Fluoro-acetate and -alkoxy Lanthanide Precursors for Lanthanide Fluoride-Based Ion Sensors

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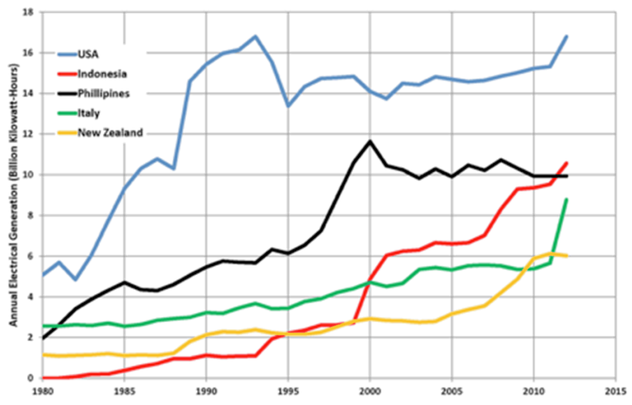
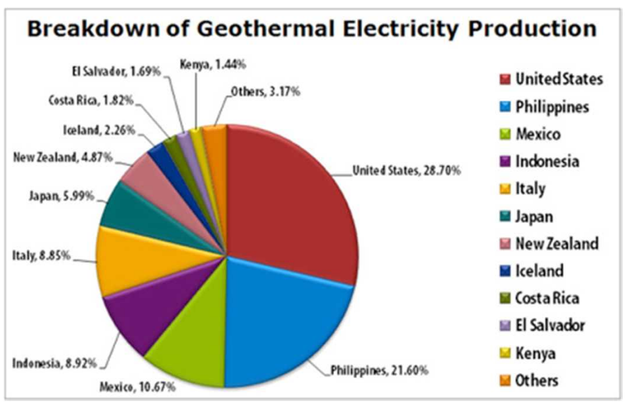
Geothermal Power

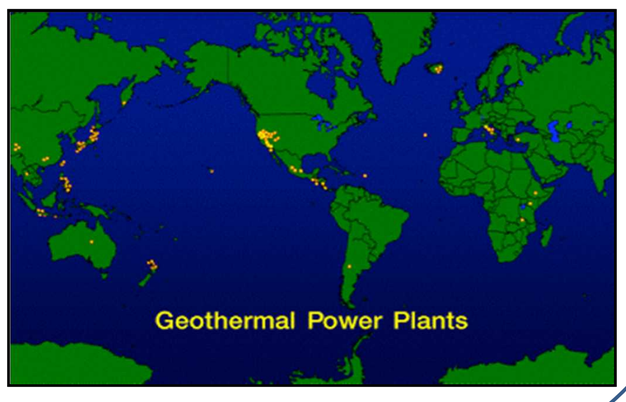
Over the course of the last century geothermal power has become a steadily growing form for energy generation. The first plant, installed in 1904 (4 lightbulbs lit), opened the door to a new alternative energy source. Since then it has proved to be a viable source of energy for numerous countries.





Of the top five users of geothermal energy, all countries have seen a large increase in utilization over the course of the last 30+ years. Additionally these countries show a promising upward trend of their usage of geothermal energy for the years ahead, making research in the production of geothermal power a must.

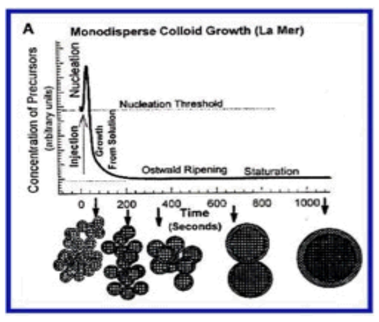
If given the correct geological conditions, geothermal energy is an extremely cheap and effective method of generating electricity. This is why internationally geothermal power is seeing steady growth especially in developing countries that require an ever growing supply of reliable energy.



