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TITLE:

Molten-Salt Synthesis of Complex Metal Oxide Nanoparticles

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SUMMARY:

Here, we demonstrate a unique, relatively low-temperature, molten-salt synthesis method for preparing uniform complex metal oxide lanthanum hafnate nanoparticles.

ABSTRACT:

The development of feasible synthesis methods is critical for the successful exploration of novel properties and potential applications of nanomaterials. Here, we introduce the molten-salt synthesis (MSS) method for making metal oxide nanomaterials. Advantages over other methods include its simplicity, greenness, reliability, scalability, and generalizability. Using pyrochlore lanthanum hafnium oxide ($La_2Hf_2O_7$) as a representative, we describe the MSS protocol for the successful synthesis of complex metal oxide nanoparticles (NPs). Furthermore, this method has the unique ability to produce NPs with different material features by changing various synthesis parameters such as pH, temperature, duration, and post-annealing. By fine-tuning these parameters, we are able to synthesize highly uniform, non-agglomerated, and highly crystalline NPs. As a specific example, we vary the particle size of the $La_2Hf_2O_7$ NPs by changing the concentration of the ammonium hydroxide solution used in the MSS process, which allows us to further explore the effect of particle size on various properties. It is expected that the MSS method will become a more popular synthesis method for nanomaterials and more widely employed in the nanoscience and nanotechnology community in the upcoming years.

INTRODUCTION:

Molten-salt synthesis (MSS) involves the use of a molten salt as the reaction medium for preparing nanomaterials from their constituent precursors. The molten salt acts as the solvent and facilitates the enhanced reaction rate by increasing the contact area between reactants and their mobility. The choice of molten salts is of paramount importance for the success of the MSS method. The salt must meet some important quality requirements such as low melting point, compatibility with reacting species, and optimum aqueous solubility. Molten salt has been used previously to enhance the rate of solid-state reactions; however, in a flux system, only a small amount of molten salt is used (unlike in MSS, in which a large quantity is added to form a soluble medium for the reaction and control the properties of the synthesized nanomaterials, such as particle size, shape, and crystallinity, *etc.*). In this sense, MSS is a modification of the powder metallurgical method and different from the flux method[1-3]. The employment of molten salt can (1) increase reaction kinetic rate[4] while decreasing synthesis temperature[5], (2) increase the degree of reactant homogeneity[6], (3) control crystalline size and morphology[7], and (4) reduce the level of agglomeration.

Nanomaterials have been in high demand in scientific research and novel industrial applications because of their superior electrical, chemical, magnetic, optical, electronic, and thermal properties. Their properties are highly dependent on the particle size, shape, and crystallinity. Compared with other synthesis methods for nanomaterials, MSS has several obvious advantages; although, it is not yet as well-known as other synthesis methods in the nanoscience and nanotechnology community. As described below, these advantages include its simplicity, reliability, scalability, generalizability, environmental friendliness, cost effectiveness, relative low synthesis temperature, and free agglomeration of NPs with clean surface[8].

Simplicity: The MSS process can be easily carried out in a simple laboratory with basic facilities. No sophisticated instrumentation is needed. Precursors and molten salts are air stable with no need for glove box handling.

Reliability: Once all initial synthesis parameters such as concentration, pH, processing time, and annealing temperature are optimized, high-quality and pure products are assured when using the MSS method. If all synthesis steps are carried out properly, the final products may attain all basic criteria needed for good-quality NPs. A novice to the MSS method will not change the synthesis outcome, as long as all synthesis parameters are properly and carefully followed.

Scalability: The MSS method’s ability to produce large quantities of size- and shape-controlled particles is crucial. This critical factor is important because it allows for the determination of industrial usefulness and efficiency. Compared to other synthesis techniques, MSS can easily generate a sufficient amount of products by adjusting stoichiometric amounts during the process. This is an important feature of the method because it allows for convenience at the industrial level, making it a more desired approach due to this scalability[9,10].

Generalizability: The MSS method is also a generalizable technique to produce nanoparticles with various compositions. Other than simple metal oxides and some fluorides, nanomaterials of complex metal oxides that have been successfully synthesized by the MSS method include perovskites (ABO_3)[10-14], spinel (AB_2O_4)[15,16], pyrochlore ($A_2B_2O_7$)[4,17-19], and orthorhombic structures ($A_2B_4O_9$)[2,3,20]. More specifically, these nanomaterials include ferrites, titanates, niobates, mullite, aluminium borate, wollastonite, and carbonated apatite[7,9,21]. The MSS method has also been used to produce nanomaterials of various morphologies such as nanospheres[4], ceramics powder bodies[22], nanoflakes[23], nanoplates[7], nanorods[24], and core-shell nanoparticles (NPs)[25], depending on synthesis conditions and crystal structure of the products.

Environmental friendliness: Several traditional methods for making nanomaterials involve the use of large amounts of organic solvents and toxic agents that generate environmental issues. The partial or total elimination of the use of them and the generation of waste by sustainable processes is in demand of green chemistry nowadays[8]. The MSS method is an environmentally friendly approach to synthesize nanomaterials by employing nontoxic chemical and renewable materials and minimizing waste, byproducts, and energy.

Relative low synthesis temperature: The processing temperature of the MSS method is relatively low compared to that required in a conventional solid-state reaction[26] or a sol-gel combustion reaction[27]. This lower temperature saves energy while producing high-quality NPs.

Cost effectiveness: The MSS method does not require any harsh or costly reactants or solvents nor any specialized instrumentation. Water is the main solvent used for washing away the used molten salts, which are also cheap. Moreover, experimental setup needed includes only simple glassware and a furnace without specialized instrumentation, while nanomaterials with complex composition and refractory nature can be produced.

Agglomeration free with clean surface: During the MSS process, the formed nanoparticles are well-dispersed in the molten salt medium due to its large quantity, used along with its high ionic strength and viscosity[1,6,8]. Unlike colloidal synthesis and most hydrothermal/solvothermal processes, no protective surface layer is necessary to prevent the continuous growth and agglomeration of the formed NPs.

Exemplary synthesis of complex metal oxide NPs by the MSS method: The MSS method as a universal and cost-effective approach to rationally and large-scale synthesize nanomaterials for a sufficiently wide spectrum of material may be highly welcomed by scientists working in nanoscience and nanotechnology. Here, lanthanum hafnate ($La_2Hf_2O_7$) was selected because of its multifunctional applications in the areas of X-ray imaging, high *k*-dielectric, luminescence, thermographic phosphor, thermal barrier coating, and nuclear waste host. $La_2Hf_2O_7$ is also a good host for doped scintillators due to its high density, large effective atomic number, and the possibility of its crystal structure to be engineered along with an order-disorder phase transition. It belongs to the $A_2B_2O_7$ family of compounds, in which “A” is a rare-earth element with a +3 oxidation state, and “B” represents a transition metallic element with a +4 oxidation state. However, due to the refractory nature and complex chemical composition, there has been a lack of proper low-temperature and large-scale synthesis methods for $La_2Hf_2O_7$ NPs.

For fundamental scientific investigation and advanced technological applications, it is a prerequisite to make monodisperse, high-quality, and uniform $A_2B_2O_7$ NPs. Here we use the synthesis of highly crystalline $La_2Hf_2O_7$ NPs as an example to demonstrate the advantages of the MSS method. As schematically shown in **Figure 1**, $La_2Hf_2O_7$ NPs were prepared by the MSS method with a two-step process following our previous reports. First, a single-source complex precursor of $La(OH)_3 \cdot HfO(OH)_2 \cdot nH_2O$ was prepared via a coprecipitation route. In the second step, size-controllable $La_2Hf_2O_7$ NPs were synthesized through the facile MSS process using the single-source complex precursor and nitrate mixture ($NaNO_3$:KNO_3 = 1:1, molar ratio) at 650 °C for 6 h.

