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Solvent-free microwave assisted green synthesis of Ln-doped ceria nanoparticles

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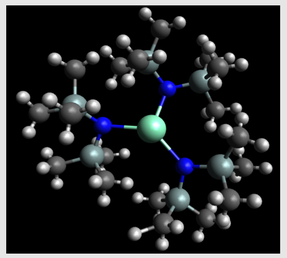
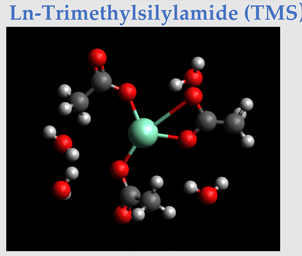
The ability to control the physical properties of nanomaterials is critical to advance manufacturing technologies and applications

Synthesis of nanomaterials is a non-trivial task especially for size/morphology control and doping, which is critical in tailoring their applicable properties. The synthesis of nanomaterials mostly involve solvents and surfactant as well as numerous other reaction conditions to control the physical and chemical motif of the nanomaterial. More specifically, the majority of Ln-doped ceria nanoparticles require high temperatures (>500 °C), long reaction times, harmful reducing agents, or non-environmentally friendly precursor/reactants. Therefore, developing a synthetic route that can reduce the aforementioned parasitic variables while simultaneously generating tailored size/morphology control is needed to advance and study Ln-doped ceria nanoparticle as function of their properties-physical/chemical motif. To ensure the production of high quality nanomaterials, a range of precursors including in-house synthesized metal amides and commercially available metal acetates/ nitrates were investigated for optimum control over the physical properties (i.e., crystalline phase, size, and morphology) of the resultant nanomaterials.

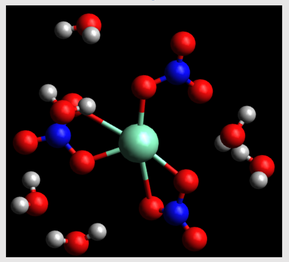
Influence of Precursor on Nanoparticle Motif



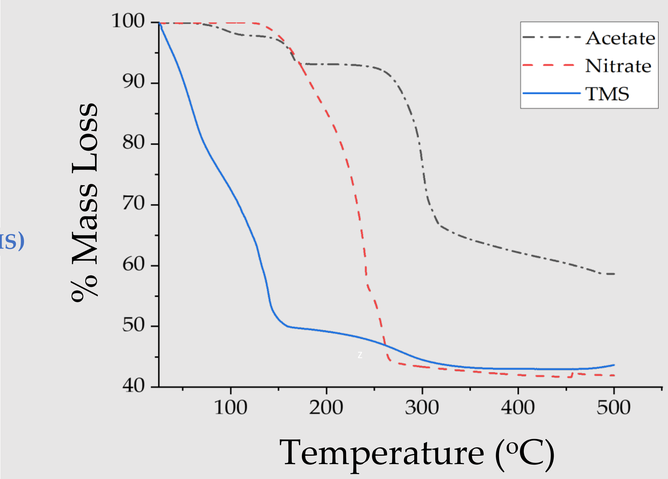
Ln-Trimethylsilylamide (TMS)



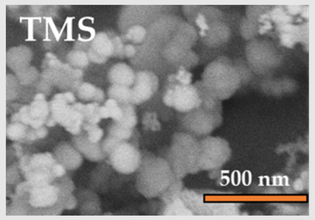
Ln-Acetate Hydrate

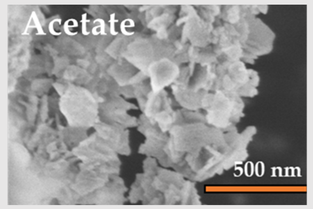


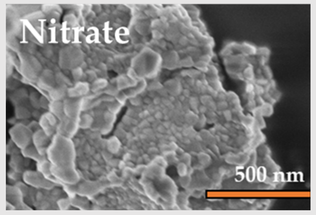
Ln-Nitrate Hexahydrate



Uniform nucleation due to single step thermal decomposition leads to spherical nanoparticle formation when using Ln-TMS based precursors.