Well Conditions

Well conditions present a variety of intricate and unique problems. The high operating temperatures necessary cause several issues for electronics used to monitor the well. Additionally the high brine levels found in the wells can provide various pH levels that have to be considered for a successful sensor. The depth and pressures found in these wells require a robust material that can survive these extremes, however due to minimal space in the well these materials must also be compact. Finally the last limitation is the well operator. These devices need to be simple enough that anyone can use and interpret the information. Our method for dealing with these issues will be to develop a sensor utilizing LnF_3 nanomaterials that will provide live feedback to the well operator.

Nanomaterial Benefits

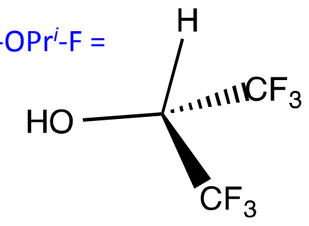


La Mer growth diagram and Ostwald ripening

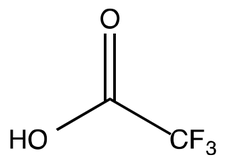
Nanomaterials provide a unique set of characteristics that can be exploited to benefit a variety of applications. Their high surface area may allow for improved detection. Similarly they can provide a possible answer to any potential material limitations such as pH, high pressures and high temperatures due to the extreme conditions found in the well.

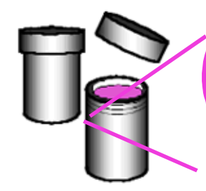
Two ligands have come to the forefront for LnF_3 synthesis: hexafluoro–*iso*-propanol and trifluoroacetic acid.

H-OPr^i-F =

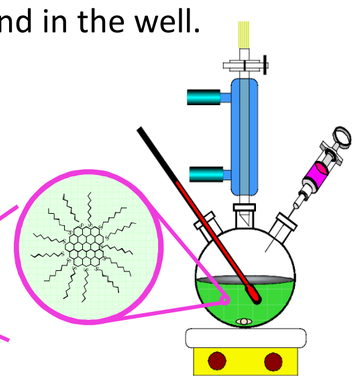


H-TFA =





Solvothermal

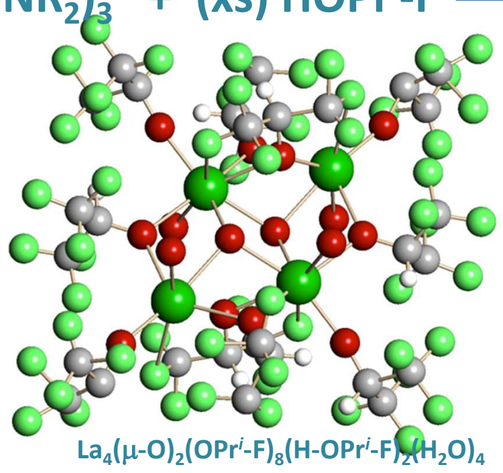


Solution precipitation

Precursor Synthesis

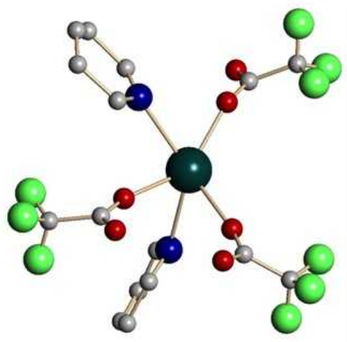
While the focus of this project is to provide a means to develop LaF_3 nanomaterials, the entire lanthanide series is of interest to determine the coordination effects of the ligands and to provide a potential substitute in the form of another LnF_3. As such a variety of different precursors have been synthesized using both the HOPri-F ligand as well as the H-TFA ligand. All reactions were performed in an inert atmosphere and developed a set of highly controllable and predictable precursors that have been confirmed via single crystal x-ray diffraction. These materials are also being tested via complexometric titrations and are being used to produce nanomaterials.

