Title:

Molten-Salt Synthesis of Complex Metal Oxide Nanoparticles

Authors and Affiliations:

Jose P. Zuniga[1], Maya Abdou[1], Santosh K. Gupta[1,2], and Yuanbing Mao[1,3]*
[1]Department of Chemistry, University of Texas Rio Grande Valley, 1201 West University Drive, Edinburg, Texas 78539, USA
[2]Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085
[3]School of Earth, Environmental, and Marine Sciences, University of Texas Rio Grande Valley, 1201 West University Drive, Edinburg, Texas 78539, USA

Corresponding Author:

Yuanbing Mao
yuanbing.mao@utrgv.edu
Tel.: (956)-665-2986

Email Addresses of Co-authors:
Jose P. Zuniga (jose.p.zuniga01@utrgv.edu)
Maya Abdou (maya.abdou01@utrgv.edu)
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 orderdisorder 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 °C 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 ~~iswill~~ 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~~ sensitiv~~e~~ity 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~~.

Formatted: Not Superscript/ Subscript

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

Formatted: Subscript

Formatted: Subscript

Formatted: Subscript

Formatted: Subscript

Formatted: Subscript

Formatted: Subscript

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.

Acknowledgements:

The authors thank the financial support by the National Science Foundation under CHE (award #1710160) and the USDA National Institute of Food and Agriculture (award #2015-38422-24059). The Department of Chemistry at the University of Texas Rio Grande Valley is grateful for the generous support provided by a Departmental Grant from the Robert A. Welch Foundation (Grant No. BX-0048). SKG would like to thanks United States-India Education Foundation (USIEF) and International institute of Education (IIE) for his Fulbright Nehru Postdoctoral Fellowship (Award# 2268/FNPDR/2017).

Disclosures:

There are no conflicts to declare.

References:

1 Kimura, T. Molten Salt Synthesis of Ceramic Powders. *InTech.* **Chapter 4,** 75-100, (2011).

2 Mao, Y., Park, T.-J. & Wong, S. S. Synthesis of classes of ternary metal oxide nanostructures. *Chemical Communications.* **0,** (46), 5721-5735, (2005).

3 Mao, Y., Zhou, H. & Wong, S. S. Perovskite-phase metal oxide nanostructures: synthesis, properties, and applications. *Material Matters.* **5,** 50-53, (2010).

4 Mao, Y., Guo, X., Huang, J. Y., Wang, K. L. & Chang, J. P. Luminescent Nanocrystals with $A_2B_2O_7$ Composition Synthesized by a Kinetically Modified Molten Salt Method. *The Journal of Physical Chemistry C.* **113,** (4), 1204-1208, (2009).

5 Yu, Y., Wang, S., Li, W. & Chen, Z. Low temperature synthesis of LaB_6 nanoparticles by a molten salt route *Powder Technology.* **323,** 203-207, (2018).

6 Liu, X., Fechler, N. & Antonietti, M. Salt melt synthesis of ceramics, semiconductors and carbon nanostructures. *Chemical Society Reviews.* **42,** (21), 8237-8265, (2013).

7 Chang, Y., Wu, J., Zhang, M., Kupp, E. & Messing, C. L. Molten salt synthesis of morphology controlled alpha-alumina platelets *Ceramics international.* **43,** (15), 12684-12688, (2017).

8 Mao, Y., Park, T.-J., Zhang, F., Zhou, H. & Wong, S. S. Environmentally friendly methodologies for nanostructure synthesis. *Small.* **3,** (7), 1122-1139, (2007).

9 Liu, J. R., Hong, R. Y., Feng, W. G., D.Badami & Wang, Y. Q. Large scale production of strontium ferrite by molten salt assited coprecipitation. *Powder Technology.* **262,** 142-149, (2014).

10 Yuanbing Mao, Sarbajit Banerjee & Stanislaus S. Wong. Large-scale synthesis of single-crystalline perovskite nanostructures. *Journal of the American Chemical Society.* **125,** (51),

15718-15719, (2003).