[Place **Figure 1** here]

PROTOCOL:

1. Preparation of a Single-Source Complex Precursor via a Coprecipitation Route

1.1. Preparation of lanthanum and hafnium precursor solution

1.1.1. Measure 200 mL of distilled water in a 500 mL beaker and start stirring at 300 rpm.

1.1.2. Dissolve lanthanum and hafnium precursors in the stirring water [*i.e.,* 2.165 g of lanthanum nitrate hexahydrate ($La(NO_3)_3 \bullet 6H_2O$) and 2.0476 g of hafnium dichloride oxide octahydrate ($HfOCl_2 \bullet 8H_2O$)].

1.1.3. Let the solution stir for 30 min before starting the titration.

1.2. Preparation of diluted ammonia solution

1.2.1. Prepare 200 mL of diluted ammonia solution with different concentrations, including 0.75%, 1.5%, 3.0%, 6.0%, and 7.5%. For example, add 20 mL of concentrated ammonia solution (NH_4OH 28-30%) to 180 mL of distilled water in a separate beaker to make 3.0% diluted ammonia solution.

1.3. Titration and washing the single source complex precursor

1.3.1. Add the diluted ammonia solution prepared in the previous step into a burette and ensure that the burette is covered at all times, since ammonia solution tends to evaporate which decreases its concentration.

1.3.2. Add the diluted ammonia solution in the burette into the stirring solution of lanthanum nitrate and hafnium dichloride oxide dropwise.

1.3.3. Adjust the dropping speed of the ammonia solution accordingly so that it will be added over a period of 2 h.

1.3.4. After several mL of ammonia solution have been delivered, ensure that the solution becomes cloudy. This is a simple sign that the precipitate of the single-source complex precursor of $La(OH)_3 \cdot HfO(OH)_2 \cdot nH_2O$ is forming.

1.3.5. After 2 h, remove the stirring bar and allow the precipitate to age overnight.

1.3.6. Check the pH of the coprecipitated solution before washing. Wash the precipitate with distilled water until the supernatant reaches a neutral pH, which normally takes 5-8 washes.

1.4. Vacuum filtration and drying of precursor

1.4.1. Vacuum filter the coprecipitated solution using a filter paper with a coarse porosity (40-60 µm; see **Table of Materials**) to separate the solid precipitate from the supernatant.

1.4.2. Ensure that all complex precursor remnants are washed from the walls of the beaker.

1.4.3. Air dry the resulting single-source complex precursor $La(OH)_3 \cdot HfO(OH)_2 \cdot nH_2O$ at room temperature overnight.

2. Molten-Salt Synthesis of Lanthanum Hafnate NPs

2.1. Preparation of salt and precursor mixture

2.1.1. Measure 30 mmol (3.033 g) of potassium nitrate (KNO_3) and 30 mmol (2.549 g) of sodium nitrate ($NaNO_3$).

2.1.2. Combine the measured salts with 0.35 g of the as-prepared single-source complex precursor $La(OH)_3 \cdot HfO(OH)_2 \cdot nH_2O$.

2.1.3. If necessary, add 1-5 mL of acetone or ethanol to the mixture to facilitate the grinding. Ensure that all the solvent is evaporated before placing the mixture into a crucible.

2.1.4. Grind the mixed salts and precursor as fine as possible for about 30 min using a mortar and pestle.

2.2. Molten-salt processing

2.2.1. Place the resulting mixture in a corundum crucible, then place it in a muffle furnace.

2.2.2. Set the furnace at 650 °C for 6 h with a ramp rate of 10 °C/min.

2.2.3. After the sample and furnace have cooled to room temperature, take out the crucible and soak the sample in a beaker filled with distilled water overnight.

2.3. Washing and drying the $La_2Hf_2O_7$ NPs

2.3.1. Empty the sample from the crucible into a 1 L beaker.

2.3.2. Wash the sample with distilled water 5-8 times until the supernatant is clear of salts and not cloudy anymore.

2.3.3. Purify the product by centrifugation or vacuum filtration to remove any residual impurity.

2.3.4. Dry the product in the oven at 90 °C overnight.

REPRESENTATIVE RESULTS:

The as-synthesized $La_2Hf_2O_7$ NPs may exist in the ordered pyrochlore phase. However, chemical doping, pressure, and temperature could modify the phase to defect fluorite. It is possible for our material to have multiple phases; however, here we focus only on the pyrochlore phase for simplicity. X-ray diffraction (XRD) and Raman spectroscopy have been used to systematically characterize their phase purity, structure, and phase. The crystalline size can be calculated using Debye-Scherrer's formula. On the other hand, Raman spectroscopy is used as a secondary structural characterization technique due to it high sensitivity to M-O vibrational modes[28]. It identifies the exact crystallographic phase of the $La_2Hf_2O_7$ NPs[29].

Compared to other synthetic techniques such as solid-state reactions, MSS has a high reaction constant, meaning that the reaction is more likely to go in the forward direction[30]. The production of pyrochlore $La_2Hf_2O_7$ is achieved by increasing the contact interfacial area and mobility of the reactant species inside the molten salt system. **Figure 2** illustrates the XRD patterns of the synthesized $La_2Hf_2O_7$ NPs made by the MSS method from the single-source complex precursors using different concentrations of ammonia solution. XRD results shows the formation of pure $La_2Hf_2O_7$ with high crystallinity. The peak position and Miller indices may be indexed based on the Joint Committee on Powder Diffraction Standard (JCPDS) pattern #78-1292. No visible impurity phases such as La_2O_3, Eu_2O_3, or HfO_2 were detected. There is no change in XRD pattern as a function of the used ammonia concentration except for the increase of particle size. **Table 1** shows the corresponding calculated crystal parameter and particle size of the $La_2Hf_2O_7$ NPs.

[Place **Figure 2** here]

[Place **Table 1** here]

There are two common phases of the $A_2B_2O_7$ compounds: the disordered fluorite phase and ordered pyrochlore phase. The disordered fluorite phase exists in the $Fm\bar{3}m$ space group, wherein all the cationic ions (A^{3+} and B^{4+}) are randomly distributed, allowing for one active mode. On the other hand, ordered pyrochlore phase exists in $Fd\bar{3}m$ space group. Therefore, it exhibits close structural resemblance to fluorite phase except that there are two cationic sites, three anionic sites [48f(O_I), 8a(O_{II}), and 8b(O_{III})], and 1/8th of the oxygen ions (O_{III}) at 8b site absent in the pyrochlore structure, allowing for 6 active modes[19,28,29]. Based on the group theory, the defect fluorite structure has one vibrational mode due to T_{2g}, while a pyrochlore phase has six vibrational modes in the range of 200-1000 cm^{-1}. This information is vital for the correct phase identification of the $La_2Hf_2O_7$ NPs (**Figure 3**). In this case, the prepared $La_2Hf_2O_7$ NPs are in pure pyrochlore form.

[Place **Figure 3** here]

FIGURE AND TABLE LEGENDS:

Figure 1: Schematic of the synthesis steps for $La_2Hf_2O_7$ NPs via the MSS method.

Figure 2: X-ray diffraction patterns of the $La_2Hf_2O_7$ NPs prepared by adjusting the used ammonia solution concentration then indexed based on the defect fluorite pattern.

Figure 3: Raman spectra of the $La_2Hf_2O_7$ NPs prepared by adjusting the used ammonia solution concentration, with six active modes pertaining to the pyrochlore phase.

Figure 4: Flowchart of the critical steps of MSS indicating the controlling factors of the synthetic procedure for NPs with potential pathways to fine-tune their characteristics.

Table 1: Crystallographic parameter and particle size of the $La_2Hf_2O_7$ NPs prepared by adjusting the used ammonia solution concentration showing a continuous particle size growth. FWHM = full-width at half-maximum.

DISCUSSION:

The chart in **Figure 4** provides several reliable controlling factors of the MSS method and accounts for alternative pathways to fine-tune the features of synthesized nanomaterials. In addition, it helps identify critical steps in the MSS process.