$La(NR_2)_3$ + (xs) HOPr^i-F $\xrightarrow{tol}$

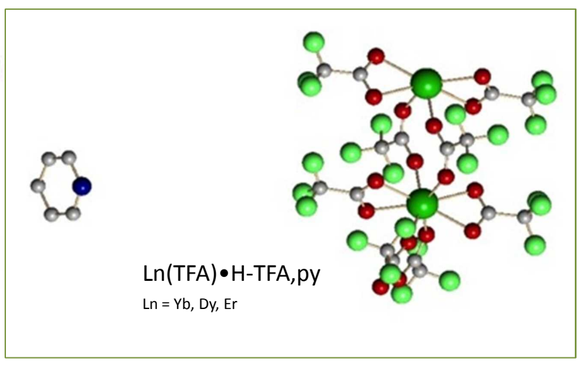


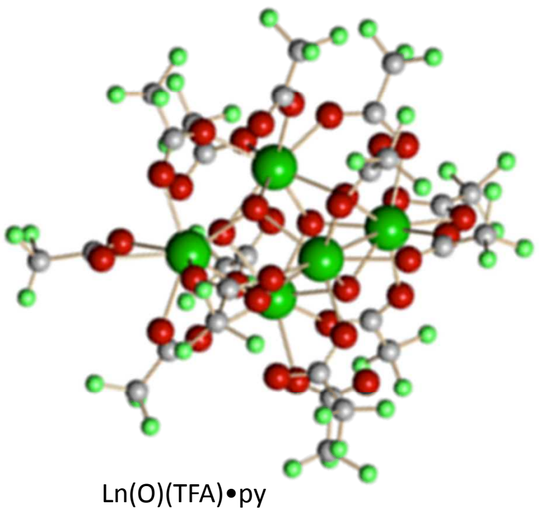
$La_4(\mu\text{-}O)_2(OPr^i\text{-}F)_8(H\text{-}OPr^i\text{-}F)_2(H_2O)_4$

$Ln(NR_2)_3$ +(xs)H-TFA $\xrightarrow{py}$



$[Tm(TFA)_3(py)_2]_n$

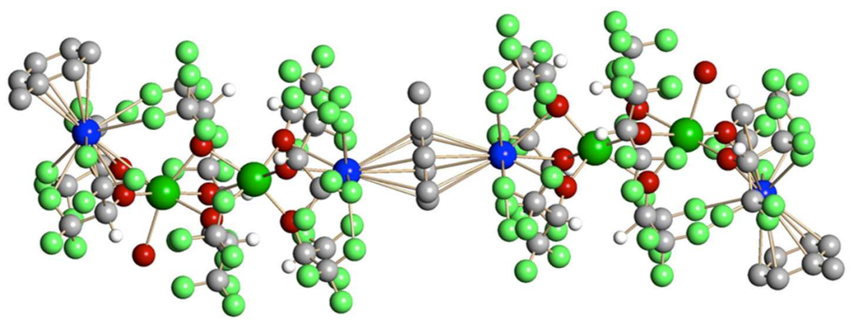




Ln(O)(TFA)•py

Ln = Dy, Ho

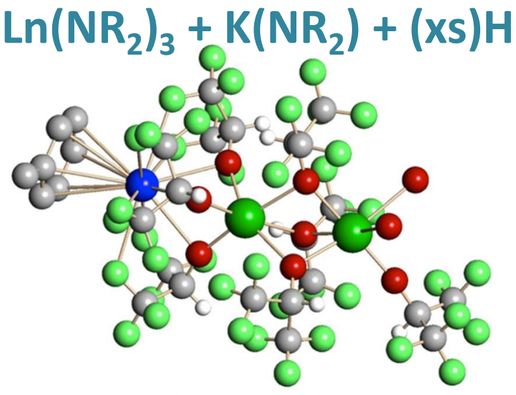
$Ln(NR_2)_3 + K(NR_2) + (xs)HOPr^i\text{-}F$



$[(\eta^6\text{-tol})K(\mu\text{-}OPr^i\text{-}F)_2(H_2O)Ln(\mu\text{-}OPr^i\text{-}F)_3Ln(\mu\text{-}OPr^i\text{-}F)_3K]_2(\eta^{12}\text{-tol})$

(K-octamer)

