

**Experimental Chronology and Investigation of Yttrium Aluminum
Garnet Nanoparticle Syntheses**

**A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville**

**Matthew McDonald
May 2022**

Copyright © 2022 by Matthew McDonald.
All rights reserved.

DEDICATION

To the Schweitzer Lab and my wife and family.
I am very fortunate and grateful for this opportunity.

“If you want to make an apple pie from scratch, you must first create the universe.”
-Carl Sagan

ACKNOWLEDGEMENTS

First and foremost, I would like to thank Dr. George K. Schweitzer for his help, guidance, knowledge, encouragement, humor, and time that he has invested into my education. This graduate career was made all the better by his insight, jokes, friendship. There is no one else to whom I owe a greater debt of gratitude.

Second, I would like to thank my committee members: Dr. Craig Barnes, Dr. Brian Long, and Dr. Charles Melcher for their time, constructive comments, and guidance. Thanks to Dr. Barnes for the classes he taught that I was able to take and Dr. Melcher for the committee substitution.

Third, I would like to thank Dr. Dunlap of the JIAMS Microscopy Center who took most of the SEM and TEM images showcased throughout the dissertation. His time and efforts with that were key to guiding the work performed. Also, I would like to thank Bo Bishop for his expertise in glassblowing and fixing the broken things I would bring down, Tim Free for his knowledge and help with machining specialty parts and setups, Matt Nelepa for teaching me soldering and basic electronic skills, and the folks in the business office who dealt with the numerous orders placed for this project to proceed. A special thanks as well to the administrative staff who work tirelessly behind the scenes to keep this department running.

Fourth, to the other members of the Schweitzer lab, past and present. This includes Dr. Jake Stewart, Dr. Melissa Bailey, Dr. Kaitlyn McDonald, Mr. Mark Hipshire, Jr., and Mr. Neal Aites. Having the opportunity to collaborate with, learn from,

and talk to about various topics made this experience all the better. I have appreciated working with each one of you.

Fifth is my undergraduate research advisor, Dr. Richard Dluhy who accepted me into his lab and sparked my interest in research. His input and knowledge excited me immensely about research and it was from him I saw how someone could be so passionate. His graduate student, Dr. Sharron Martin took me under her wing and showed me laboratory skills and let me grow in my project.

Sixth, to my family and my wife. The adventures we have gone on and the memories we have are what kept me going throughout this endeavor. Looking forward to the future and how we will continue to grow.

ABSTRACT

Yttrium aluminum garnet (YAG) has been a material of intense interest since its discovery in 1964. Recently, efforts have been made to find alternate ways of producing YAG and other analogous oxides as dense materials for applications in lasers, scintillators, and optics. Methods of densification necessitate the use of nanomaterials as the building blocks for their development.

The production of nano-oxides is a diverse field with numerous methods, each with its own benefits and drawbacks. Methods like ball milling and solution combustion were chosen because of their projected simplicity, meanwhile flame spray pyrolysis and precipitation were chosen because of the control each offered in their syntheses. Hydrothermal synthesis was attempted as a supplementary technique to precipitation.

To find the ideal method to produce these materials, each approach was explored in detail and evaluated according to ideal criteria. The aim of this work was to provide a solid foundational exploration of different synthetic techniques, choose one and explore it further. During the investigation, the method selected had room for improvement regarding metal ion concentration which exceeded expectations for nanoparticle synthesis. Presented herein is the novel technique of frit assisted precipitation and a foundational study of its ability to produce nanoparticles.

TABLE OF CONTENTS

CHAPTER 1 Introduction.....	1
A Brief Introduction to Yttrium Aluminum Garnet and Nanoparticles.....	1
Introduction to the Methods.....	3
Process Introduction and Literature Survey.....	3
Ball Milling.....	4
Solution Combustion Synthesis	7
Microwave Combustion.....	10
Flame Spray Pyrolysis	12
Precipitation	15
Hydrothermal	18
Evaluation and Expansion of the Process Criteria.....	20
Summary of the Literature Survey.....	24
CHAPTER 2 Analytical Equipment	26
Scanning Electron Microscopy (SEM)	26
Transmission Electron Microscopy (TEM)	26
Inductively Couple Plasma Optical Emission Spectroscopy (ICP-OES)	26
Fourier Transmission Infrared Spectroscopy (FTIR)	26
Thermogravimetric Analysis (TGA).....	26
Powder X-Ray Diffraction (PXRD).....	27
CHAPTER 3 Experimental Chronology.....	28
Ball Milling/Mechanochemistry	28
Materials	30
Apparatus	30
Procedure	30
Conclusion	31
Solution Combustion, Template Assisted, and Microwave Assisted Combustion Synthesis of YAG	36
Introduction.....	36
Materials	37
Apparatus	37
Procedure – Solution Combustion	38
Procedure – Template Assisted Combustion Synthesis.....	38
Procedure – Microwave Assisted Combustion Synthesis.....	38
Results.....	39
Conclusion	47
Flame Spray Pyrolysis for the Synthesis of YAG	47
Introduction.....	47
Materials	48
Apparatus	49
Procedure	50
Results and Discussion	50
Conclusion	53

Coprecipitation of YAG.....	54
Introduction.....	54
Materials	59
Apparatus	60
Procedure	60
Results and Discussion	60
Conclusion	61
Hydrothermal Synthesis of YAG.....	65
Introduction.....	65
Materials	66
Apparatus	66
Procedure	66
Results and Discussion	67
Conclusion	74
Experimental Chronology Conclusion.....	74
Experimental Summary	74
CHAPTER 4 Continued Examinations of the Coprecipitation of YAG.....	80
Introduction.....	80
Experimental	83
Materials	83
Apparatus	83
Procedure	88
Results.....	90
Conclusion	104
CHAPTER 5 Frit-Assisted Precipitation	106
Introduction.....	106
Experimental	109
Materials	109
Apparatus	109
Procedure	111
Results.....	115
Conclusion	160
CHAPTER 6 Overall Summary and Prospects.....	163
REFERENCES	169
VITA.....	194

LIST OF TABLES

Table 1 Expanded Darr criteria applied to the techniques and reflecting the literature. ..	25
Table 2 Comparison of the physical properties, which pertain to milling, of YAG and GAGG	29
Table 3 Expanded Darr criteria applied to the grading of the techniques after experimental experience with each.	79
Table 4 Judging the broader precipitation processes based on the expanded Darr criteria.	105
Table 5 Showing the bends and stretches of the precipitants and modifiers	135
Table 6 Comparison of the precipitation techniques with a delineation to highlight the frit assisted technique.....	162

LIST OF FIGURES

Figure 1 A diagram showcasing a planetary ball mill and the collision between two balls compacting material and imparting energy.....	5
Figure 2 Diagram of combustion synthesis demonstrating three stages of heating in a furnace, the transition to combustion, and the final resultant powder.	8
Figure 3 A diagram showing the stages of microwave combustion synthesis with the heating via microwaves, eventual decomposition and combustion, and final powder that results.	11
Figure 4 Diagram of the setup for a filter-capture flame spray pyrolysis setup. Here the example flammable mix of metal nitrates and organic liquids is aspirated by a pre-mixed fuel-oxygen which are then ignited by a pilot light of mixed propane and air. Residence time through a tube to allow for full combustion eventually leads to a filter for particle capture.	13
Figure 5 Setup of a drop-wise precipitation with a focus on the drop from the metals coming into the precipitating solution and resulting in the particles. Full addition eventually results in a suspension of particles.	16
Figure 6 Hydrothermal setup of a reactor, pre-loaded with precursor, in a muffle furnace to give a final powder.	19
Figure 7 Two graphs, the top showing balls of 10mm and their impact energy and the second graph showing balls of 20mm diameter.....	32
Figure 8 The effect of RPM speed on the amount of energy imparted per impact.....	33
Figure 9 Worn out tungsten carbide (top left), zirconium oxide balls (top right), and silicon nitride (bottom row). Reprinted with permission. ^[1]	34
Figure 10 Degradation of tungsten carbide milling media results in stark black contamination of normally white-green GAGG powder after milling for 10 hours. Reprinted with permission. ^[1]	35
Figure 11 Traditional combustion synthesis performed over a Meker burner for easier viewing.....	40
Figure 12 XRD pattern of the results from the combustion syntheses which have been sintered in a furnace at 900°C to obtain a crystalline pattern. A YAG standard from NIST is referenced for comparison.....	41
Figure 13 SEM images of the results from combustion syntheses. Only the top left urea image is a 200nm scale bar, the others are 1 or 2 μm scale bars.	42
Figure 14 Pictures of a cellulose filter paper imbued with a metal nitrate and urea solution. The flame front can be seen travelling across the experiment.	44
Figure 15 XRD pattern of the microwave assisted combustion synthesis using urea.	45
Figure 16 Example of the corrosion and wear from repeated use in microwave assisted solution combustion synthesis experiments.....	46
Figure 17 Top is a picture of testing the nozzle's flow with alcohol to simulate the FSP mixture. Bottom is the nozzle in position of the setup spraying the FSP mixture through the pilot light and down the tube to the filter	52
Figure 18 An example of a boil over if the solution was not fully cooled and alcohol was added. The darker yellow color is attributed to dissolved NO _x	55