[Place **Figure 4** here]

First, the identity of precursors is critical, especially for the synthesis of complex metal oxide NPs. When producing $A_2B_2O_7$ NPs, it is important to first generate a single-source complex precursor that contains the main elements making up the final product [*i.e.,* A and B, at an atomic level with the formula of $A(OH)_3{\cdot}BO(OH)_2{\cdot}nH_2O$]. In this experiment, the particle size of the final $La_2Hf_2O_7$ NPs could be controlled during this step by adjusting the concentration of the titrant ammonia solution, where a higher ammonia solution concentration generated bigger $La_2Hf_2O_7$ NPs. Other trials have also been performed to make $A_2B_2O_7$ NPs using different precursors, such as commercially available nitrates or oxides containing the main elements of $A_2B_2O_7$; however, none have worked[4]. The advantages of this amorphous single-source complex precursor are that the composing elements of $A_2B_2O_7$ are mixed at an atomic level and are homogeneously distributed in the same order as the final $A_2B_2O_7$ product, decreasing the space or range the reactants that need to be transported.

Second, the selection of proper molten salt has major importance in obtaining nanomaterials with desirable morphology and characteristics. The melting point of the selected salt should be appropriate for the synthesis of the required phase of nanomaterials. The formation of nanomaterials is ultimately governed by the melting point of salts used as molten solvents, such as alkali chloride, sulfate, carbonate, or hydroxide[1,6,31,32]. It has been reported that the use of different molten salts can modify the formation temperature, thereby altering the particle size and morphology[18].

In addition, the ramp rate tends to affect the synthesis of the NPs. A fast ramp rate tends to generate agglomerated NPs[33], which affects their properties. In the case of luminescent and scintillation materials, high agglomeration is not desirable, as it can scatter excited and emitted light[17,19]. A slow ramp rate is thus more suitable and allows enough time to reach the actual temperature inside the crucible. A slower cooling process usually allows for NPs with a spherical shape to form[34].

Another important criterion for the selection of the salt is that it should have sufficient aqueous solubility. With simple washing by water, the used molten salt should be easily washed away after the MSS.

Finally, the addition of a volatile liquid such as acetone and ethanol during the mixing of the salts used and single-source complex precursor helps ease the grinding process but is not essential. The addition of a liquid is helpful to make a homogenous mixture in a shorter time and requires less effort, which is important in generating pure products. The added volatile liquid does not affect the characteristics of the resultant NPs since it fully evaporates by the end of the grinding process. Due to its high volatility, the amount added may range anywhere from 1 to 5 mL.

The MSS method is a straightforward and simple way to synthesize NPs at any university and industrial location. However, modifications of the protocol can be made. For example, in case a vacuum filter system is not available, the single-source complex precursor obtained from the coprecipitation step can be centrifuged. Different eutectic salt mixtures can be used to engineer NPs with desired characteristics.

Even though the MSS method is generally easy to be employed, limitations include (1) the possibility of the product formation being limited by the contact area of the dissimilar reactants in the reaction[1]. Additionally, (2) not every nanostructured product can be formed within selected molten salts. These cases are rare but can certainly happen[35]. It is desirable that the selected salts act only as pure solvents and do not react with the reactants or products. Furthermore, common mistakes that may hinder the quality of the final nanoparticle products include the following: (1) First, if the burette is not covered during the titration, this may change the concentration of the ammonium hydroxide and eventually change the size of obtained nanoparticles. Another common mistake is (2) not giving the coprecipitation a period of two hours to form. Adding the ammonia titrant too fast affects the coprecipitation kinetics, which might render inhomogeneous complex precursor. The third pitfall is (3) not grinding the salt(s) and precursor(s) as fine as possible, which generates impure products or inhomogeneous particles.

The MSS method is simple, effective, fast, low-temperature, and cost-efficient as proven with previously reported results, compared to conventional solid-state and sol–gel/combustion synthesis methods[27]. It is also scalable, reliable, and generalizable in regards to making agglomeration-free NPs without a surface protective layer, unlike colloidal and hydrothermal/solvothermal synthesis methods.

Application of the MSS method has widely spread in the last couple of decades, from ferroelectric and ferromagnetic materials to materials for Li-ion batteries[36], semiconductors[17,37], phosphors[17,19], and electro-catalysts[38,39], mainly for nanosized materials, especially those with complex compositions. In conclusion, the MSS method provides a suitable pathway in the synthesis of simple and complex metal oxide NPs. It is expected that the MSS method will become an even more popular synthesis method for nanomaterials and more widely employed in the nanoscience and nanotechnology community in the upcoming years.

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DISCLOSURES:

There are no conflicts to declare.

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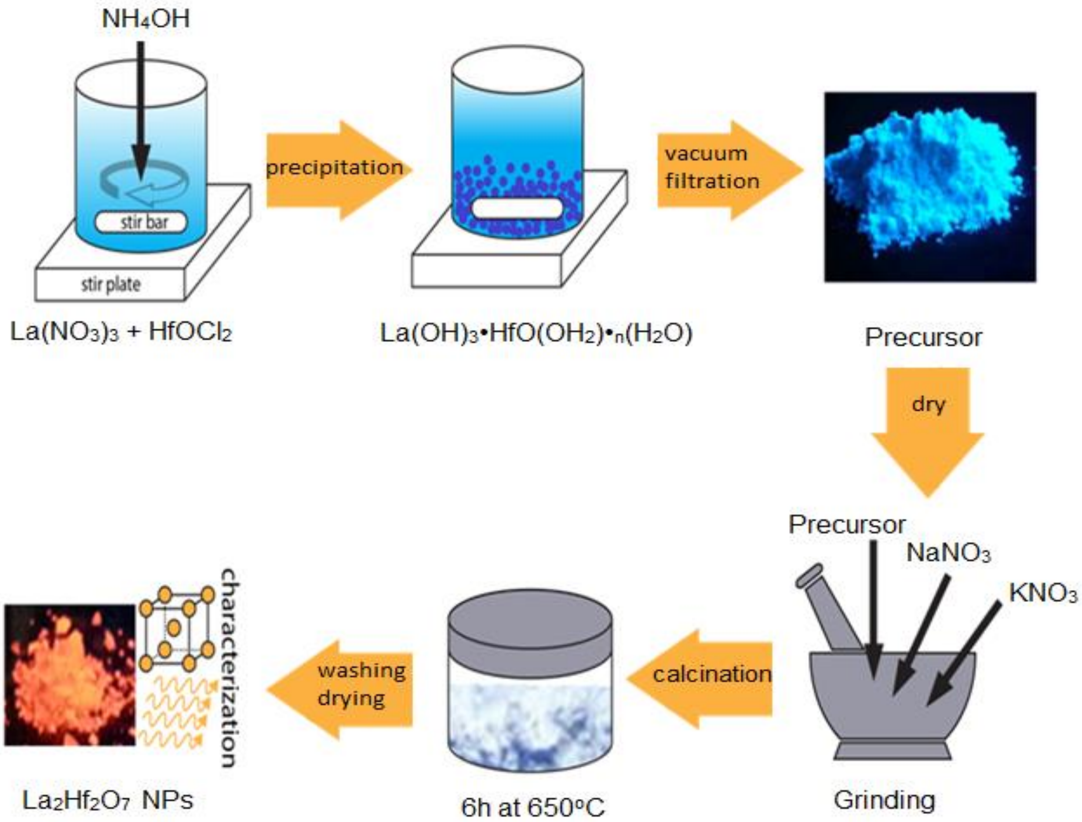
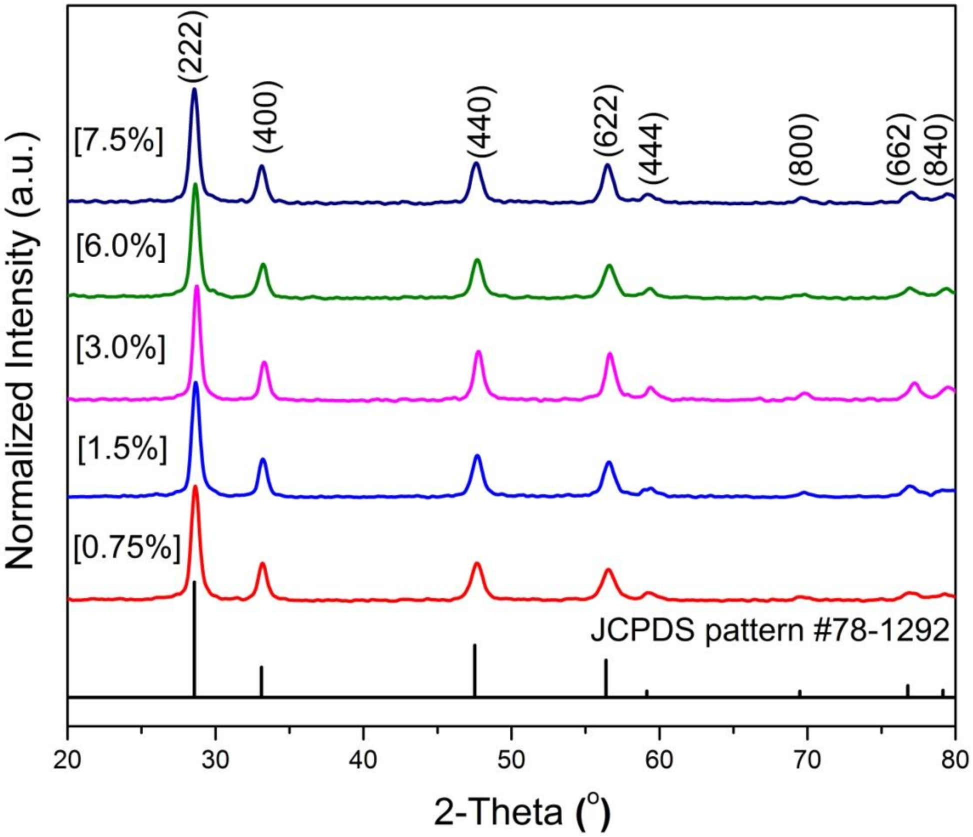
Figure 1