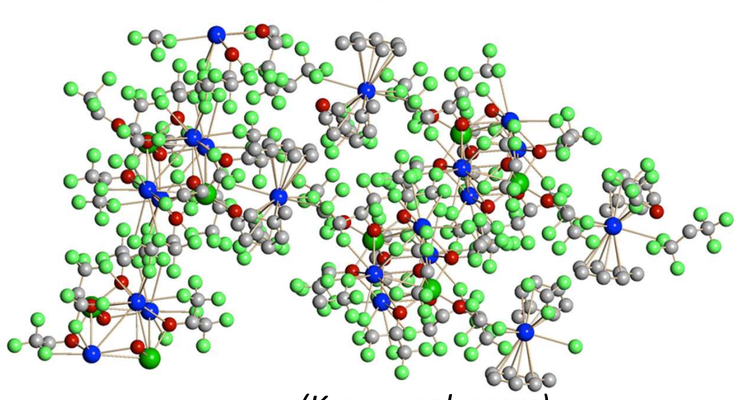
$2\ Ln(NR_2)_3 + K(NR_2) + (xs)HOPr^i\text{-}F$



$[(\eta^6\text{-tol})K(\mu\text{-}OPr^i\text{-}F)_3Ln(\mu\text{-}OPr^i\text{-}F)_3Ln(OPr^i\text{-}F)(H_2O)_2]$

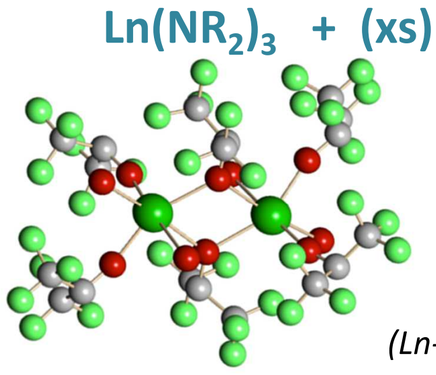
(K-dimer)

$Ln(NR_2)_3 + 2K(NR_2) + (xs)HOPr^i\text{-}F$

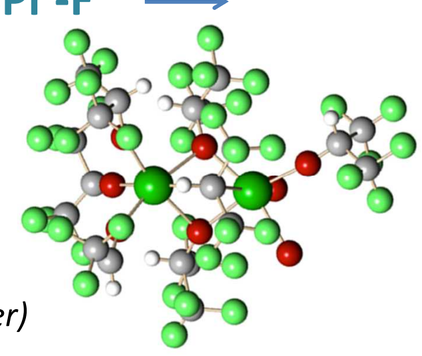


(K-razy polymers)

$Ln(NR_2)_3$ + (xs) HOPr^i-F $\xrightarrow{tol}$



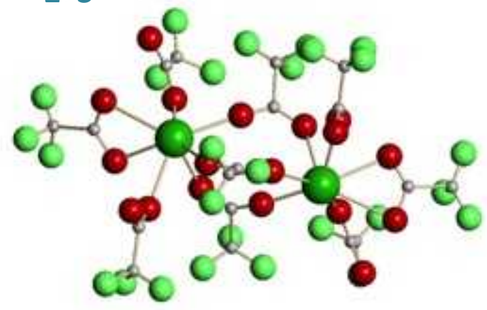
$[(H_2O)_2(OPr^i\text{-}F)_2Ln(\mu\text{-}OPr^i\text{-}F)]_2$



$[(OPr^i\text{-}F)_3Ln(\mu\text{-}OPr^i\text{-}F)_2Ln(OPr^i\text{-}F)(H_2O)_2]$

(Ln-dimer)

$Ln(NR_2)_3$ +(xs)H-TFA $\xrightarrow[\text{H-TFA}]{\text{Tol}}$



$[Ln_2(TFA)_6(HTFA)_3]_\infty$

Ln = Nd, Eu, Pr, Y, La, Ce, Gd, Ho

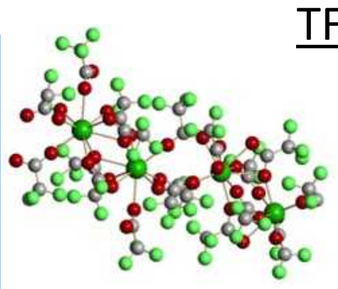
Nanoparticle Synthesis

Solution routes are of interest for a variety of reasons. They provide a relatively simple process of production with a variety of controllable variables such as time, temperature, and surfactants used. They are also easily scalable to large batch reactions.