Figure 19 SEM images of the particles produced with the homemade setup. Note the jagged features and lack of any sphericity. This material was scraped from the walls of the tube, not captured in the filter which may contribute to their lack of sphericity.	56
Figure 20 Particles prepared by a professional apparatus. These particles are more spherical with some morphological outliers. The size can vary drastically in these powders.	57
Figure 21 Diagram of the dropwise precipitation setup.	62
Figure 22 SEM images of precipitation of YAG in water with ammonium bicarbonate.	63
Figure 23 SEM images of the water/alcohol precipitation powders.	64
Figure 24 FTIR Stretches and bend of the hydrothermally treated powder	68
Figure 25 Comparison of the precursor and hydrothermal powders which had segregated.	69
Figure 26 Picture of the segregated powder.	70
Figure 27 XRD of the segregated powders calcined at 650°C	72
Figure 28 Comparison of the hydrothermally treated YAG precipitants sintered at 1000°C for 6 hours	73
Figure 29 Ultrasonic diagram and pictures of the setup from the side and top-down view.	85
Figure 30 Spray precipitation setup diagram showing the flow of materials and resultant particle suspension.	86
Figure 31 Ultrasonic nebulization spray setup diagram. Compared to the previous setup, the oxygen concentrator has been replaced by the ultrasonic generator.	87
Figure 32 Proposed setup for an electrospray precipitation using an overhead stirrer.	89
Figure 33 Sonochemiluminescence from luminol excitation in the bath reactor. The bottle has drifted towards the wall in the second top-down picture and shows significantly more activity. The bottom picture is of a bottle near the side showing activity only in the area below the waterline of the bath.	91
Figure 34 SEM images of powder precipitated from the ultrasonic bath reactor. The top is an initial sample, and the bottom is another sample attempt with the same chemicals.	92
Figure 35 SEM images from the spray precipitation of YAG. The left most picture has a scale bar of 10 micrometers, the middle and right pictures are 1 micrometer.	94
Figure 36 Precipitation of Al at a slower flow rate via spray pyrolysis	96
Figure 37 Powder resulting from the dripping of solution into the spray co-precipitated setup when a lid was put on to catch the ejected liquid.	97
Figure 38 Powder resulting from ultrasonic nebulization spray at 130kHz.	99
Figure 39 Precipitated spray powder collecting on the lip of the beaker from the turbulent air ejecting the ultrasonic spray.	100
Figure 40 Alternative setup of the ultrasonic spraying to try and limit turbulence from overhead stirring by using magnetic stirring.	101
Figure 41 Different angles of the electrospray setup with Taylor cones formed in each picture.	103

Figure 42 Diagram of the frit-assisted precipitation setup. Item ① is the metal ion precursor solution, item ② is the pump, item ③ is the frit, item ④ is the overhead stirrer, and item ⑤ is the precipitating solution.....	110
Figure 43 Computer generated rendition of the titanium frit holder (light grey) and retention plate (dark gray) and lines to demonstrate the route liquid will take through the holder when setup.	112
Figure 44 Side profile (left) and front profile (right) of the evolution of frits designed and improved for these studies.	113
Figure 45 SEM images of powders precipitated with NH_4OH through a fine glass frit. Image bars are A) 2 μm , B) 1 μm , C) 200 nm, and D) 300 nm.....	117
Figure 46 SEM images of powders precipitated with NH_4OH while being sprayed into the solution. Image bars are A) 2 μm , B) 1 μm , C) 200 nm, and D) 200 nm.	118
Figure 47 SEM images of powders precipitated with NH_4HCO_3 through a fine glass frit. Image bars are A) 2 μm , B) 1 μm , C) 200 nm, and D) 2 μm	119
Figure 48 SEM images of YAG powders from a 1:1 diluted precursor solution passed through a fine glass frit and precipitated with ethylenediamine heated to 50°C. Image bars are A) 2 μm , B) 100 nm, C) 100 nm, and D) 100 nm.	121
Figure 49 SEM images of YAG powders from a 2:1 diluted precursor solution passed through a fine glass frit and precipitated with ethylenediamine heated to 50°C. Image bars are A) 2 μm , B) 100 nm, C) 100 nm, and D) 100 nm.	122
Figure 50 SEM images of YAG powders from a 3:1 diluted precursor solution passed through a fine glass frit and precipitated with ethylenediamine heated to 50°C. Image bars are A) 2 μm , B) 200 nm, C) 100 nm, and D) 100 nm.	123
Figure 51 SEM images of YAG powders from a 3:1 diluted precursor solution dripped into an ethylenediamine solution heated to 50°C. Image bars are A) 2 μm , B) 100 nm, C) 100 nm, and D) 100 nm.	124
Figure 52 SEM images of YAG powders diluted 1:1 and mixed with p-TSA as a capping agent. These were precipitated with ammonium carbonate by passing the precursor YAG solution through a fine glass frit. Image bars are A) 3 μm , B) 200 nm, C) 200 nm, and D) 1 μm	127
Figure 53 SEM images of YAG powders diluted 1:1 and mixed with stearic acid as a capping agent. These were precipitated with ammonium carbonate by passing the precursor YAG solution through a fine glass frit. Image bars are A) 10 μm , B) 2 μm , C) 200 nm, and D) 200 nm.	128
Figure 54 SEM images of YAG powders diluted 1:1 and no capping agent. These were precipitated with ammonium carbonate by passing the precursor YAG solution through a fine glass frit. Image bars are A) 20 μm , B) 10 μm , C) 200 nm, and D) 200 nm.	129
Figure 55 Pressed sample of the p-TSA capped powder (left) and a transparent standard (right) processed by an outside group.	130
Figure 56 Combined plot of all PXRDs of the powders sintered at 1000°C. Labelled A) OH only, B) HCO_3^- only, C) CO_3^{2-} only, D) OH-+ACAC, E) HCO_3^- +ACAC, F) CO_3^{2-} +ACAC, G) OH-+2EHA, E) HCO_3^- +2EHA, F) CO_3^{2-} +2EHA.....	132
Figure 57 Combined TGAs of the precipitated material.	133

Figure 58 Combined figure of the nine systems FTIR's where column A) No organic, B) ACAC, and C) 2EHA. Row 1) OH ⁻ , 2) HCO ₃ ⁻ , 3) CO ₃ ⁻² precipitants.....	137
Figure 59 A near-field view of the powder calcined at 650°C where column A) No organic, B) ACAC, and C) 2EHA. Row 1) OH ⁻ , 2) HCO ₃ ⁻ , 3) CO ₃ ⁻² precipitants. The scale bars are 100 nm in size.....	139
Figure 60 A combined image setup showing the frit (top) and dropwise (bottom) additions in a far and close-up view. Left is a 200nm scale bar, right is a 100nm scale bar.	141
Figure 61 YAG powder precipitated by passing the 0.85 molar solution through an ultrafine titanium frit into an ammonium bicarbonate solution.	143
Figure 62 Left is a wide field view (100 nm scale bar) of the Ti frit produced powder spread across an SEM platform, an enlarged section (right) can be seen with a measurement of a particle of 12 nm.	145
Figure 63 Left is a wide field view (1 μm scale bar) of the Ti frit produced powder spread across an SEM platform, an enlarged section (right) can be seen with a measurement of a particle of 25 nm.	146
Figure 64 YAG precipitation comparison between the fine glass frit and the ultrafine titanium frit at 3 mL per minute. Scale bars for the top row are 300 and 200 nm (left and right), for the bottom they are 300 and 100 nm (left and right).	147
Figure 65 FTIR spectrum of a precipitation performed with ammonium bicarbonate and calcined at 650°C for 6 hours under oxygen (blue) and then microwave calcined at 650°C for 6 hours under air (orange). The carbonate stretches are marked by the box.....	149
Figure 66 Thermogravimetric analysis of the YAG sample calcined at 650°C for 6 hours under oxygen and then microwave calcined at 650°C for 6 hours under air.	150
Figure 67 FTIR spectrum of a precipitation performed with ammonium hydroxide and 2-ethylhexanoic acid and calcined at 650°C for 6 hours under oxygen (Blue) and then microwave calcined at 650°C for 6 hours under air (Orange). The carbonate stretches are marked by the box.....	151
Figure 68 FTIR spectrum of another precipitation performed with ammonium bicarbonate and calcined at 650°C for 6 hours under oxygen (Blue) and then microwave calcined at 650°C for 6 hours under air (Orange). The carbonate stretches are marked by the box.....	152
Figure 69 FTIR spectrum of a precipitation performed with ammonium hydroxide and 2-ethylhexanoic acid and calcined at 650°C for 6 hours under oxygen (Blue) and then microwave calcined at 725°C for 6 hours under air (Orange). The carbonate stretches are marked by the box.....	153
Figure 70 FTIR spectrum of another precipitation performed with ammonium bicarbonate and calcined at 650°C for 6 hours under oxygen (Blue) and then microwave calcined at 725°C for 6 hours under air (Orange). The carbonate stretches are marked by the box.....	154
Figure 71 YAG calcination at 650°C for 6 hours under oxygen followed by microwave calcination at 725°C for 6 hours under air. A standard is included as a reference for the high temperature response where the crystalline phase sets in	155

Figure 72 Diagram of the setup for steaming the powder in a loosely covered crucible contained within a desiccator.....	158
Figure 73 Calcination of carbonate residue contaminated powder. It has been recorded as it was originally calcined, calcined again in a furnace, then in a microwave, then steamed, and a final microwave treatment. All calcinations were done a 650°C for 6 hours.....	159

CHAPTER 1

INTRODUCTION

A Brief Introduction to Yttrium Aluminum Garnet and Nanoparticles

Yttrium aluminum garnet doped with cerium (YAG:Ce) has drawn a lot of interest because of its uses as a laser^[1], phosphor^[2], and analogue to other garnet scintillators^[3]. Its prevalence in the literature also makes it a good standard to compare against in these fields. Interest in YAG has grown substantially as attention to other novel garnets and rare earth compounds has risen.^[4-7] Concurrent to this is the need for simpler synthetic techniques which bypass the molten growths or high temperature melts. Focus has been on polycrystalline materials derived from pressed nanopowders and is an area of highly active research.^{[8][9]}

It has been well established that the smaller the particle's size, the higher the density achievable is from pressing or casting methods.^{[10][11]} To make viable dense ceramics of YAG the material is derived from a synthetic bottom-up approach by producing nanopowders for use as a precursor to a compact body, which is sintered to a final dense crystalline material.^[12-14] Because of the importance given to nanoparticle size, care must be taken for the selection of a synthetic method to produce such desired ceramic materials.