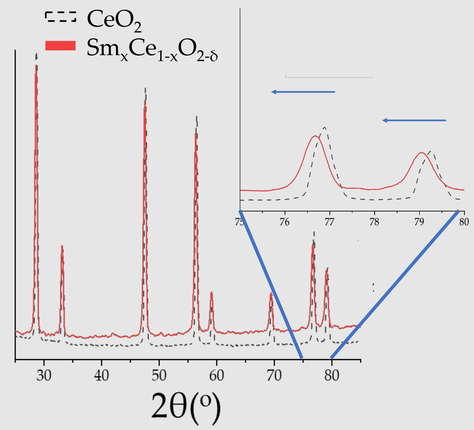




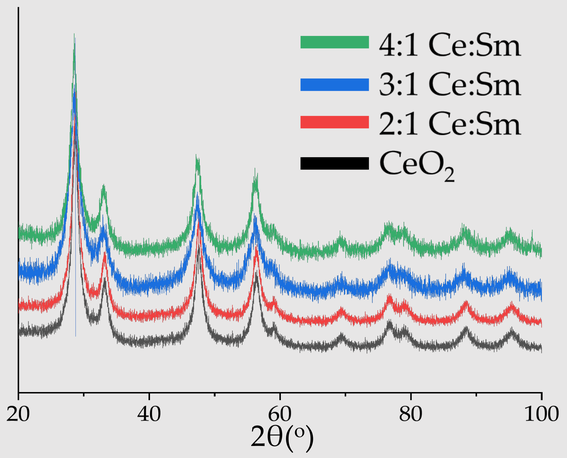


Synthesis of Sm-doped Ceria Nanoparticles

Sm-Precusor + Ce-Precursor → Grind with mortar and pestle → BP-210 Microwave → $Sm_xCe_{1-x}O_{2-\delta}$

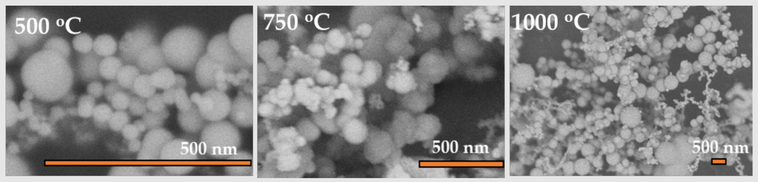


pXRD spectra shows the formation of CeO_2, **cubic fluorite** space group. Incorporation of Sm ions leads to downshifting of entire spectra



Various Ce:Sm ratios leads to increase in the Sm concentration indicated by the continuous downshifts of the pXRD spectra

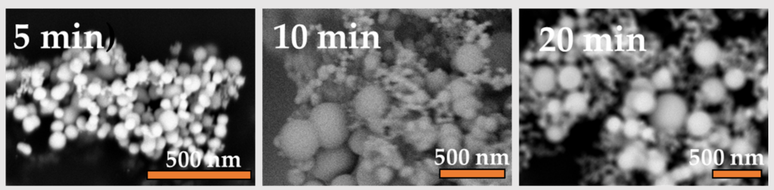
Effect of Temperature on Nanoparticle Size



Temperature	Average Size
500 °C	53 nm
750 °C	130 nm
1000 °C	279 nm

Spherical nanoparticles were produced at **varying reaction temperatures** with an initial Ce:Sm molar ratio of 4:1 and a reaction time of 10 minutes.

Temporal Study for Nanoparticle Size Control



Time	Average Size
5 min	60 nm
10 min	89 nm
20 min	217 nm

Spherical nanoparticles were produced with **various reaction times**, a reaction temperature of 750 °C and an initial Ce:Sm molar ratio of 2:1.

Conclusions

For the first time, we successfully produced Sm-doped Ceria nanoparticles using a microwave assisted-solid state synthesis route. The use of TMS based precursors yielded spherical nanoparticles due to their single decomposition event. Further exploration of reaction temperature, initial metal ion ratio, and reaction time demonstrated control of final particle size. This work demonstrates the potential for solvent-free, high-yield synthesis of morphology controlled rare-earth oxide materials using tailored precursors in a microwave reactor.

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