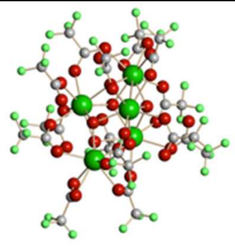
Solvothermal Route

Solution Precipitation Route

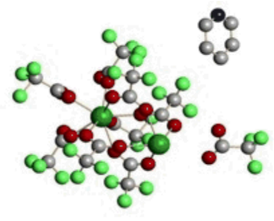
TFA derivatives



$[La_4(TFA)_{12}(H\text{-}TFA)_8]_\infty$

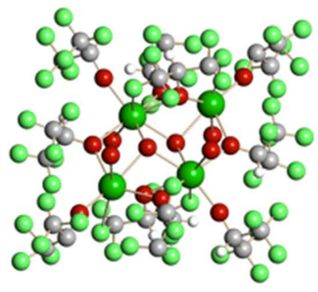


Dy(O)(TFA)•py

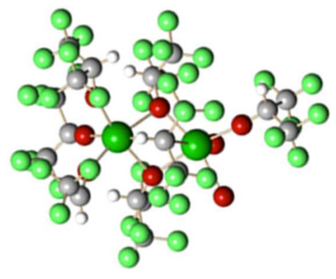


$[Yb(TFA)_3(HTFA)_2]_\infty$•py

OPr^i-F derivatives



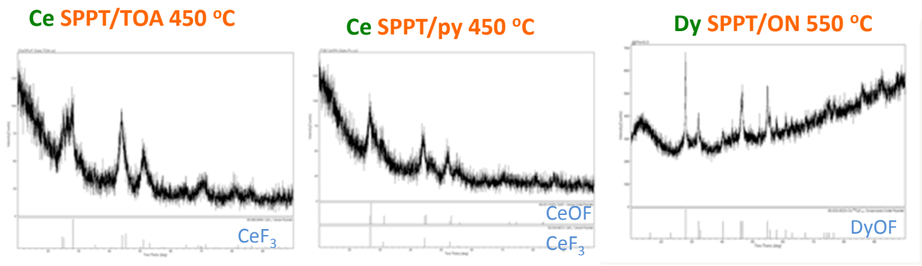
$La_4(\mu_3\text{-}O)_2(OPr^i\text{-}F)_8(H\text{-}OPr^i\text{-}F)_2(H_2O)_4$

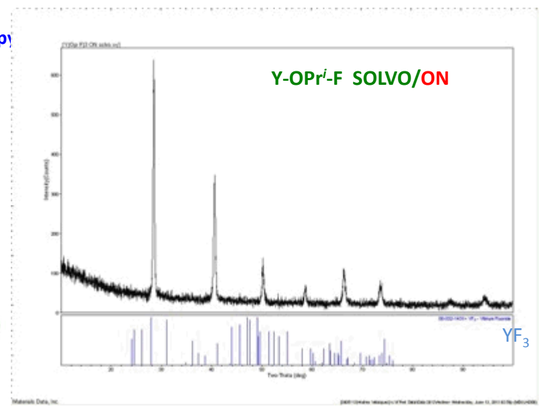


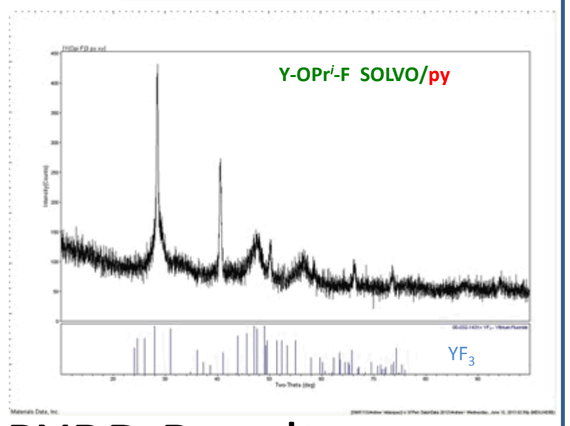
$[(OPr^i\text{-}F)_3Ln(\mu\text{-}OPr^i\text{-}F)_2Ln(OPr^i\text{-}F)(H_2O)_x]$