Previous melt methods, like Czochralski^[15] and Bridgman^[16], require large amounts of energy, time, and specialized apparatus to make a single crystal. The field has begun to optimize alternate routes using nanomaterial precursors to compact and sinter together to form dense, polycrystalline ceramics.^[12-14] Interest and demand for nanomaterials has increased to fill this niche and out of this has evolved the search for the

best synthetic approaches. Belyakov et al. (2011) summarizes four routes to nanopowders as either using a liquid or gas medium, solid state reaction, or plasma reaction.^[17]

Methods for the ideal synthetic approach to properly-sized nanoparticles range from grinding to combustion of precursors in a controlled manner to the precipitation of metal ions from solution. To help gauge the capabilities of synthetic approaches a list of desirable properties from Darr, et al. (2017) has guided the efforts:^[18]

- Allow controllable manufacture of homogenous nanoparticles (<100nm diameter particle) with desired composition and characteristics.
- Be energy and resource efficient (i.e. avoids the use of wasteful organic solvents or large amounts of energy and ideally uses a green solvent such as water).
- Be fast and flexible and use relatively few steps (preferably a one step or rapid process).
- Should possess consistent quality with ideally no batch-to-batch variations (e.g. as in a continuous process).
- If possible, should allow constant ‘in-process’ or ‘in-line’ monitoring for quality control measures.
- Allow flexibility to affect or control particle attributes by changing process conditions, for example, pressure, flow rate, temperature, etc.
- Give access to unique nanomaterials that are difficult to make using other methods (unique phase compositions, unique combination of particle properties).

- Should minimize hazards to workers or end users, for example, process being of minimal internal volume or readily shutdown in an emergency, or produce nanoparticles that cannot be readily inhaled by the process operator.

This broad set of characteristics can be applied to the numerous synthetic techniques for the production of nanoparticles and will be expanded later in this chapter. YAG nanoparticle syntheses ranging from combustion synthesis^[19], flame spray pyrolysis^[20], microwave synthesis^[21], ball milling^[22], and coprecipitation^[23] will be explored, as well as variations of some of these methods in order to promote certain desirable characteristics in an attempt to find the best method for the economical production of large quantities of nanopowders.

This dissertation will follow the experimental timeline of methods to produce YAG by numerous attempted syntheses. Each of these approaches will be detailed in its execution and results and comments about the benefits and shortcomings of them. What is learned from these is then applied in a novel technique which has shown great promise to allow for manipulation and production of nano YAG material. Some time will also be given to future investigations of this method and development of it with a solid foundation of research.

Introduction to the Methods

Process Introduction and Literature Survey

To familiarize the reader with the approaches and variations for nanoparticle syntheses explored in this dissertation, this is an introduction to each process to cover the broad reviews of the technique, prospect of the chemistry, and what might be accomplished

in the pursuit of this method. Each of these was attempted in the hopes of identifying a candidate method for use and improvement, excelling at the characteristics laid out previously.

Ball Milling

Grinding and milling has been known since antiquity with one of the earliest documented experiments being performed by Theophrastus, who ground cinnabar (mercury sulfide, HgS) in a brass or copper mortar and pestle with some acetic acid.^[24] This resulted in the formation of liquid mercury, and was novel because it avoided the need for fire to form quicksilver (elemental mercury metal). Currently milling is primarily in the pharmaceutical industry^[25], and for the production of pigments^{[26][27]} and alloys^{[28][29]}.

Modern use of milling is focused primarily on the solvent-free or reduced solvent use syntheses in organic procedures.^[25] Inorganic oxides and other inorganic materials have shown that ball milling is adept at syntheses of materials that may be difficult in conventional procedures.^[30] Because of its top-down approach, using bulk materials and mixing them together has the benefit of cheap and broad material selection.^[24] Especially in oxide synthesis where the use of alternate starting materials like carbonates, sulfates, and oxalates can give finer powders, but may leave unreacted residue. Using the oxides themselves gives a more direct result.^[24]

Unlike traditional plate grinding or tumble milling, planetary ball milling takes advantage of a launched ball across the cavity of the milling cup which impacts the wall or another ball, grinding the material caught between the ball and the wall or another ball. (Figure 1) Part of the energy from the ball's velocity is released upon impact and powder

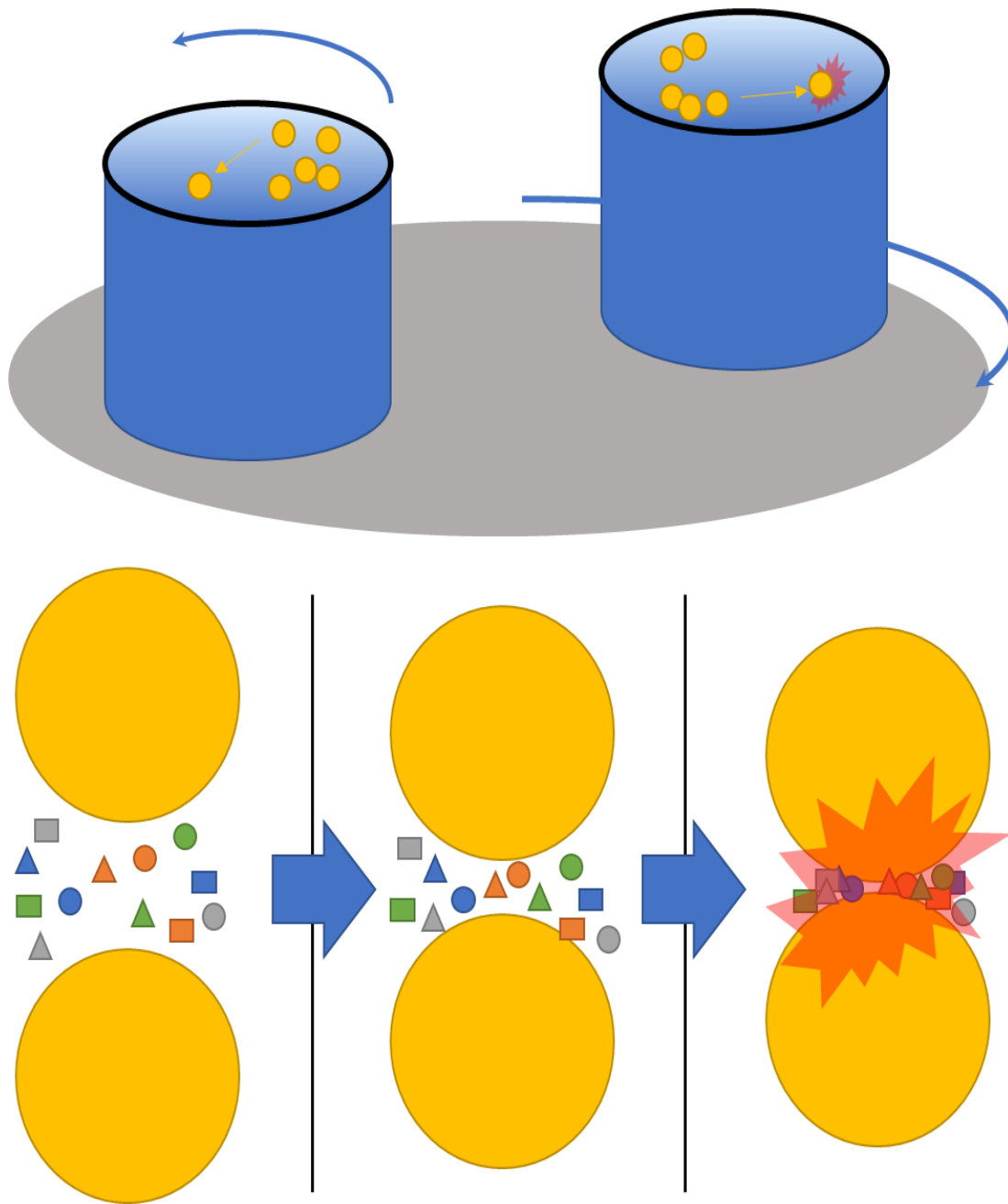


Figure 1 A diagram showcasing a planetary ball mill and the collision between two balls compacting material and imparting energy.

caught between the wall and ball have a hotspot imparted onto them. Over enough time and numerous impacts this begins to promote a solid-state reaction. Using the Rojac modified^[31] Burgio equation^[32], it is predicted that increasing the ball's mass and having the widest vessel for this reaction can yield the most energy per impact and reduce grinding time. A paper from our group covers this in more depth, as does the dissertation of K. A. McDonald.^[33]

Guo and Sakurai (2000) are some of the earliest researchers to produce YAG by ball milling, initially by drawing the equivalence of mechanical alloying by ball milling to that of mixing metal oxides in a similar fashion. They start with the goal of making YAG and yttrium aluminum perovskite (YAP) from simple oxide materials ground in a tungsten carbide cup by tungsten carbide milling media. In total, they mill for twenty-four hours and note residue of the tungsten carbide being present in the resulting analyses. The researchers conclude they have succeeded in making their two desired materials at lower temperatures, bypassing the need for high temperature heating processes.^[33] Zhang and Satio (2003) report the synthesis of YAG using different aluminum oxide precursors derived from $\text{Al}(\text{OH})_3$ heated at different temperatures. Milling was performed in a zirconium oxide cup and by zirconium oxide milling media for up to six hours. They conclude that by the end of six hours and using an $\text{Al}(\text{OH})_3$ starting material calcined at 400°C , they begin to see the start of YAG formation as shown by an x-ray diffraction (XRD) pattern. Treatments of the aluminum starting material at higher temperatures gave little to no improvement and caused other phases to arise. These researchers settle on a process of milling for six hours and heating to 700°C to give a pure phase of YAG but make no mention of cup or material

degradation, nor does the XRD pattern show any.^[35] Li, et al (2012) are one of the few groups to achieve a transparent ceramic using ball milling as the primary synthesis technique. They mill with aluminum oxide balls and cup for up to ten hours, adding tetraethyl orthosilicate as a sintering aid for transparency. They only have XRD patterns of high temperature processing at $>1600^{\circ}\text{C}$, but in a scanning electron microscopy electron dispersive x-ray analysis (SEM-EDX) display they note large granular impurities in the pressed material of aluminum oxide, likely from the milling media.^[36]

The promise of this method's simple setup, small material requirement, low specific demand of reactant types, and fast reaction times were investigated to test these benefits for rare earth garnets syntheses.