NH₄OH
stir bar
stir plate
$La(NO_3)_3 + HfOCl_2$
precipitation
$La(OH)_3{\bullet}HfO(OH_2){\bullet}_n(H_2O)$
vacuum filtration
Precursor
dry
Precursor
$NaNO_3$
KNO_3
Grinding
calcination
6h at 650°C
washing drying
characterization
$La_2Hf_2O_7$ NPs


Normalized Intensity (a.u.)
2-Theta (°)
20
30
40
50
60
70
80
(222)
(400)
(440)
(622)
(444)
(800)
(662)
(840)
[7.5%]
[6.0%]
[3.0%]
[1.5%]
[0.75%]
JCPDS pattern #78-1292

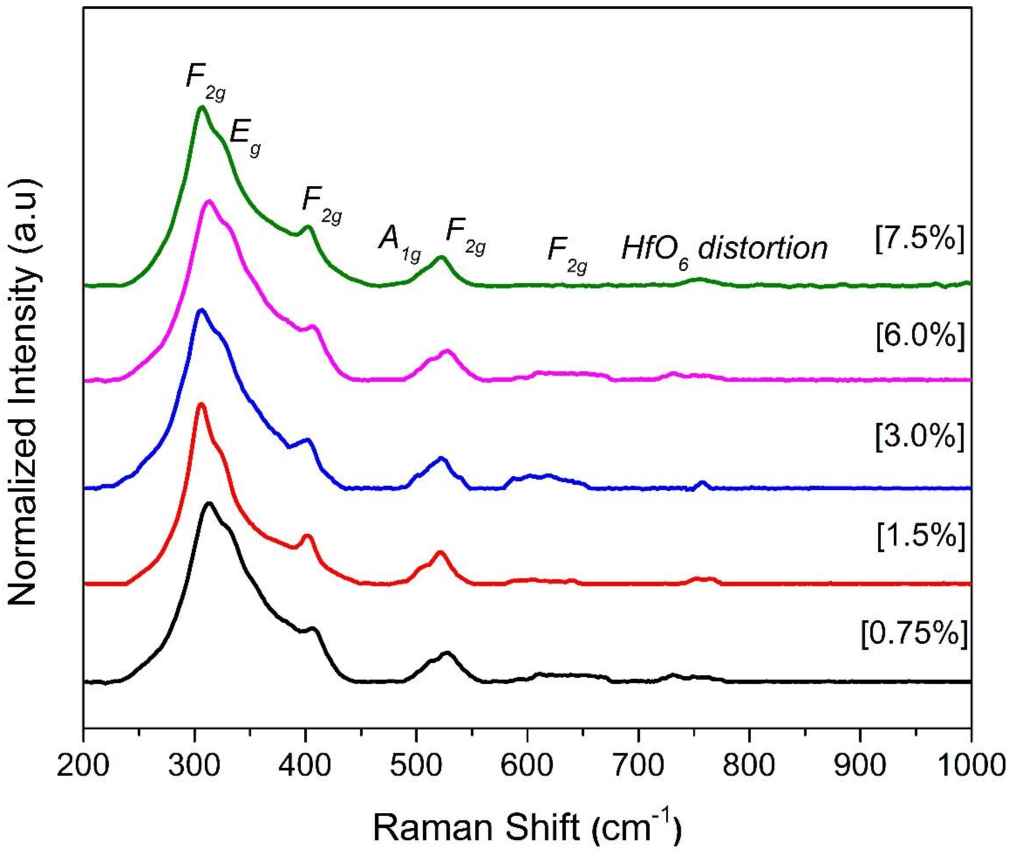

F_{2g}
E_g
F_{2g}
A_{1g}
F_{2g}
F_{2g}
HfO_6 distortion
[7.5%]
[6.0%]
[3.0%]
[1.5%]
[0.75%]
Normalized Intensity (a.u)
200
300
400
500
600
700
800
900
1000
Raman Shift (cm^{-1})

Figure 4


Synthesis steps
Controlling factors
Precursor(s)
❖ Chemical identity
❖ Physical features
Mixing
❖ Type of salts
❖ Amount of salts
❖ Mixing methods
MSS
❖ Temperature
❖ Duration
❖ Ramp Rate
❖ Atmosphere
Washing
❖ Choice of solvent
❖ Quantity of solvent
❖ Repetitions
Drying
❖ Drying methods

Concentration of NH_4OH(aq) used	**XRD data of the synthesized $La_2Hf_2O_7$ NPs**			
	2θ (°)	**FWHM (β)**	**Lattice parameters (Å)**	**Particle size (nm)**
[0.75%]	28.57	0.4	10.81	19.00
[1.5%]	28.64	0.39	10.79	20.00
[3.0%]	28.67	0.37	10.78	21.00
[6.0%]	28.69	0.31	10.77	26.00
[7.5%]	28.74	0.27	10.75	29.00

Table of Materials

Name of Reagent/Material	Company
Acetone, ACS, 99.5+%	Alfa Aesar
Hafnium dichloride oxide octahydrate, 98+% (metals basis excluding Zr), Zr <1.5%	Alfa Aesar
Lanthanum(III) nitrate hexahydrate	Aldrich
Potassium nitrate, ReagentPlus R, ≥99.0%	Sigma-Aldrich
Sodium nitrate, ReagentPlus R, ≥99.0%	Sigma-Aldrich
Ammonium hydroxide, 28% NH3, NH4OH	Alfa Aesar
Filter paper, P8 grade	Fisherbrand

CAS Number	Comments
67-64-1	Dried over 4A sieves
14456-34-9	Hygroscopic
10277-43-7	Hygroscopic
7757-79-1	Hygroscopic
7631-99-4	
1336-21-6	

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Author(s):	Jose P. Zuniga, Maya Abdou, Santosh K. Gupta, Yuanbing Mao

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Name: Yuanbing Mao
Department: Chemistry
Institution: University of Texas Rio Grande Valley
Article Title: Molten-Salt Synthesis of Complex Metal Oxide Nanoparticles
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Date: 5/15/2018

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July 20, 2018

Dear Dr. Phillip Steindel,

We thank the referees and the production team for the comments expressed for our manuscript (Manuscript No: JoVE58482R1) entitled "Molten-Salt Synthesis of Complex Metal Oxide Nanoparticles" and proceed to address them as follows.