Ln = *all but Sm*

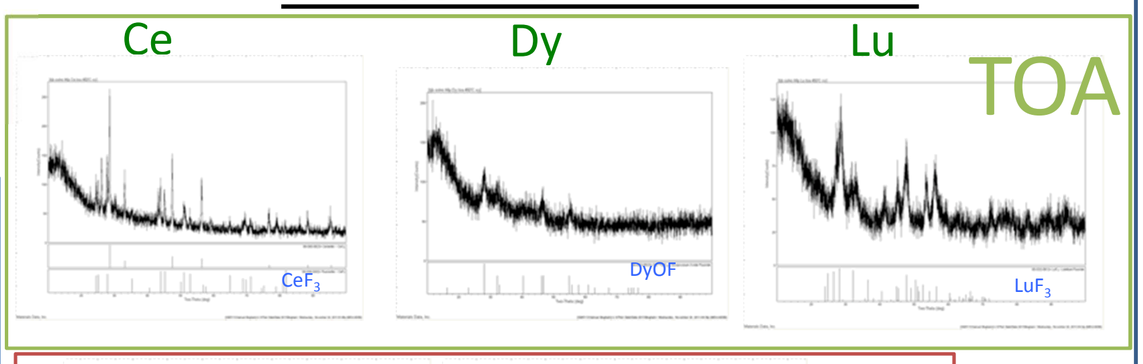
Opri-F SPPT PXRD Results

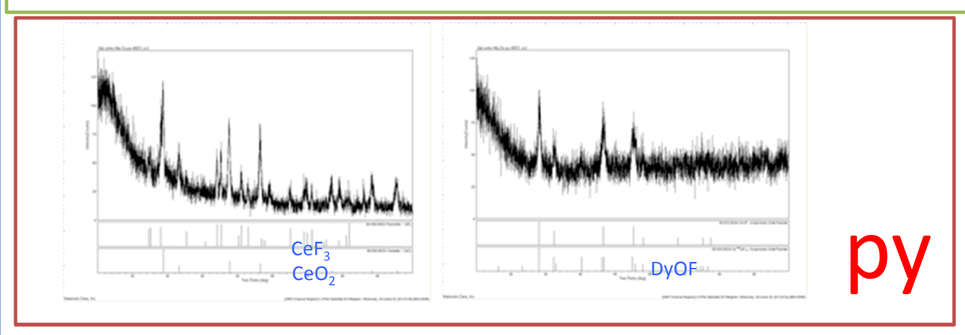






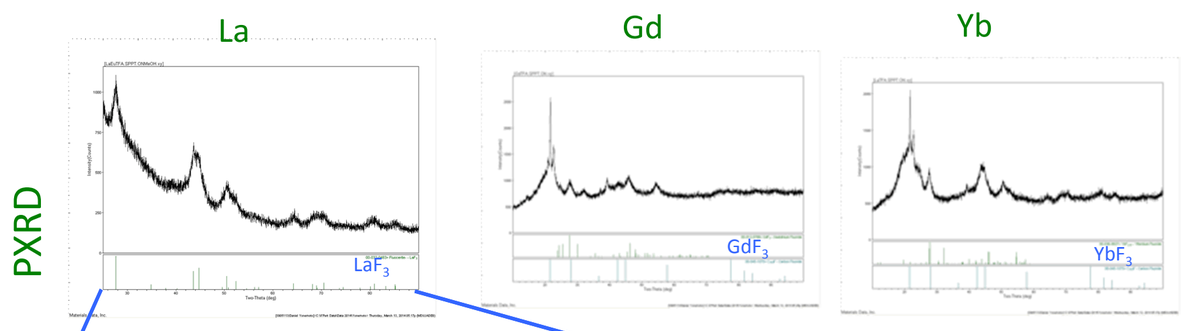
TFA SOLVO PXRD Results





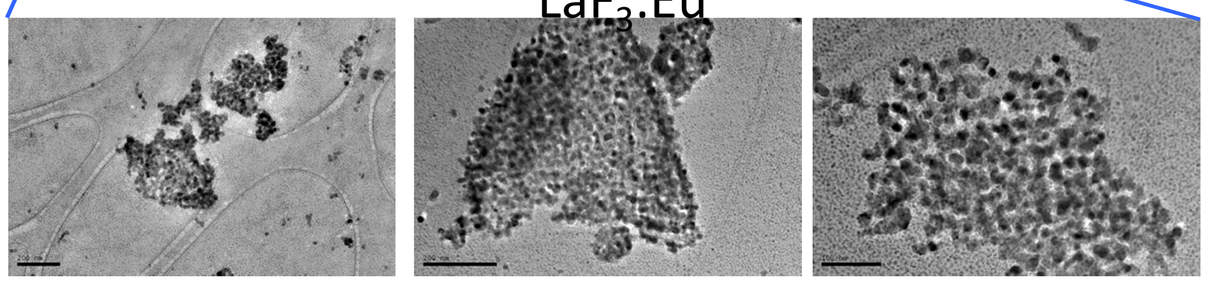
Through our investigations we have deteremined that high temperature solvents convert the fluorinated precursors to LnF3 where as the low temperature solvents prefer the oxyfluoride derivatives.