Solution Combustion Synthesis

Alternatively known as sol-gel combustion, solution combustion synthesis (SCS) is an unusual, yet simple technique which results in a powder from a highly exothermic reaction.^[37] This is achieved by mixing an aqueous metal ion solution, typically composed of metal nitrates, with a large excess of reducible fuel, and heating the solution until it begins to undergo a vigorous redox reaction, eventually resulting in a foamed product.^[38] Figure 2 shows a diagram of this setup.

The fuels are critical to provide some dilution to the metal ions in solution and to evolve gases during the combustion for the foaming and physical spacing of powders, a diagram of which can be seen in Figure 2. Because of this, a high ratio of fuel to metal ions is necessary to obtain ideal powders, typically a $>4:1$ fuel to metal ion molar ratio.^[39] The fuels are often comprised of nitrogen containing compounds because of their highly

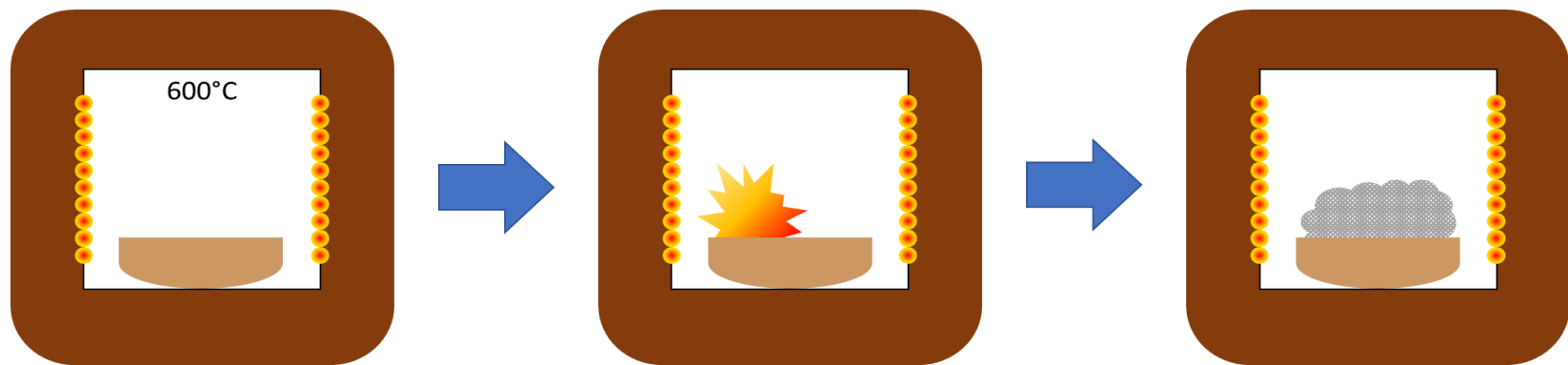


Figure 2 Diagram of combustion synthesis demonstrating three stages of heating in a furnace, the transition to combustion, and the final resultant powder.

exothermic nature and low activation energies to promote the exothermic breakdown for combustion. A table of common fuels can be found in the review by Varma, et al. (2016).^[37]

A classic example of a self-propagating metal and fuel combination is ammonium dichromate ($(\text{NH}_4)_2\text{Cr}_2\text{O}_7$), often used in an experiment called the ‘tabletop volcano’.^[40] Heating of this salt leads to a run-away reaction that produces green Cr_2O_3 , nitrogen gas, and water vapor, not stopping until all precursor is consumed. This is one of the simplest examples of oxide synthesis, but many other oxides have been synthesized by combining metal nitrates with a fuel.

The process is useful for the formation of complex oxides, which have a significant interest in recent times for use as ceramics, pigments, phosphors, solid electrolytes, and scintillators.^[41] One of the earliest synthesis of YAG by combustion synthesis was by Kingsley, et al. (1990) who demonstrated that a combination of urea and rare earth metal nitrates can produce an oxide and that combining with aluminum can give rare earth aluminates, YAG being one of the many they tested.^[42] YAG was also produced by Ramanathan, et al. (2002) using glycine as the fuel and noted that a carbon residue persisted and had to be burned out after the reaction.^[43] Laishram, et al. (2011) explored the combination of urea and glycine and the effects it had at various ratios, eventually settling on 2:5 metal ion to fuel molar ratio to produce pure YAG after calcination at 700°C.^[44] Finally, Wu, et al. (2015) take it to an extreme by combining metal nitrates and fuel in a 1:40 molar ratio to result in pure phase YAG in a short time.^[45] Their main experiment was studying the effects of cerium content, up to 20 molar percent, and they used an excess of fuel to achieve this reproducibly.^[46]

Experiments using this technique will be explored because of the simplicity in both chemistry and apparatus, rapid synthesis time, and produced oxides with minor residual material left over. Those properties will be useful for comparing to the other techniques.

Microwave Combustion

Different from resistance heating, microwaves are known to heat more uniformly than traditional resistance heating.^[47] Through dielectric loss microwave radiation is absorbed by the sample and dispersed throughout the sample.^[48] The higher power microwave instruments are capable of heating more quickly and thoroughly which appeals to researchers because of its ability for uniform heating and the low cost of commercial, high wattage microwave systems.

A variation of solution combustion synthesis, this method replaces the external heating with one that heats internally, uniformly, and thoroughly, shown in Figure 3. This can reduce processing time and ensures a more consistent yield since materials are exposed to consistent microwave radiation.^[21] The earliest use of microwaves to make YAG by combustion synthesis was performed by Fu (2005) who mixed metal nitrates with urea in an 8:15 metal to fuel molar ratio. Using a 650-watt microwave generator the reaction was reported to take 30 minutes to make a powder which was then calcined at 1100°C and characterized. Some other phases can be seen in the XRD pattern and the SEM images shows jagged materials, but the overall approach was a success.^[50] Vaidhyanathan and Binner (2006) used citric acid as an alternative fuel to produce a gel that was exposed to microwave heat until fully calcined, after about 30 minutes. This method follows a sol-gel technique known as the Pechini method^[51] with the only variation being the application of

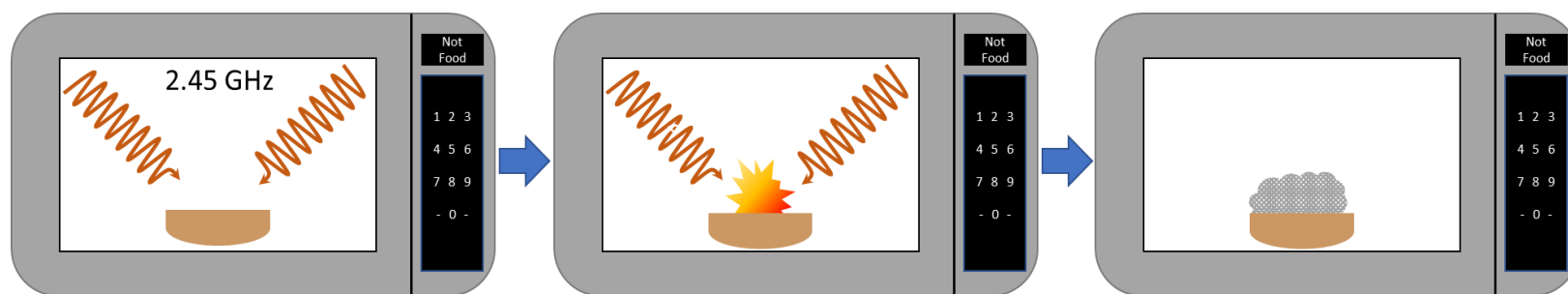


Figure 3 A diagram showing the stages of microwave combustion synthesis with the heating via microwaves, eventual decomposition and combustion, and final powder that results.

microwave heating. Secondary phases can be seen in the XRD pattern but are not attributed to any known phases and persist even after high temperature calcination. The SEM pictures show small particles, and they conclude it is an overall success in making YAG in a short time.^[52] Potdevin, et al. (2012) return to the use of urea as a fuel in a 2:5 molar ratio of metal to urea. Their final product looks very porous in SEM images and the phase purity contains a perovskite form of yttrium and aluminum oxides. They conclude their synthesis is a success because of the high luminescent yield of this doped form of YAG and the short processing time it took them to produce the material.^[53]

Because of these papers and the previously mentioned factors, microwave combustion synthesis has the same benefits as externally heated combustion synthesis, but with the hopes of bolstering the process through more thorough and less demanding heating. Investigations of this method were conducted to familiarize myself with the concepts and properties of this approach.

Flame Spray Pyrolysis

Flame spray pyrolysis (FSP) is one of the more prolific methods used by industry today for its high throughput.^[54] This method differentiates itself from solution combustion by using flammable organic solvents to host the metal ions and the aspiration of the solution through a flame, as portrayed in Figure 4.^[55] This promotes combustion and breakdown of material in the flame resulting in a soot of product.