Editorial and production comments:

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

Thank you. The manuscript has been proofread by all authors to avoid spelling or grammar issues.

2. Figure 1: Please include a space between numbers and their units (i.e., 6 h, 650 °C).

Thank you for the comment. Figure 1 has been modify as suggested in the revised manuscript.

3. Please upload Table 1 to your Editorial Manager account as an .xls or .xlsx file.

Thank you. Table 1 has been converted to .xlsx format and uploaded.

4. Keywords: Please provide at least 6 keywords or phrases.

Thank you. A sixth keyword "precursor" has been added.

5. Please use SI abbreviations for all units: L, mL, µL, h, min, s, etc.

Thank you. All units have been corrected to SI abbreviations.

6. Please include a space between all numbers and their corresponding units: 15 mL, 37 °C, 60 s; etc.

Thank you. A space has been included as suggested.

7. Please revise the protocol to contain only action items that direct the reader to do something (e.g., "Do this," "Ensure that," etc.). The actions should be described in the imperative tense in complete sentences wherever possible. Avoid usage of phrases such as "could be," "should be,"

and “would be” throughout the Protocol. Any text that cannot be written in the imperative tense may be added as a “Note.” Please include all safety procedures and use of hoods, etc. Please move the discussion about the protocol to the Discussion.

Thank you. All protocol steps have been revised accordingly. All needed safety procedures have been added. In addition, all the discussion about the protocol has been moved to the Discussion.

8. 1.3.2: What is the total volume of ammonia solution added?

Thank you for the question. The total volume of ammonia solution is 200 mL. This information has been added to the revised manuscript.

9. 1.4.1: What is the pore size of the filter paper?

Thank you for the question. The filter paper used for the precursor filtration step is made of cellulose fiber suitable for gravity and vacuum filtration systems. The porosity of the filter paper is coarse (40-60 µm) with a particle retention of 20–25 µm and a flowrate 160 mL/min. The information pertaining to the pore size has been added in our manuscript “Vacuum filtration and drying of precursor” section. It reads as “1.4.1) Vacuum filter the coprecipitated solution using a filter paper with a coarse porosity (40-60 µm) (Fisherbrand, P8) to separate the solid precipitate from the supernatant.”

10. 2.1.1: Please specify the mass measured.

Thank you. The measured mass has been specified in the revised manuscript. Now it reads as:
2.1.1) Measure 30 mmol (3.033 g) of potassium nitrate (KNO_3) and 30 mmol (2.549 g) of sodium nitrate ($NaNO_3$).
2.1.2) Combine the measured salts with 0.35 g of the as-prepared single-source complex precursor $La(OH)_3 \cdot HfO(OH)_2 \cdot nH_2O$.

11. 2.1.4: Please specify the volume of acetone or ethanol added.

Thank you. The volume of acetone or ethanol added has been provided in the revised manuscript.

12. References: Please do not abbreviate journal titles. Please include volume and issue numbers for all references.

Thank you for the comment. All references have been updated as suggested.

Changes to be made by the Author(s) regarding the video:

1. Titles of the manuscript and the video do not match.

Thank you for catching the error, which has been corrected in the revised manuscript.

2. 00:32: Please change ml to mL.

Thank you for the comment. Now ml has been changed to mL in the video.

3. 01:05-02:24, 05:09-06:35: Please remove the introduction and discussion about the protocol from the protocol section. Protocol should contain only action items that direct the reader to do something.

Thank you for the comment. Both the Introduction and Discussion about the protocol have been removed from the protocol section.

4. 03:08: This specific detail "Add diluted ammonia solution to the burette" in the video is not stated in the written manuscript.

Thank you for the comment. The detail has been added to the revised manuscript. It reads as "1.3.1) Add the diluted ammonia solution prepared in the previous step into a burette, and ensure that the burette is covered at all times, since ammonia solution tends to evaporate which decreases its concentration."

5. Please upload a revised high-resolution video here:
http://www.jove.com/files_upload.php?src=17837058

A revised high-resolution video has been added accordingly.

Video quality issues

- The videography quality does not meet our standards. Overall, there is too much camera movement. Additionally, many of the actions are out of focus and several of the shots are underexposed. This video would need to be reshot using static framing and accurate focus.

Thank you for the comments. Shots have been retaken accordingly as seen in the revised high-resolution video.

Editing issues

- 0:24, 6:36 - The audio and video are fading out while the speaker is still speaking. This should happen after they are finished.

Thank you for the comment. This issue has been solved accordingly.

Frame size/proportions issues

- 7:49-9:00 - The white backgrounds of these figures should be extended to fill the frame.

Thank you for the comment. A full-screen white background has been added to all figures.

Reviewers' comments:

Concerns regarding Reviewer #1:

1. While the manuscript/video are well made, one area which could be improved on is the discussion of common mistakes which may be made in the synthesis. This could be important if the reader/viewer is attempting to make a material not directly covered. Specifically, it would be useful if the authors discussed some pitfalls which may occur during both synthesis steps which might lead to impurities or unwanted products. (Manuscript)

We thank the reviewer for the encouraging comments and suggestion. We have modified our manuscript in the Limitation of the MSS method section accordingly and added the following: "Furthermore, common mistakes that could hinder the quality of the final nanoparticle products include the following: first is not covering the burette during the titration, which changes the concentration of the ammonium hydroxide and eventually changes the size of obtained nanoparticles. Another common mistake is not to give the coprecipitation a period of two hours to form. Adding the ammonia titrant too fast affects the coprecipitation kinetics which might render inhomogeneous complex precursor. The third pitfall is not to grind the salt(s) and precursor(s) as fine as possible, which generate impure products or inhomogeneous particles."

2. There are sections of the video where there is a transition from the speaker to an experiment. In these sections, it is difficult to hear what the speaker is saying. It may be good to slightly re-edit the video or to add captions so that everything is clear. (Video)

We thank the reviewer for the comments. The video has been re-edited to improve the transition and clarity as suggested.

3. One section of the text lists the need to identify the crystal structure using Raman (line 239). This appears a bit out of the blue but it is discussed two paragraphs later. It would be good to mention earlier in the text that there are multiple phases of these materials and the authors are focusing on the pyrochlore phase. (Manuscript)

We thank the reviewer for the suggestion. We have modified the manuscript and now it reads as “The as-synthesized $La_2Hf_2O_7$ NPs could exist in the ordered pyrochlore phase. However, chemical doping, pressure, temperature could modify the phase to defect fluorite. It is possible for our material to have multiple phases but in this paper, we focus only on the pyrochlore phase for simplicity. X-ray diffraction (XRD) and Raman spectroscopy have been used to systematically characterize their phase purity, structure and phase.”

4. It would be good to discuss in more detail the role of adding solvents to the grinding process prior to the molten salt reaction. Does this change the morphology? How much should be added? etc.(Manuscript)

We thank the reviewer for the comment and questions. A new paragraph has been added to the Critical step section in the revised manuscript. It reads as “Finally, the addition of a volatile liquid such as acetone and ethanol during the mixing of the salts used and the single-source complex precursor helps ease the grinding process but is not essential. The addition of a liquid is helpful to make a homogenous mixture in shorter time and less effort, which is important to generate pure products. The added volatile liquid does not affect the characteristics of the resultant NPs since it fully evaporates by the end of the grinding process. Due to its high volatility, the amount added could range anywhere from 1 mL to 5 mL.”

Please feel free to contact me in the event of any questions or concerns.

Sincerely,
Mao Yuanbing

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Associate Professor
Department of Chemistry
University of Texas Rio Grande Valley
1201 West University Drive
Edinburg, TX 78539-2999
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Title:

Molten-Salt Synthesis of Complex Metal Oxide Nanoparticles

Authors and Affiliations:

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Santosh K. Gupta (santufrnd@gmail.com)

Keywords:

co~~-~~precipitation, molten-salt synthesis, complex metal oxides, lanthanum hafnium oxide, nanoparticles, precursor.