TFA SPPT Results



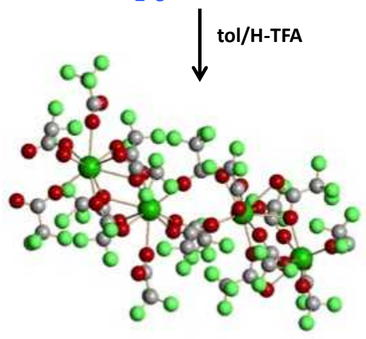
LaF_3:Eu

TEM



$La(NR_2)_3$ + (xs) H-TFA

tol/H-TFA



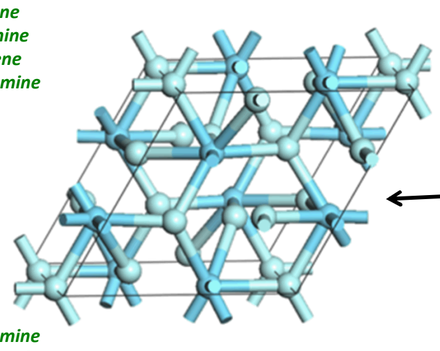
$[La(TFA)_3(HTFA)_x]_n$

SPPT
> 300 °C

Oleylamine
Trioctylamine
Octadecene
Hexadecylamine

SOLVO
185 °C
24 h

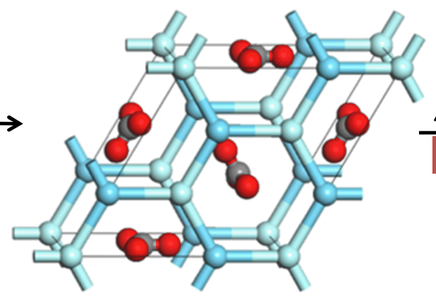
Oleylamine
Trioctylamine
Octadecene
Octylamine