The precursor materials for viable flame spray pyrolysis are typically nitrates, carboxylic acids, or acetylacetonates.^[56] These materials dissolve readily in select solvents, like alcohol and/or hydrocarbons, and decompose readily to oxides under proper flame

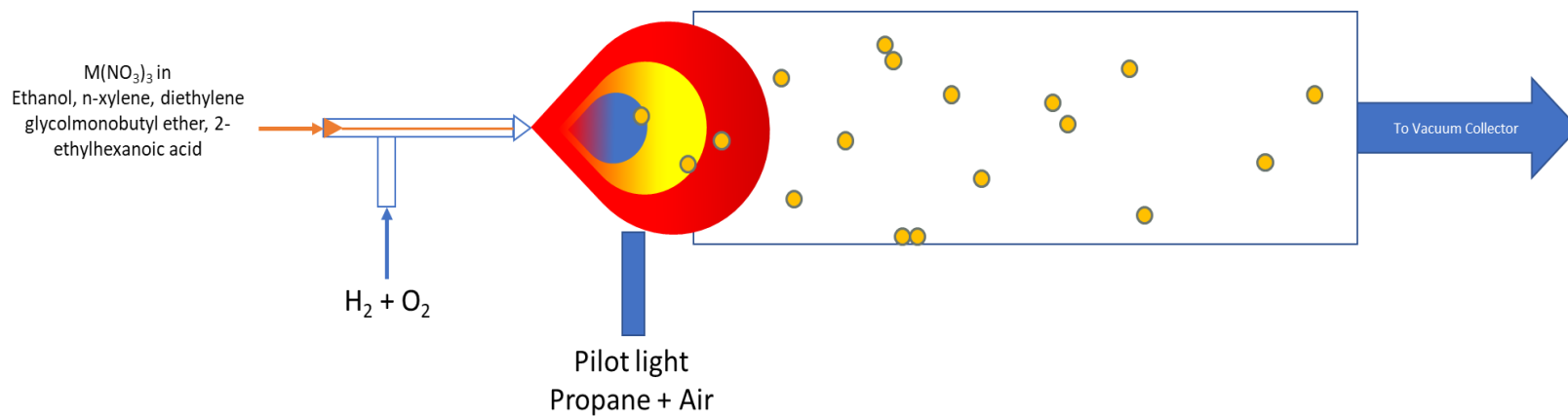


Figure 4 Diagram of the setup for a filter-capture flame spray pyrolysis setup. Here the example flammable mix of metal nitrates and organic liquids is aspirated by a pre-mixed fuel-oxygen which are then ignited by a pilot light of mixed propane and air. Residence time through a tube to allow for full combustion eventually leads to a filter for particle capture.

conditions.^[55] Rosebrock, et al. (2016) found that residence time in the flame also dictates the ‘proper’ outcome for the product to yield spherical particles.^[57]

A recent review described FSP as “manufacturing of nanoscale materials by flame more attractive compared to the alternative classical wet-chemistry” touting its large-scale applications.^[56] S. Pratsinis in another paper^[58] details the seven points of flame spray pyrolysis which lend it to being the ideal method for nanoparticle syntheses: 1) continuous flame spray requires simple and few unit operations (e.g. burner, tubing, valves, etc.) which enables a short and fast processing chain, 2) powder collection by filtration is an integral part of the manufacturing process, 3) little to no waste is produced by the process, 4) high purity metal oxides products without any organic contaminants can be made, 5) unique morphologies can be made, like those for high surface area applications, 6) the short length, high temperature gradient can produce metastable crystal phases, and 7) flame and aerosol processes are well defined classically, reducing the need for experimental trial and error.

YAG has been reported several times in the literature and one of the earliest and more comprehensive is from J. Marchal, et al. (2004) where they explore the effects of different starting materials (metal nitrates and metal-organics like acetylacetonates, propionates, 2-ethylhexanoates, and methoxyacetate) and solvent mixtures upon the resulting YAG powder. They find that both of these components play a critical role in the powder production, giving large micron-sized spheres in the case of the nitrates, and a very fine powder in the case of propionates and acetylacetonates. Metal-ion concentrations were reported to be less than 0.1M concentration based on yield percentages. Initial calcination studies show a myriad of combined yttrium and aluminum monoclinic and perovskite

phases. After annealing, these phases are reported to convert to the garnet phase, but no other XRD patterns are shown, except for one sample which showcases a myriad of crystalline phases.^[20] J. S. Lee, et al. (2009) report a novel approach to make YAG using the metal nitrates dissolved in ethanol with the addition of concentrated urea. The ratio is 0.1 molar metal ions stoichiometrically mixed to YAG (3:5 yttrium to aluminum) to 3 moles of urea. They have done this to act as a fuel and aid in combustion in the flame. XRD patterns show a predominant YAG phase of the powder, with some other phases present. SEM images show the particles are consistently 20 nm in size.^[59] A. Purwanto (2014) corroborates the work of Lee, et al. using a fuel-assisted spray pyrolysis and compares it to a sample with no urea at combined metal ion concentrations of 0.1 molar. They show a significant size reduction from micron-sized particles without urea to sub-50 nm particles with the addition of urea. The drawback to their work is the significant phase impurity they recorded in XRD patterns.^[60] These papers highlight that it is likely better to avoid fuel-assisted syntheses and use an organic mixture at more dilute concentrations.

Because of these enticing characteristics and a promising literature survey, flame spray pyrolysis will be explored for its capability to produce YAG. Evaluation of its procedures and costs will help determine how it compares to other methods.

Precipitation

This is a broad approach, chemically defined as the formation of a solid from a supersaturated solution. Precipitation is widely used for the formation of a solid from mixing two solutions together, as can be seen in Figure 5.^[61] Classic examples of this are lead (II) iodide, silver (I) chloride, and barium sulfate which are commonly used as

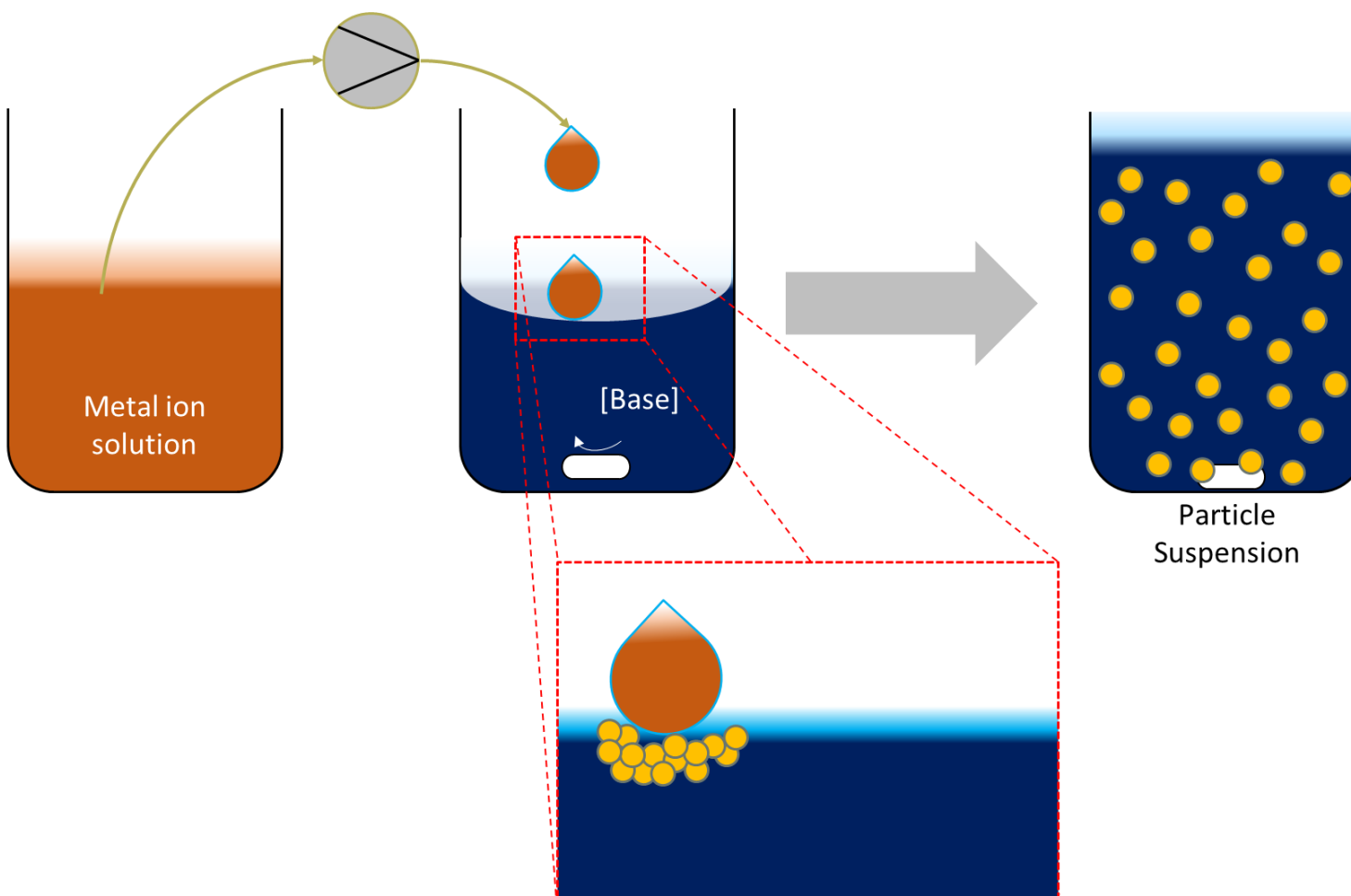


Figure 5 Setup of a drop-wise precipitation with a focus on the drop from the metals coming into the precipitating solution and resulting in the particles. Full addition eventually results in a suspension of particles.

standards for solubility products, electrochemical investigations, and introductory chemistry experiments.^[62-67] This method extends beyond inorganic materials to include organic precipitations^{[68][69]} and precipitations of materials within alloys^[70]. The focus of this overview will be on inorganic precipitations that can be treated by post-processing to yield metal oxides.