Short Abstract:

A unique relative low temperature molten-salt synthesis method for preparing uniform complex metal oxide lanthanum hafnate nanoparticles has been demonstrated.

Long Abstract:

Development of feasible synthesis methods is critical for the successful exploration of novel properties and potential applications of nanomaterials. Here we are introducing the molten-salt synthesis (MSS) method for making metal oxide nanomaterials started with its advantages over other methods, such as simplicity, greenness, reliability, scalability and generalizability, to just name a few. Using pyrochlore lanthanum hafnium oxide $La_2Hf_2O_7$ as a representative, we described the MSS protocol for the successful synthesis of complex metal oxide nanoparticles (NPs). Furthermore, this method ~~have~~ has the unique ability to produce NPs with different material features by changing various synthesis parameters such as pH, temperature, duration, and post-annealing. By fine-tuning these parameters, we have been able to synthesize highly uniform, non-agglomerated and highly crystalline NPs. As a specific example, we varied the particle size of the $La_2Hf_2O_7$ NPs by changing the concentration of the used ammonium hydroxide solution in the MSS process, which allowed us to further explore the effect of particle size on various properties. It is expected that the MSS method will become an even more popular synthesis method for nanomaterials and be more widely employed in the nanoscience and

nanotechnology community in the upcoming years.

Introduction:

Molten-salt synthesis (MSS) involves the use of a molten salt as the reaction medium for preparing nanomaterials from their constituent precursors. The molten salt acts as the solvent and facilitate the enhanced reaction rate by increasing the contact area between reactants and their mobility. The choice of molten salts is of paramount importance for the success of the MSS method. They must meet some important quality requirements such as low melting point, compatibility with reacting species, and optimum aqueous solubility. Molten salt has been used before to enhance the rate of solid-state reactions. However, in a flux system, only a small amount of molten salt is used, unlike the MSS where large quantity of salt is added to form a soluble medium for the reaction and control the properties of the synthesized nanomaterials, such as particle size, shape, and crystallinity, etc. In this sense, MSS is a modification of the powder metallurgical method and different from the flux method.[1-3] The employment of molten salt can (1) increase reaction kinetic rate[4] while decreasing synthesis temperature[5], (2) increase the degree of reactant homogeneity[6], (3) control crystalline size and morphology[7], and (4) reduce the level of agglomeration.

Nanomaterials have been in high demand in scientific research and novel industrial applications because of their superior electrical, chemical, magnetic, optical, electronic and thermal properties. Their properties are highly dependent on the particle size, shape and crystallinity. Compared with other synthesis methods for nanomaterials, MSS has several obvious advantages even though it is not yet as well-known as other synthesis methods in the nanoscience and nanotechnology community. As described below, these advantages include its simplicity, reliability, scalability, generalizability, and environmental friendliness, cost effectiveness, relative low synthesis temperature, and free agglomeration of NPs with clean surface, etc.[8]

Simplicity: The MSS process can be easily carried out in a simple laboratory with basis facility. No sophisticated instrumentation is needed. Precursors and molten salts are air stable with no need ~~of~~ for glove box handling.

Reliability: Once all initial synthesis parameters such as concentration, pH, processing time, and annealing temperature, etc. are optimized, one is sure to make high quality and pure products by the MSS method. If one carries out all synthesis steps properly, the final products could attain all basic criteria needed for good quality NPs. A novice to the MSS method does not change the synthesis outcome as long as s/he follows all synthesis parameters properly and carefully.

Scalability: The MSS method’s ability to produce large quantities of size- and shape-controlled particles is crucial. This critical factor is important because it allows for the determination of industrial usefulness and efficiency. Compared to other synthesis techniques, it can easily generate a sufficient amount of products by adjusting stoichiometric amounts during the MSS synthesis. This is an important feature of the MSS method because it allows for convenience at the industrial level making it a more desired approach due to its scalability.[9,10]

Generalizability: The MSS method ~~it~~ is also a generalizable technique to make nanoparticles with various compositions. Other than simple metal oxides and some fluorides, nanomaterials of complex metal oxides which have been successfully synthesized by the MSS method include perovskites (ABO_3)[10-14], spinel (AB_2O_4)[15,16], pyrochlore ($A_2B_2O_7$)[4,17-19] and orthorhombic structures ($A_2B_4O_9$)[2,3,20]. More specifically, these nanomaterials include ferrites, titanates, niobates, mullite, aluminium borate, wollastonite and carbonated apatite.[7,9,21] The MSS method has also been used to produce nanomaterials of various morphologies such as nanosphere[4], ceramics powder bodies[22], nanoflakes[23], nanoplates[7], nanorods[24], and core-shell nanoparticles (NPs)[25] depending on synthesis conditions and crystal structure of the products.

Environmental friendliness: Several traditional methods for making nanomaterials involve the use of large amounts of organic solvents and toxic agents that generate environmental issues. The partial or total elimination of the use of them and the generation of waste by sustainable processes is in demand of green chemistry nowadays.[8] The MSS method is an environmentally friendly approach to synthesize nanomaterials by employing nontoxic chemical and renewable materials and minimizing waste, byproducts and energy.

Relative low synthesis temperature: The processing temperature of the MSS method is relatively low compared to that required in a conventional solid-state reaction[26] and sol-gel combustion reaction.[27] It saves energy during the low temperature approach while producing high quality NPs.

Cost effectiveness: The MSS method does not require any harsh or costly reactants or solvents ~~and~~ nor any specialized instrumentation. Water is the main solvent used for washing away the used molten salts, which are also cheap. Moreover, experimental setup needed includes only simple glassware and furnace without specialized instrumentation while nanomaterials with complex composition and refractory nature could be produced.

Agglomeration free with clean surface: During the MSS process, the formed nanoparticles are well-dispersed in the molten salt medium due to its large quantity used along with its high ionic strength and viscosity.[1,6,8] Unlike colloidal synthesis and most hydrothermal/solvothermal processes, no protective surface layer is necessary to prevent the continuous growth and agglomeration of the formed NPs.

Exemplary synthesis of complex metal oxide NPs by the MSS method:

The MSS method as a universal and cost-effective approach to rationally and large-scale synthesize nanomaterials for a sufficiently wide spectrum of material is highly welcomed by scientists working in the area of nanoscience and nanotechnology. Here, lanthanum hafnate $La_2Hf_2O_7$ is selected because of its multifunctional applications in the areas of X-ray imaging, high *k*-dielectric, luminescence, thermographic phosphor, thermal barrier coating, and nuclear waste host. $La_2Hf_2O_7$ is also a good host for doped scintillators due to its high density, large effective atomic number, and the possibility of its crystal structure to be engineered along with an order-disorder phase transition. It belongs to $A_2B_2O_7$ family of compounds (where A is a rare-earth element with +3 oxidation state, and B represents a transition metallic element with +4 oxidation state). However, due to the refractory nature and complex chemical composition, there was the lack of proper low temperature and large-scale synthesis method for $La_2Hf_2O_7$ NPs.

For fundamental scientific investigation and advanced technological applications, it is a prerequisite to make monodisperse, high quality and uniform $A_2B_2O_7$ NPs. Here we use the synthesis of highly crystalline $La_2Hf_2O_7$ NPs as an example to demonstrate the advantages of the MSS method. As schematically shown in Figure 1, $La_2Hf_2O_7$ NPs were prepared by the MSS method with a two-step process following our previous reports. First, a single-source complex precursor of $La(OH)_3 \cdot HfO(OH)_2 \cdot nH_2O$ was prepared via a co~~-~~precipitation route. In the second step, size-controllable $La_2Hf_2O_7$ NPs were synthesized through the facile MSS process using the single-source complex precursor and nitrate mixture ($NaNO_3$:KNO_3 = 1:1, molar ratio) at 650 ℃ for 6 h~~ours~~.