LnF_3

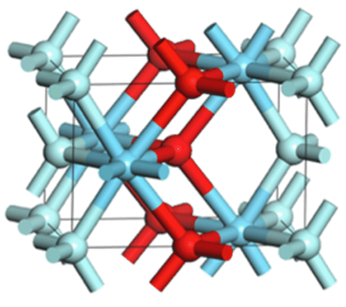
SOLVO
185 °C
24 h

Pyridine



$La(CO_3)F$

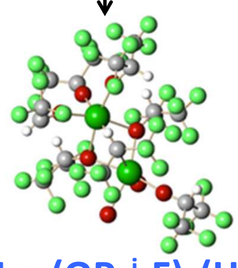
450 °C
AIR



LnOF

$Ln(NR_2)_3$ + (xs) H-OPr^i-F

tol/H-OPR^i-F



$Ln_2(OPr^i\text{-}F)_6(H_2O)_x$

SPPT
> 300 °C

Oleylamine
trioctylamine

Δ

AIR

Ln = La (450), toa
Ce (450), on
Dy (550), on
Tb (450), on

SOLVO
185 °C
24 h

py

?????

py

SPPT
<300 °C

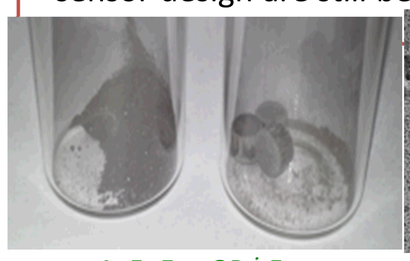
450 °C

AIR

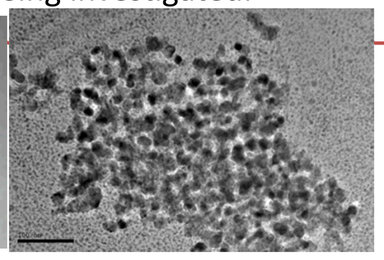
CeOF

Summary and Conclusion

Materials tests are now underway on LaF3:Eu to determine their effectiveness in regard to the bulk commercial powders. While synthesis and identification of these materials are complete, pellet issues, survivability and ion sensor design are still being investigated.



LaF_3:Eu ; OPr^i-F



LaF_3:Eu ; TFA

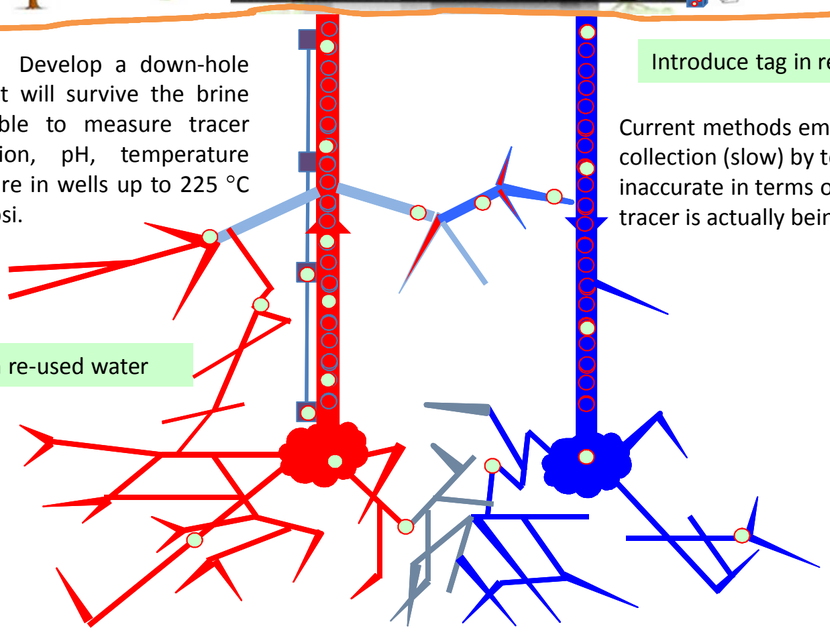
Sun, X. et al. *Chem. Eur. J.* **2007** *13*, 2320-2332.

Approach: Develop a down-hole sensor that will survive the brine and be able to measure tracer concentration, pH, temperature and pressure in wells up to 225 °C and 5000 psi.

Introduce tag in return water

Current methods employ surface collection (slow) by technician and inaccurate in terms of where the tracer is actually being circulated.

Detect tag in re-used water



The largest geothermal plant in the world is located at
The Geysers (Santa Rosa, CA, USA).