One of the benefits of precipitation is the wide selectivity of precipitants that can be used. To produce oxides, commonly carbonates^{[71][72]} or hydroxides^[73] are used because of their low cost and simplicity. Alternatives like carboxylates^[74], urea^[75], or amines^{[76][77]} have been pursued. Another variable which can be manipulated is the solvent the reaction is taking place in. If a solvent is chosen which the product is less soluble in than others, like water, this is commonly known as antisolvent precipitations.^{[69][78]}

Typical methods of introducing the two solutions together, a precipitant and a metal ion solution, require a dilute concentration of metal ions which ensures discrete nucleation to make nanoparticles. This has been a limitation to the precipitation approach and attempts to push beyond low concentrations result in agglomerated particles.^[79]

Experiments involving precipitation were pursued because of the ability to manipulate conditions involving solvent, precipitant, and concentration. Particular attention will be paid to the expected shortcomings and what has been done to bolster this system to overcome those. An assessment of these will be useful in comparing it to the other methods.

Hydrothermal

High temperature and pressure processing in the cases of hydrothermal, solvothermal, and autoclave syntheses can promote novel reactions that are typically not attainable through conventional means.^[80] The mechanism for producing nanoparticles is similar to that of precipitation requiring tenth to hundredth molar concentrated metal ion solutions and different types of precipitants to make materials.^[18]

There are two approaches for hydrothermal synthesis to make nanoparticles: one where the particles are formed before proceeding into a hydrothermal treatment, and another where the materials are precipitated under hydrothermal conditions.^[18] The first approach benefits from the ability to separate materials from solution before treatment, avoiding halogens, nitrates, or incompatible solvents from degrading the hydrothermal reactor and to promote certain morphologies by allowing for aging time for structures like zeolites^[80] and pre-mixing of metal-organic-frameworks^[81]. The second approach is a one-pot synthesis and reduces the number of steps and materials needed. Small scale approaches can be performed using a hydrothermal reactor, relying on batch-wise syntheses, as shown in Figure 6.^[77]

One of the earliest instances of YAG synthesis by the hydrothermal method was not looking for nanoparticles, but actually microparticles as efficient phosphors. Takamori and Lawrence (1986) used citrate precursors and a concentration of 0.4 molar to make YAG particles that were purposefully large. They investigated the effects of seeding to promote the growth of particles, along with a control with no seed powder, and found that seeding led to larger particle, likely from nucleation sites on the seeds.^[82] L. Xia, et al. (2004) demonstrate a mixed alcohol/water system to make nanoparticles of YAG by

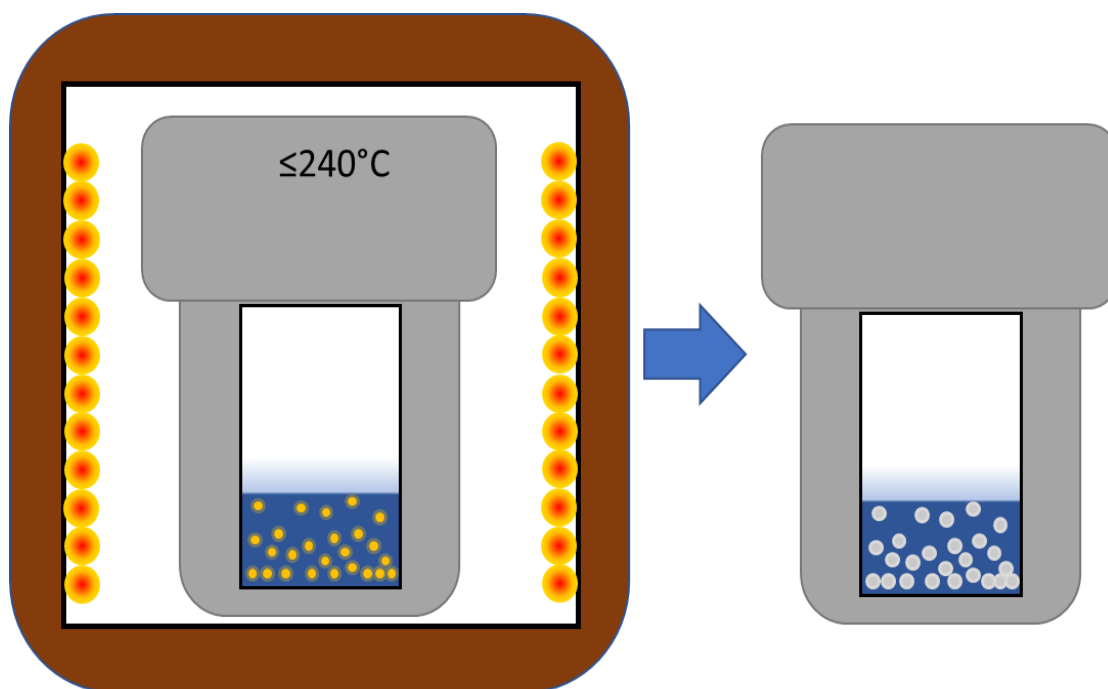


Figure 6 Hydrothermal setup of a reactor, pre-loaded with precursor, in a muffle furnace to give a final powder.

hydrothermal synthesis. They do not detail final concentrations, but the particles resulting from the setup were consistent and spherical with a refined garnet structure.^[83] Syntheses using supercritical water have also shown great utility in producing YAG nanoparticles. W. Linxiang, et al. (2010) report using high temperature close to 400°C to make crystalline nanoparticles of YAG after synthesis of an yttrium and aluminum carbonate precursor. They were curious about the effects of time on the experiment's results, leaving some samples in for up to 12 hours. No real change was noted in the particles except for a slight migration to marginally larger particles at longer time intervals. Concentration is not given, but the SEM images show particles are greater than 100 nm in size and morphologically has flat, crystalline faces.^[84] These syntheses lay a decent foundation of what to expect from hydrothermal treatments. While the special apparatus for supercritical phases may not be feasible yet, the research shows that this may be a worthwhile route if funding permits.

Because of its capability to produce oxides from introduced materials, this method will be explored. Evaluation of its batch-wise capabilities and reactor heat limitations will give valuable experimental reference material for how it compares against other methods.

Evaluation and Expansion of the Process Criteria

As mentioned previously in the introduction, Darr, et al. (2017) laid out a broad set of criteria which would be useful for comparing nanoparticle synthesis methods.^[18] However, some of these points are too broad and nuance is lost for a sufficient comparison. The original points are verbatim from the paper and comments follow about how these should be refined into more detailed guidelines. Darr states that “any viable and safe

process of high-quality nanomaterials should preferably display the following characteristics:"

1. Allow controllable manufacture of homogenous nanoparticles (<100nm diameter particle) with desired composition and characteristics

This point may be broken up into the two points of composition and characteristics to better gauge properties such as stoichiometry and morphology of nanoparticles produced.

2. Be energy and resource efficient (i.e. avoids the use of wasteful organic solvents or large amounts of energy and ideally uses a green solvent such as water)

Efficiency may be broken up into three separate points regarding energy, cost, and yield. Energy is taken directly from Darr's point, but resource can be broken into cost and yield because resource efficiency is defined by how well it works and how much it makes. An underlying point of these which may not be obvious is time efficiency which contributes to both cost and yield.

3. Be fast and flexible and use relatively few steps (preferably a one step or rapid process)

Time and adaptability are two key considerations for a process. Being able to rapidly produce product is ideal. Adaptability to changes in the process or product demands make any process stand out. This point may be broken up into two separate points about flexibility and number of steps. Time, taken from the concept of being fast, will be partially included with the previously mentioned efficiency points and represented in the number of steps a method takes.

4. Should possess consistent quality with ideally no batch-to-batch variations (e.g. as in a continuous process)

This point highlights two critical criteria which may be separated: product quality and continuous flow. Reproducibility is highly desirable for any process and should be paramount if the technique is to be viable. Product quality also implies the potential of residues or contamination, which can be carried over from precursors and should be considered. Continuous operation makes a process much more appealing for industrial use and time is critical here too for a fast and efficient synthesis.

5. If possible, should allow constant ‘in-process’ or ‘in-line’ monitoring for quality control measures

This is a difficult point to gauge after an initial reading, but this is very pertinent to follow a synthesis and works well in conjunction with a continuous flow system.

6. Allow flexibility to affect or control particle attributes by changing process conditions, for example, pressure, flow rate, temperature, etc.

Flexibility appears again as a criterion emphasizing how critical it is to Darr and the other researchers.

7. Give access to unique nanomaterials that are difficult to make using other methods (unique phase compositions, unique combination of particle properties)

Alternate materials are great to showcase the versatility of an approach, but this point can fit into the concept of flexibility.

8. Should minimize hazards to workers or end users, for example, process being of minimal internal volume or readily shutdown in an emergency, or produce nanoparticles that cannot be readily inhaled by the process operator

Hazards and waste are both critical attributes to consider because how they can impact the usefulness of a process. These should be two points to consider on their own.

To summarize the points derived from Darr's initial list in the order which they were realized, the process should:

1. Have nanoparticles that meet desired composition
2. Have nanoparticles that meet desired characteristics
3. Be energy efficient
4. Be cost efficient
5. Be yield efficient
6. Be flexible
7. Have a minimum of steps
8. Have a product that is reproducible
9. Ensure residual contamination is eliminated
10. Be capable of continuous production
11. Have the ability to be monitored 'in-line'
12. Have minimal hazards
13. Have waste and disposal that are manageable

These expanded points can be seen in a table in the next section. Broadening the characteristics will bring out more of the nuances that each of the processes should have and be the best gauge for determining its advantages and drawbacks.

Summary of the Literature Survey

The above six methods were to be explored to understand each one's unique capabilities for the synthesis of yttrium aluminum garnet nanoparticles. Based on the literature survey, there are shortcomings and benefits to each route and the resulting powders. This necessitates replication in the lab so a greater understanding of these approaches can be reached.