Protocol:

1. Preparation of single-source complex precursor via a co~~-~~participation route

1.1) Preparation of lanthanum and hafnium precursor solution

1.1.1) Measure 200 ~~ml~~mL of distilled water in a 500 ~~ml~~ mL beaker and start stirring at 300 rpm.

1.1.2) Dissolve lanthanum and hafnium precursors in the stirring water, i.e. 2.165 g of lanthanum nitrate hexahydrate ($La(NO_3)_3 \bullet 6H_2O$) and 2.0476 g of hafnium dichloride oxide octahydrate ($HfOCl_2 \bullet 8H_2O$).

1.1.3) Leave the solution stirred for 30 min before starting the titration.

1.2) Preparation of diluted ammonia solution

1.2.1) Prepare 200 mL of diluted ammonia solution with different concentrations including 0.75%, 1.5%, 3.0%, 6.0%, and 7.5%. For example, add 20 ~~ml~~ mL of concentrated ammonia solution (NH_4OH 28-30%) to 180 ~~ml~~ mL of distilled water in a separate beaker to make 3.0% diluted ammonia solution. ~~Note, that particle size of the $La_2Hf_2O_7$ NPs can be controlled in this step by adjusting the concentration of the titrant ammonia solution. In this case, higher ammonia solution concentration generates bigger $La_2Hf_2O_7$ NPs.~~

1.3) Titration and washing the single source complex precursor~~precursor of $La(OH)_3 \cdot HfO(OH)_2 \cdot nH_2O$~~

1.3.1) Add the diluted ammonia solution prepared in the previous step into a burette, and ensure that the burette is covered at all times, since ~~the~~ ammonia solution tends to evaporate which decreases~~changing~~ its~~he initial~~ concentration.

1.3.2~~1~~) Add the diluted ammonia solution in the burette ~~prepared in the previous step~~ into the stirring solution of lanthanum nitrate and hafnium dichloride oxide dropwise.

1.3~~.2~~.3) Adjust the dropping speed of the ammonia solution ~~drops~~ accordingly so that~~e~~ it~~200 mL solution~~ will be added over a period ~~of~~ of ~~titration lasts~~ 2 h~~ours~~.

~~1.3.34) Note,Ensure that the burette is must be covered at all times, since the ammonia solution tend to evaporate which changdecreasesing ithe initials concentration.~~

1.3.4) After several mL of ammonia solution delivered, ensure that the solution is~~will~~ becomes~~inge~~ cloudy. This is a simple sign that the precipitate of the ~~a~~ single-source complex precursor of $La(OH)_3 \cdot HfO(OH)_2 \cdot nH_2O$ is forming.

1.3.5) After ~~two hours~~2 h remove the stirring bar and allow the precipitate to age overnight.

1.3.6) Check the pH of the co-precipitated solution before washing. Wash the precipitate with distilled water until the supernatant reaches a neutral pH, which normally takes 5-8 washes.

1.4) Vacuum filtration and drying of precursor

1.4.1) Vacuum filter the co-precipitated solution using a ~~funnel with a~~ filter paper ~~with a coarse porosity~~ with a coarse porosity (40-60 µm) (Fisherbrand P8) to separate the solid precipitate from the supernatant~~remove any residual impurity~~.

1.4.2) Ensure that all complex precursor remnants are washed from the walls of the beaker.

1.4.3~~2~~) Air dry the resulting single-source complex precursor $La(OH)_3 \cdot HfO(OH)_2 \cdot nH_2O$ at room temperature overnight.

2. Molten-salt synthesis of lanthanum hafnate ~~of $La_2Hf_2O_7$~~ NPs

2.1) Preparation of salt and precursor mixture

2.1.1) Measure 30 mmol (3.033 g) of potassium nitrate (KNO_3) and 30 mmol (2.549 g) of sodium nitrate ($NaNO_3$).

2.1.2) Combine the measured salts with 0.35 g of the as-prepared single-source complex precursor $La(OH)_3 \cdot HfO(OH)_2 \cdot nH_2O$.

~~2.1.3) Grind the mixed salts and precursor as fine as possible for about 30 minutes using a mortar and pestle.~~

2.1.~~4~~3) 1-5 mL of ~~Acetone~~ acetone or ethanol can be added to the mixture to facilitate the grinding. Ensure that all solvent is evaporated ~~and that the final mixture is as fine as possible.~~before placing the mixture into ~~the~~a crucible.

2.1.4) Grind the mixed salts and precursor as fine as possible for about 30 min using a mortar and pestle.

2.2) Molten-salt processing ~~of $La_2Hf_2O_7$ NPs~~

2.2.1) Place the resulting mixture in a corundum crucible, and place it in a muffle furnace.

2.2.2) Set the furnace at 650 °C for 6 h ~~hours~~ with a ramp rate of 10 °C/min.

2.2.3) After the sample and furnace cooled down to room temperature, take out the crucible and soak the sample in a beaker filled with distilled water overnight.

2.3) Washing and drying the $La_2Hf_2O_7$ NPs

2.3.1) Empty the sample from the crucible into a ~~200 ml~~1 L beaker.

2.3.2) Wash the sample with distilled water 5-8 times until the supernatant is clear of salts and not cloudy anymore.

2.3.3) Purify the product by centrifugation or vacuum filtration to remove any residual impurity.

2.3.4) Dry the product in the oven at 90 °C overnight.

Representative Results:

The as-synthesized $La_2Hf_2O_7$ NPs could exist~~s~~ in the ordered pyrochlore phase. However, chemical doping, pressure, temperature could modify the phase to defect fluorite. It is possible for our material to have multiple phases but in this paper, we focus only on the pyrochlore phase for simplicity. X-ray diffraction (XRD) and Raman spectroscopy ~~can~~have been used to ~~were~~ systematically ~~characterized~~characterize their~~for~~ phase purity, structure and ~~morphology~~ phase~~using powder X-ray diffraction (XRD),~~ and ~~Raman spectroscopy and scanning electron microscopy (SEM)~~. The crystalline size ~~were~~ can be~~was~~ calculated using Debye-Scherer's formula. On the other hand, ~~–~~Raman spectroscopy is used as a secondary structural characterization technique due to it high~~since it is highly~~ sensitivity~~e~~ to M-O vibrational modes.[28] It identifies the exact crystallographic phase of the $La_2Hf_2O_7$ NPs.[29] ~~SEM is used to determine the size and morphology of the $La_2Hf_2O_7$ NPs.~~

Compared to other synthetic techniques such as solid-state reaction, MSS has a high reaction constant, meaning that the reaction is more likely to go ~~to~~ in the forward direction[30]. The production of pyrochlore $La_2Hf_2O_7$ is achieved by increasing the contact interfacial area and the mobility of the reactant species inside the molten salt system. [*Place Figure 2 here]* illustrates the XRD patterns ~~from~~ of the synthesized $La_2Hf_2O_7$ NPs made by the MSS method from the single-source complex precursors using different concentrations of ammonia solution. XRD results shows the formation of pure $La_2Hf_2O_7$ with high crystallinity. The peak position and Miller indices could be indexed based on the JCPDS pattern #78-1292. No visible impurity phases such as La_2O_3, Eu_2O_3, ~~and~~ or HfO_2 were detected. There is no change in XRD pattern as a function of the used ammonia concentration except the increase of the particle size. *[Place Table 1 here]* shows the corresponding calculated crystal parameter and particle size of the $La_2Hf_2O_7$ NPs.

There are two common phases of the $A_2B_2O_7$ compounds, i.e. disordered fluorite and ordered pyrochlore phases. The disordered fluorite phase exists in $Fm\bar{3}m$ space group wherein all the cationic ions (A^{3+} and B^{4+}) are randomly distributed allowing for one active mode. On the other hand, ordered pyrochlore phase exists in $Fd\bar{3}m$ space group. Therefore, it exhibits close structural resemblance to fluorite phase except that there are two cationic sites, three anionic sites 48f(O_I), 8a(O_{II}), and 8b(O_{III}), and 1/8th of the oxygen ions (O_{III}) at 8b site absent in the pyrochlore structure allowing for 6 active modes[19,28,29]. Based on the group theory, the defect fluorite structure has one vibrational mode due to T_{2g}, while a pyrochlore phase has six vibrational modes in the range of 200-1000 cm^{-1}. This information is vital for the correct phase identification of the $La_2Hf_2O_7$ NPs [*Place Figure 3 here]*. In our case, the prepared $La_2Hf_2O_7$ NPs are in pure pyrochlore form.