11 Mao, Y. Facile synthesis of ferromagnetic double perovskite oxide La_2BMnO_6 nanoparticles. *RSC Advances.* **2,** (33), 12675-12678, (2012).

12 Hailili, R., Wang, C. & Lichtfouse, E. Perovskite nanostructures assembled in molten salt based on halogen anions KX (X = F, Cl and Br): Regulated morphology and defect-mediated photocatalytic activity. *Applied Catalysis B: Enviromental.* **232,** 531-543, (2018).

13 Yuanbing Mao, J. P., John S. McCloy. Magnetic properties of double perovskite oxide La_2BMnO_6 nanocrystals. *Nanoscale.* **5,** (11), 4720-4728, (2013).

14 Mao, Y. & Wong, S. S. Reproducible composition and shape control of crystalline $Ca_{1-x}Sr_xTiO_3$ perovskite nanoparticles. *Advanced Materials.* **17,** (18), 2194-2199, (2005).

15 Rojas-Hernandez, R. E. *et al.* Original Synthetic Route To Obtain a $SrAl_2O_4$ Phosphor by the Molten Salt Method: Insights into the Reaction Mechanism and Enhancement of the Persistent Luminescence. *Inorganic Chemistry.* **54,** (20), 9896-9907, (2015).

16 Reddy, M. V., Xu, Y., Rajarajan, V., Ouyang, T. & Chowdari, B. V. R. Template Free Facile Molten Synthesis and Energy Storage Studies on MCo_2O_4 (M = Mg, Mn) as Anode for Li-Ion Batteries. *ACS Sustainable Chemistry and Engineering.* **3,** (12), 3035-3042, (2015).

17 Zuniga, J. P., Gupta, S. K., Pokhrel, M. & Mao, Y. Exploring optical properties of $La_2Hf_2O_7$:Pr^{3+} nanoparticles under UV and X-ray excitations for potential lighting and scintillating applications. *New Journal of Chemistry.* **42,** (12), 9381-9392, (2018).

18 Pokhrel, M., Wahid, K. & Mao, Y. Systematic Studies on $RE_2Hf_2O_7$:5%Eu^{3+} (RE = Y, La, Pr, Gd, Er, and Lu) Nanoparticles: Effects of the A-Site RE^{3+} Cation and Calcination on Structure and Photoluminescence. *The Journal of Physical Chemistry C.* **120,** (27), 14828-14839, (2016).

19 Wahid, K., Pokhrel, M. & Mao, Y. Structural, photoluminescence and radioluminescence properties of Eu^{3+} doped $La_2Hf_2O_7$ nanoparticles. *Journal of Solid State Chemistry.* **245,** 89-97, (2017).

20 Park, T.-J., Papaefthymiou, G. C., Moodenbaugh, A. R., Mao, Y. & Wong, S. S. Synthesis and characterization of submicron single-crystalline $Bi_2Fe_4O_9$ cubes. *Journal of Materials Chemistry.* **15,** (21), 2099-2105, (2005).

21 Gilbert, M. R. Molten salt synthesis of titanate pyrochlore waste-forms. *Ceramics ~~i~~International.* **42,** (4), 5263-5270, (2016).

22 Huang, Z. *et al.* Molten salt synthesis of $La_2Zr_2O_7$ ultrafine powders. *Ceramics ~~i~~International.* **42,** (5), 6221-6227, (2016).

23 Huang, Z., Duan, H., Liu, J. & zhang, H. Preparation of lanthanum cerate powders via a simple molten salt route. *Ceramics ~~i~~International.* **42,** (8), 10482-10486, (2016).

24 Wang, G. *et al.* Fabrication of rod-like Ti_4O_7 with high conductivity by molten salt synthesis. *Materials Letters.* **186,** 361-363, (2017).