Using the criteria laid out by Darr, et al. (2017)^[18] listed in the introduction, a preliminary table was constructed to help compare the multiple techniques and better gauge their strong points and weaknesses. Table 1 will be refined in the future sections as methods are refined and experimental experience focuses the synthesis candidates. In the table a ✓ means that it meets the criterion, - means that it might meet the criterion in some circumstances, and ✕ means that it struggles to or fails to meet the criterion. These were attempted to be shown in the best light and given the benefit of the doubt that they could perform in certain ways.

Table 1 Expanded Darr criteria applied to the techniques and reflecting the literature.

<i>(In regard to oxide syntheses)</i>	Ball Milling [25][80-82]	Combustion Synthesis [37][41][83][84]	Microwave [21][47][85]	Flame Spray Pyrolysis [53][55][86]	Precipitation [2][17][58]	Hydrothermal [18][76][88]
Product meets desired composition	✗	✓	—	—	✓	✓
Product meets desired characteristics	✗	✓	✓	—	✓	—
Process is Energy Efficient	✓	✗	✓	✗	✓	✗
Process is Cost Efficient	✗	✓	✗	—	—	—
Process is Yield Efficient	✓	✓	✓	—	—	✓
Process is Flexible	✗	✗	✗	✗	—	✓
Process has a Minimum of Steps	✓	✗	✓	✓	✓	✓
Product is Reproducible	✓	✓	✓	✓	✓	✓
Residual Contamination Elimination	✓	✓	✓	—	—	✓
Capable of Continuous Operation	✗	✗	✗	✓	✓	✓
Process can be Monitored In-Line	✗	✗	✗	✗	✓	✓
Process has Minimal Hazards	✓	—	✗	—	—	—
Waste and Disposal are Manageable	✓	✓	✓	✓	—	✓

Yes	No	Maybe
✓	✗	—

CHAPTER 2

ANALYTICAL EQUIPMENT

Scanning Electron Microscopy (SEM)

A Zeiss Auriga Cross Beam FIB/SEM was used to characterize the products' morphology and size. A Phenom Pharos G2 Desktop FEG-SEM was also used when available.

Transmission Electron Microscopy (TEM)

A Zeiss Libra 200 HT FE MC was used for a closer and clearer look at particle size.

Inductively Couple Plasma Optical Emission Spectroscopy (ICP-OES)

An Agilent 5110 was used to determine residual metal content of reaction effluent and determine the concentration of metals. The latter was replaced by pyrolysis because of the higher accuracy.

Fourier Transmission Infrared Spectroscopy (FTIR)

A Thermo Scientific Nicolet iS50 FTIR spectrometer was used to characterization of carbonate and organic content to track residual carbonaceous material after calcinations and determine effectiveness of those calcinations.

Thermogravimetric Analysis (TGA)

A TA Instruments Q-50 TGA was used to record weight loss of samples as a function of temperature with a constant heating rate. This was useful for acknowledging

when decomposition of certain materials was and great for tracking the residual organic content that persists after some calcinations.

Powder X-Ray Diffraction (PXRD)

A Malvern Panalytical Empyrean PXRD was used to analyze the diffraction pattern of amorphous and crystalline materials to look at phase purity and determine crystallite sizes.

An Olympus BTX-II benchtop XRD was used when available for scanning of powders and obtaining patterns.

CHAPTER 3 EXPERIMENTAL CHRONOLOGY

Ball Milling/Mechanochemistry

This work was some of the earliest the author contributed to. Investigations were underway well before, but this portion of work takes place in 2016 and 2017. As previously mentioned, ball milling was performed in a planetary ball mill because of the benefits it has to grind material in a shorter time and with higher energy than traditional tumble milling or grinding. Previous laboratory members have covered this work in greater detail with our groups' contributions to the field of mechanochemistry.^{[92][93]} Their experience, guidance, and cooperation were beneficial for evaluation of this technique and understanding its candidacy for improvement. The simplicity and ability of using simple oxide starting materials set ball milling apart from other methods, with the option for addition of solvents and the ability to manipulate variables like RPMs, density, and ball size.^[85]

Our group's previous work used a garnet known as gadolinium aluminum gallium garnet (GAGG) as the target material. The properties of YAG and GAGG are physically similar, as shown in Table 1. Because of this, the experiments on GAGG are considered analogous and included in this chronology. The author's contributions were mainly computational, evaluating the Burgio equation^[32] and using it to correlate with the physical phenomenon seen in the experiments. Described herein are the experiments and a brief look at the computation contributions.

Table 2 Comparison of the physical properties, which pertain to milling, of YAG and GAGG

	Yttrium Aluminum Garnet (YAG)	Gadolinium Aluminum Gallium Garnet (GAGG)
Mohs Hardness	8.0	8.0
Density	4.55	6.63
Symmetry	Cubic	Cubic
Space Group	$Ia\bar{3}d$	$Ia\bar{3}d$

Materials

Gadolinium oxide (Strem 99.99%), aluminum oxide (Strem Chemicals, 99.99%), gallium oxide (Strem Chemicals, 99.99%), and cerium (IV) oxide (Strem Chemicals, 99.99%) were used in the synthesis of GAGG.

Apparatus

As described previously, a Fritsch Pulverisette 7 planetary ball mill was used to grind the material using balls and cup from Fritsch. These balls and cups were made of either silicon nitride, zirconium oxide, or tungsten carbide and the milling media of the same type was paired with the cup. Because of the weight limit, the heavy tungsten carbide cup was limited to 600 RPM to prevent damaging the machine.

Procedure

Oxides were weighed out individually and added to the cup with the number of balls specified by the manual. Typically, the 10 mm balls were used and seven of those were added to their respective cup. The cups were placed into the machine's slots and milled at a chosen RPM and for a selected time. After milling, the cup had to be left in their holders because of how hot they got. After this the balls were removed and a majority of the powder could be collected.

Early research was performed to help in predicting the results of milling with different media and the effects on energy imparted into the system using the Burgio equation. A more condensed version of the equation was derived and used to predict the total energy in a system over a given time. The formula that was derived from the Burgio-Rojac equation can be seen in Equation 1. Here E_j represents the energy in joules, d is the ball diameter, D is the density of the vial and balls, S_D is the main disc speed in RPMs, s_c is the speed of the cup in RPMs, and W is the

diameter of the cup. Graphical representations of this can be seen in Figures 1 and 2 where the diameter of the balls is varied or the speed. As can be inferred, the tungsten carbide balls being the densest, impart the most energy per impact. This correlated well with the times for synthesis of GAGG and other materials and are explained more in depth in the dissertations of K. A. McDonald (2018)^[1] and M. N. Bailey (2019)^[2]. In summary, the heavier the weight of the milling balls, the higher the energy predicted and results showed shorter synthesis times for both gadolinium aluminum gallium garnet and lutetium oxyorthosilicate. This was attributed to the more dense grinding balls imparting more energy per impact.

$$E_J = \frac{\pi d^3 D S_D S_C (W-d)}{24} \left[-\frac{s_C^2 (W-d)}{s_D^2} - 2R \right] \quad \text{Equation 1}$$

As these studies were conducted, the degradation of the balls and cups became apparent. Balls showed signs of pitting, cups were losing their straight sides, and some samples showed signs of detectable contamination, as seen in Figures 3 and 4. Working life of the cups was not studied, but other researchers estimate the cost being half the price of operation of the apparatus to replace worn components.^[87] Further, there are ‘blind spots’ in the cups where balls are unable to reach material residing there which can lead to residual starting materials.

Conclusion

Ball milling was an extremely enticing method because of its simplicity. The issues resulting from contamination are just too difficult to overlook when the milling materials constitute a significant portion of experimental cost and are so short lived. Contamination may not be an issue for organic syntheses that use ball milling because of the lower power needed to break