Figure and Table Legends:

Figure 1. Schematic of the synthesis steps of the $La_2Hf_2O_7$ NPs via the MSS method ~~depicting each step of the process~~.

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Figure 2. X-ray diffraction patterns of the $La_2Hf_2O_7$ NPs prepared by adjusting the ~~concentration of the~~ used ammonia solution concentration and indexed based on the defect fluorite pattern.

Figure 3. Raman spectra of the $La_2Hf_2O_7$ NPs prepared by adjusting the ~~concentration of the~~ used ammonia solution concentration with six active modes pertaining to the pyrochlore phase.

Figure 4. Flowchart of critical steps of the MSS method indicating the controlling factors of the synthetic procedure~~s~~ for NPs with potential pathways to fine-tune their characteristics.

Table 1. Crystallographic parameter and particle size of the $La_2Hf_2O_7$ NPs prepared by adjusting the ~~concentration of the~~ used ammonia solution concentration showing a continuous particle size growth.

Discussion:

Critical steps in the MSS protocol:

The chart in [*Place Figure 4 here*] provides several reliable controlling factors of the MSS method and accounts for alternative pathways ~~for~~ to fine-tune~~ing~~ the features of synthesized nanomaterials~~' features~~. In addition, it helps identify critical steps essential in the MSS process.

First, the identity of precursors is critical, especially for the synthesis of complex metal oxide NPs. For making $A_2B_2O_7$ NPs, it is very important to first generate a single-source complex precursor which contains the main elements that make up the final product, i.e. A and B, at an atomic level with the formula of $A(OH)_3{\cdot}BO(OH)_2{\cdot}nH_2O$. In our example, the particle size of the final $La_2Hf_2O_7$ NPs could be controlled in this step by adjusting the concentration of the titrant ammonia solution, where higher ammonia solution concentration generates bigger $La_2Hf_2O_7$ NPs. ~~Many o~~Other ~~experiments~~ trials have also been performed to make $A_2B_2O_7$ NPs using ~~other~~ different ~~starting~~ precursors, such as ~~the~~ commercially available nitrates or oxides containing the main elements of $A_2B_2O_7$, but none of them worked[4]. The advantages of this amorphous single-~~-~~source complex precursor is that the composing elements of $A_2B_2O_7$ are mixed at an atomic level, and are homogeneously distributed in the same order as the final $A_2B_2O_7$ product, decreasing the space or range the reactants need to be transported.

Second, the selection of proper molten salt~~s~~ has major importance to obtain nanomaterials with desirable morphology and characteristics. The melting point of the selected salt should be appropriate for the synthesis of the required phase of nanomaterials. The formation of nanomaterials is ultimately govern by the melting point of salts used as molten solvents such as alkali chloride, sulfate, carbonate or hydroxide[1,6,31,1,32]. It has been reported that the use of different molten salts can modify the formation temperature and thereby altering the particle size and morphology.[18]

In addition, the ramp rate tends to affect the synthesis of the NPs~~ as well~~. A fast ramp rate tends to generate agglomerated NPs,[33] which affect their properties. In case of luminescent and scintillation material, high agglomeration is not desirable as it can scatter excited and emitted light.[17,19] A slow~~er~~ ramp rate is more suitable and allows enough time to reach actual temperature inside the crucible. ~~The~~ A slow cooling process usually allows NPs with spherical shape to form.[34]

There is another important criterion for the selection of the salt: the salt should have sufficient aqueous solubility. With simple washing by water, the used molten salt should be easily washed away after the MSS.

Finally, the addition of a ~~solvent~~volatile liquid such as acetone and ethanol during the mixing of the salts used and the single-source complex precursor helps ease the grinding process ~~decrease the distance of interaction between the salts used and the precursor~~ but is not ~~necessary~~essential. ~~One can grind the salts and precursor without any solvent, however this will increase the amount of time spend grinding and effort.~~ The addition of a ~~solvent~~liquid is helpful ~~by increasing the contact surface area between the both salts and precursor allowing for~~to make a ~~more~~ homogenous mixture in shorter time and less effort, which is important to~~. A high homogenous mixture will~~ generate ~~a~~ pure products~~sample free of unreacted precursor~~. The~~By~~ added~~ing, a~~ volatile

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liquid~~solvent~~ does not affect the characteristics~~morphology~~ of the resultant ~~particles whatsoever~~NPs since it fully evaporates by the end of the grinding process. ~~The fact that acetone and ethanol have a~~Due to its high volatility, the amount added could range anywhere from 1 mL to~~less from~~ 5 mL~~l~~.~~ It is important that one should keep grinding until all solvent evaporates and the mixture is as fine as possible.~~

Modifications and troubleshooting of the MSS process:

The MSS method is straightforward and ~~very~~ simple way to synthesize NPs~~implement~~ at any university and industry. However, modifications ~~in~~ of the protocol can be made~~ in case of a troubleshooting~~. For example, in case a vacuum filter system is not available, the single-source complex precursor obtained from the co~~-~~precipitation step can be centrifuged. Different eutectic salt mixtures can be used to engineer ~~the synthesized~~ NPs with desired characteristics.

Limitations of the MSS method:

Even though the MSS method is generally easy to be employed, limitations which can occur ~~during using this method~~ include: (1) The possibility ~~ition~~ of the product formation is limited by the area of contact of the dissimilar reactants in the ~~solid-state~~ reaction[1]. (2) Not ~~all~~ every nanostructured products can be formed within ~~the eutectic salt mixture~~selected molten salts. The cases are rare, but could certainly happen~~ed~~.[35] It is desirable that the selected salts act only as pure solvents ~~only~~ and do not react with the reactants ~~and~~ or the products. Furthermore, common mistakes that could hinder the quality of the final nanoparticle products include the following: first is~~volved~~ not covering the burette during the titration, which changes~~ing~~ the concentration of the ammonium hydroxide ~~which~~and eventually~~ will~~ changes the size of obtained nanoparticles~~ size~~. ~~In addition, a~~Another common mistake is not to ~~allowing~~give the coprecipitation ~~to form during~~ a period of two hours to form. ~~By a~~Adding the ammonia titrant ~~at a~~too fast~~er rate~~ affects the coprecipitation kinetics ~~of the reaction changes~~ which might render~~cause~~ inhomogeneous~~unwanted~~ complex precursor. ~~Finally, if one~~The third pitfall is not to grind the salt(s) and precursor(s) ~~careful in the grinding process and the final mixture is not~~ as fine as possible, which generate impure products ~~the resultant product made yield larger~~or inhomogeneous particles.

The significance of the MSS method with respect to existing/alternative methods

The MSS method is simplistic, effective, fast, low temperature, and cost efficient as proved with many ~~promising~~ reported results compared with conventional solid-state and sol–gel/combustion synthesis methods.[27] It is also scalable, reliable, and generalizable to make~~, and~~ agglomeration-free NPs without surface protective layer, unlike the colloidal and hydrothermal/solvothermal synthesis methods.

Future applications or directions of the MSS method

The application of the MSS method has widely spread in the last couple of decades from ferroelectric and ferromagnetic materials to materials for Li-ion batteries[36], semiconductors[17,37], phosphors[17,19] and electro-catalysts,[38,39] ~~especially~~ mainly ~~with regard to~~for nanosized materials, especially those with complex compositions. In conclusion, the MSS method ~~can~~ provides a suitable pathway in the synthesis of simple and complex metal oxide NPs. It is expected that the MSS method will become an even more popular synthesis method for nanomaterials and be more widely employed in the nanoscience and nanotechnology community in the upcoming years.

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There are no conflicts to declare.

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