25 Pokhrel, M., Burger, A., Groza, M. & Mao, Y. Enhance the photoluminescence and radioluminescence of $La_2Zr_2O_7$:Eu^{3+} core nanoparticles by coating with a thin Y_2O_3 shell. *Optical Materials.* **68,** 35-41, (2017).

26 Ramesh, G., Subramanian, V. & Sivasubramanian, V. Dielectric properties of lead indium niobate ceramics synthesized by conventional solid state reaction method. *Materials Research Bulletin.* **45,** (12), 1871-1874, (2010).

27 Gupta, S. K. *et al.* Role of various defects in the photoluminescence characteristics of

Formatted: Subscript

Formatted: Subscript

nanocrystalline $Nd_2Zr_2O_7$: An introspection through spectroscopic and DFT calculations. *Journal of Materials Chemistry C.* **4,** (22), 4988-5000, (2016).

28 Wang, X., Zhu, Y. & Zhang, W. Preparation of lanthanum zirconate nano-powders by Molten Salt method. *Journal of Non-crystalline solids.* **356,** (20-22), 1049-1051, (2010).

29 Popov, V. V. *et al.* Fluorite-pyrochlore phase transition in nanostructured $Ln_2Hf_2O_7$ (Ln = La-Lu). *Journal of Alloys and Compounds.* **689,** 669-679, (2016).

30 Rybarczyk, M. K., Gontarek, E., Lieder, M. & Titirici, M.-M. Salt melt synthesis of curved nitrogen-doped carbon nanostructures: ORR kinetics boost. *Applied Surface Science.* **435,** 543-551, (2018).

31 Ozen, M., Mertens, M., Snikers, F., D'Hondt, H. & Cool, P. Molten-salt synthesis of tetragonal micron-sized barium titanate from a peroxo-hydroxide precursor. *Advanced Powder Technology.* **28,** (1), 146-154, (2017).

32 Fazli, R., Fazli, M., Safaei-Naeini, Y. & F.Golestani-Fard. The effects of processing parameters on formation of nano-spinel ($MgAl_2O_4$) from LiCl molten salt. *Ceramics* ~~*i*~~*International.* **39,** (6), 6265-6270, (2013).

33 Bortolani, F. & Dorey, R. A. Molten salt synthesis of PZT powder for direct write inks. *Journal of the European Ceramic Society.* **30,** (10), 2073-2079, (2010).

34 Zhou, H., Mao, Y. & Wong, S. S. Probing structure-parameter correlations in the molten synthesis of $BaZrO_3$ perovskite submicron-sized particles. *Chemistry of Materials.* **19,** (22), 5238-5249, (2007).

35 Kimura, T., Machida, M., Yamaguchi, T. & Newnham, R. E. Products of Reaction Between PbO and Nb_2O_5 in Molten KCl or NaCl. *Journal of the American Ceramic Society*. **66,** (10), 195-197, (1983).

36 Liu, S. *et al.* A novel rechargeable zinc-air battery with molten salt electrolyte. *Journal of Power sources.* **342,** 435-441, (2017).

37 Huang, Z., Li, B. & Liu, J. Molten-Salt Synthesis of Oxyapatite $La_{9.33}Si_6O_{26}$ Powders as Electrolytes for Intermediate Temperature Solid Oxide Fuel Cells. *Physica status solidi A - Applicationand Materials science.* **207,** (10), 2247-2251, (2010).

38 Ahmed, J. & Mao, Y. Synthesis, characterization and electrocatalytic properties of delafossite $CuGaO_2$. *Journal of Solid State Chemistry.* **242,** (1), 77-85, (2016).

39 Ahmed, J. & Mao, Y. Ultrafine Iridium Oxide Nanorods Synthesized by Molten Salt Method toward Electrocatalytic Oxygen and Hydrogen Evolution Reactions. *Electrochimica Acta.* **212,** 686-693, (2016).