

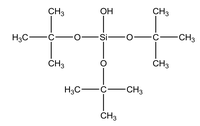

$Y(DBP)_3(py)_2$

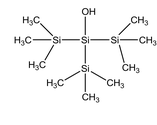
Yttrium Siloxides

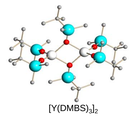
After most of the aryloxides had been synthesized, some siloxide ligands were investigated (see below). They also increase in steric bulk from left to right, but the addition of the silicon changes the electronic properties because the Si has a greater effect on the lone pairs of the O than does C. These structures are of interest for any potential changes in the yttria nanomaterials, but also for the potential to make YSiO or YSi nanomaterials.

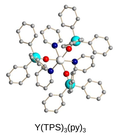
$Y(N(SiMe_3)_2)_3 + 3\ H\text{-}OSiR_3 \longrightarrow Y(OSiR_3)_3 + 3\ HN(SiMe_3)_2$


H-DMBS (*tert*-butyldimethylsilanol)


H-TOBS (tris(*tert*-butoxy)silanol)


H-SST (tris(trimethylsilyl)silanol)

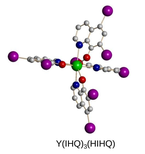

$[Y(DMBS)_3]_2$


$Y(TPS)_3(py)_3$

Other Yttrium Compounds

In addition to the novel yttrium compounds already described, some were synthesized with other commercially available ligands and in different solvents to help study the behavior of the yttrium and to see what other structure types are possible.


$Y_6(\mu_3\text{-}O)_2(2MPO)_{12}$


$Y(HQ)_3(HHQ)$

$[Y(\mu\text{-DMP})(DMP)_2(Et_2O)]_2$

Nanomaterials of Yttrium Compounds

The synthesis of nanomaterials using a representative selection of the newly characterized $Y(OR)_3$ precursors employed either the SPPT or SOLVO routes shown to the right. The resulting precipitate was collected by centrifugation, washed three times with appropriate solvent, and air dried. The six $Y(OR)_3$ precursors used were chosen because of variations in nuclearity, solvents bound, and alkoxide/siloxide ligands to study what may affect the size, shape, and morphology of the yttria produced. PXRD analyses indicate that most of the materials are amorphous, but some showed KCl contamination (see the $Y(DIP)_3(THF)_2$ pattern below). The materials will need to be calcined and new TEM and PXRD analyses performed.

SOLVO
- 25 mL pyridine
- heated at 185C for 24 h
- washed with hex

SPPT
- 20 mL trioctylamine (TOA)
- 2 mL oleic acid (OA)
- heated to 360C for 30 mins
- washed with EtOH

The isolated powder for each sample was reslurried in hexanes and a drop was placed on the TEM grid. The resulting TEM images are shown below. The SOLVO samples yielded larger particles, but all the samples showed large agglomerations of particles. There is a general lack of monodispersity and uniformity. One sample to note is the $[Y(\mu\text{-oBP})(oBP)_2(THF)]_2$ which formed rod-like structures from both synthesis routes. The unique shape could have unique materials properties as well and is being studied further.

The TEM instrument used was a Philips CM 30 operating at 300 keV accelerating voltage with a LaB_6 source and a line-to-line resoution of 0.18 nm. The instrument is equipped with a Thermo Noran System Six energy dispersive X-ray spectrometer for element characterization.

Lanthanide Dopants in Yttria Matrix

Initial dopant studies for luminescent nanomaterials focused on cerium, a common lanthanide dopant. About 0.2g of $Y(DBP)_3$ or $Y(TPS)_3(py)_3$ was doped with 1% $Ce(NR_2)_3$. The reactions followed the same SOLVO and SPPT conditions used above, respectively. The $Y(DBP)_3$:Ce yielded a black powder that turned light brown upon calcination and showed minimal luminescence under short wavelength UV light. The $Y(TPS)_3(py)_3$:Ce yielded a white powder that showed fairly bright, blue luminescence under long wavelength UV light.

$Y(DBP)_3$

$Y(TPS)_3(py)_3$

Work has also begun on synthesis of yttrium cerium alkoxides. These would result in a precursor that has the dopant already in it and the additional synthesis step to add the cerium should be unnecessary.

Mixed-Metal Yttrium Compounds and Nanomaterials

Recently, $Y(OR)_3$ have been mixed with alkali metals and alkali metal alkoxides to generate mixed-metal alkoxides. The crystal structures are much more complex than the $Y(OR)_3$ themselves and this could impact the size and shape of nanomaterials generated from these compounds. A SOLVO route was used and the results are shown next to the corresponding crystal structure. In future, these compounds will also be doped with lanthanides to try to synthesize other luminescent nanomaterials.

$Y_2Li_2(ONep)_8(HONep)_2$

$[Y_2K_2(ONep)_8][Y_4K_2(\mu_4\text{-}O)(ONep)_{12}]$

$Y_2Na_4(ONep)_{10}$

SOLVO
- 25 mL pyridine
- heated at 180C for 24 h
- washed with hex

$Y_2Cs_4(\mu_6\text{-}O)(\mu_3\text{-}ONep)_{10}(H?ONep)_2$

Summary and Future Work

- Y_2O_3 is an ideal matrix for lanthanide dopants to synthesize luminescent nanomaterials.
- Commercially available submicrometer-sized Y_2O_3 materials are difficult to disperse in aqueous solvents.
- In order to generate dispersable Y_2O_3, a novel family of $Y(OR)_3$ was synthesized.
- The shape of the precursor has a pronounced effect on the nanomaterials generated, so a subset of the novel alkoxides were used to generate Y_2O_3 nanomaterials via two solution routes.
- Cerium was the initial lanthanide dopant studied and showed bright blue luminescence when added to a SPPT reaction with $Y(TPS)_3(py)_3$.
- Mixed-metal alkoxides were generated using yttrium and the alkali metals.
- These complex structures were also used to generate nanomaterials that may be amenable to lanthanide dopants in future.

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.