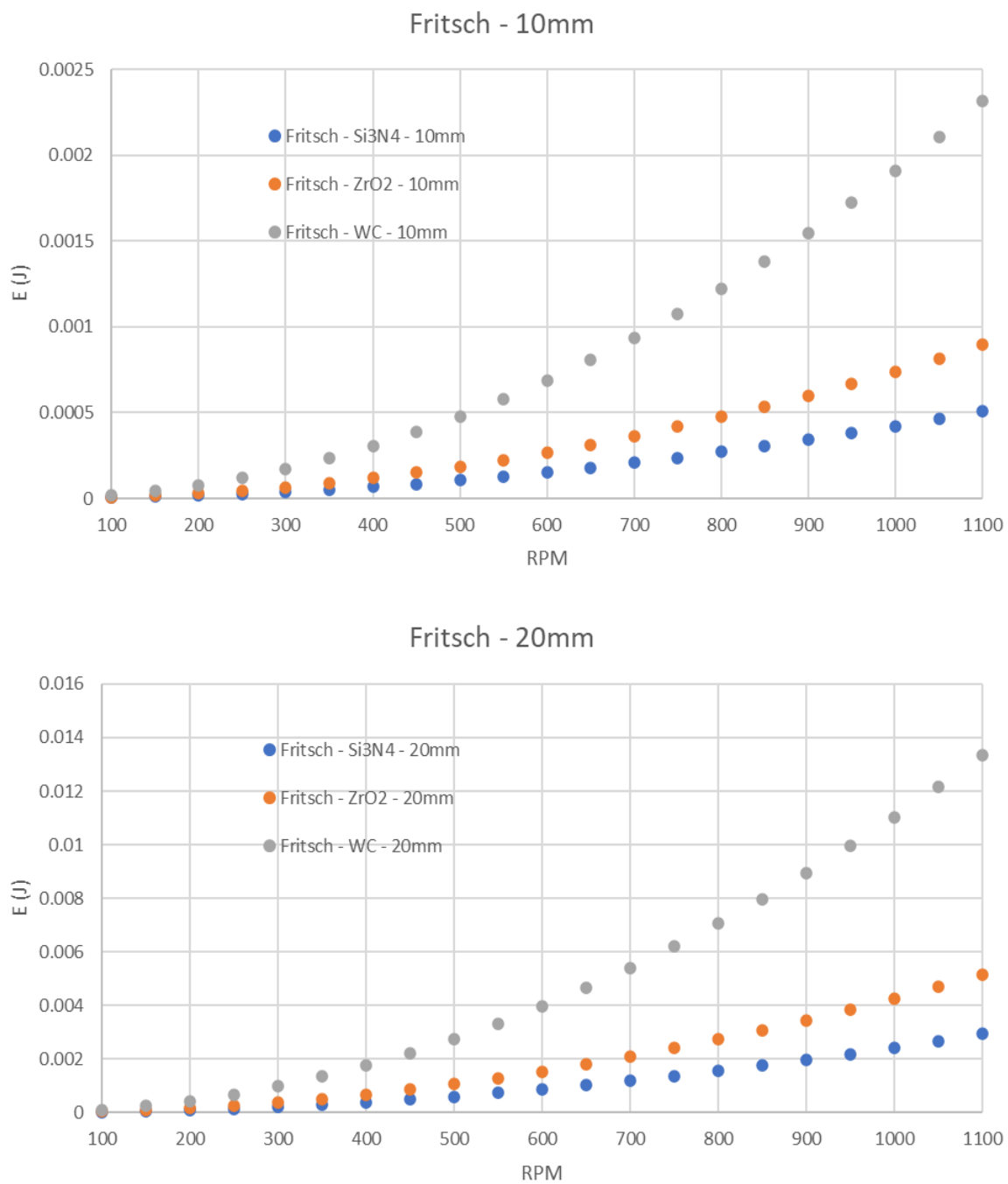


Figure 7 Two graphs, the top showing balls of 10mm and their impact energy and the second graph showing balls of 20mm diameter.

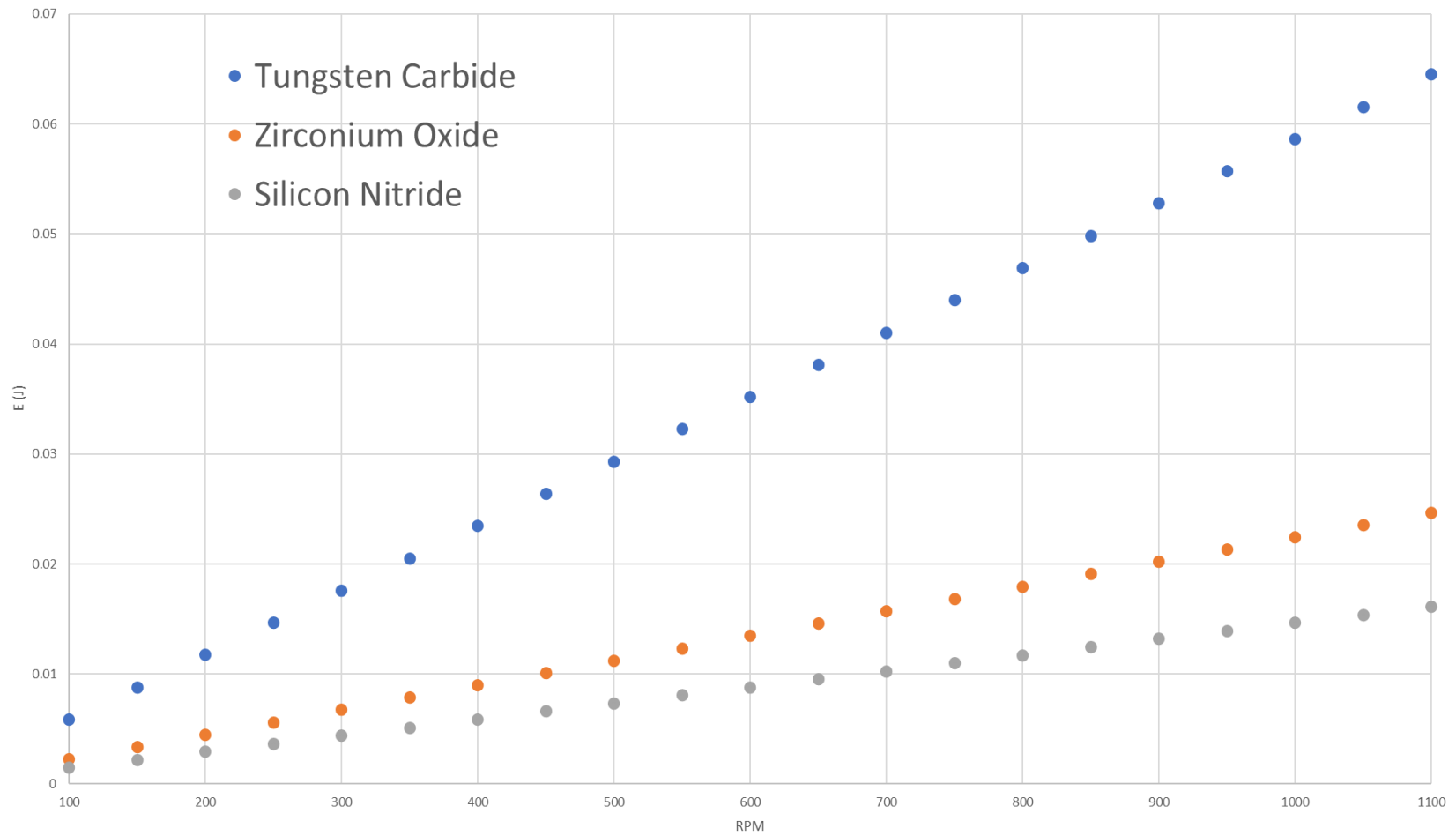


Figure 8 The effect of RPM speed on the amount of energy imparted per impact.

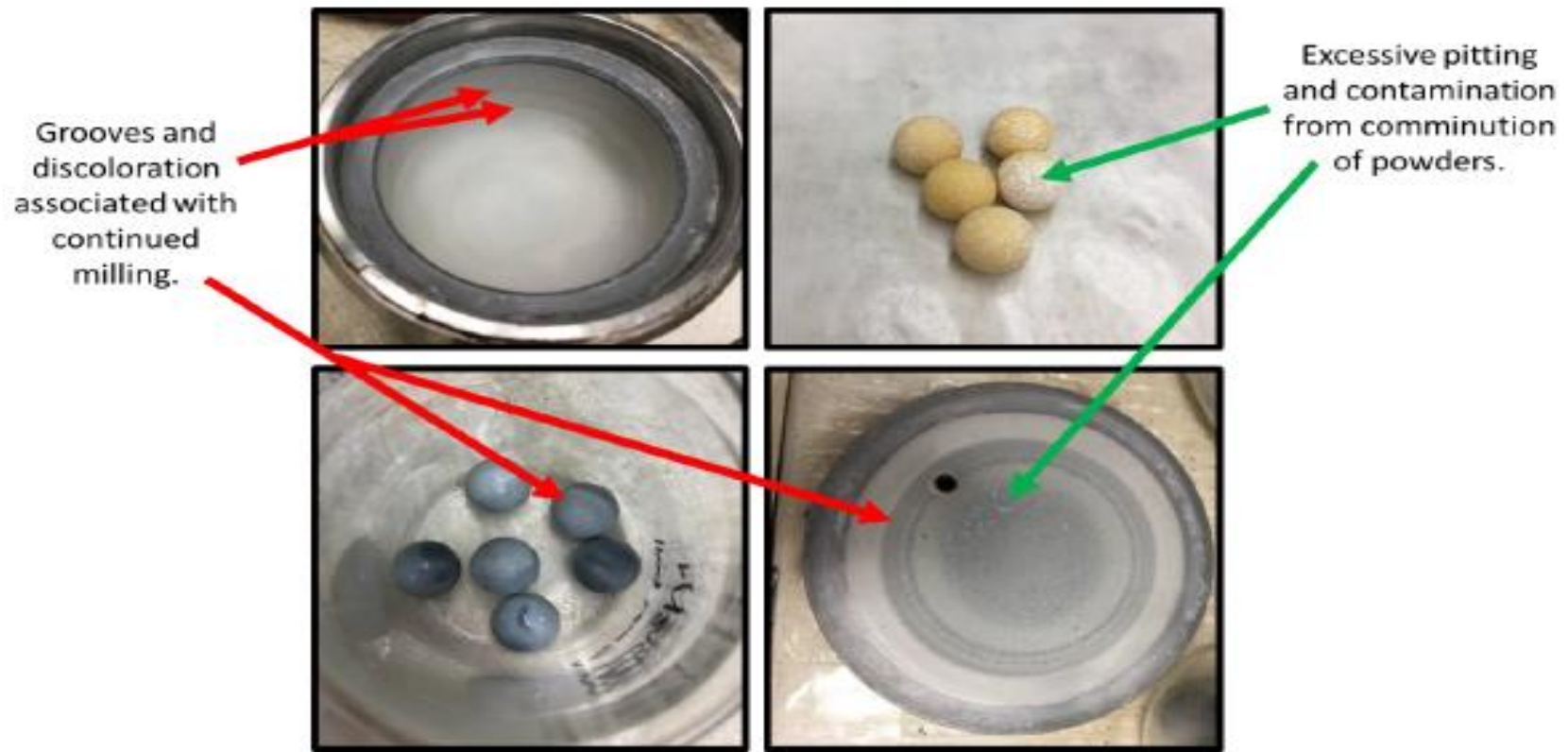


Figure 9 Worn out tungsten carbide (top left), zirconium oxide balls (top right), and silicon nitride (bottom row).
Reprinted with permission.^[1]

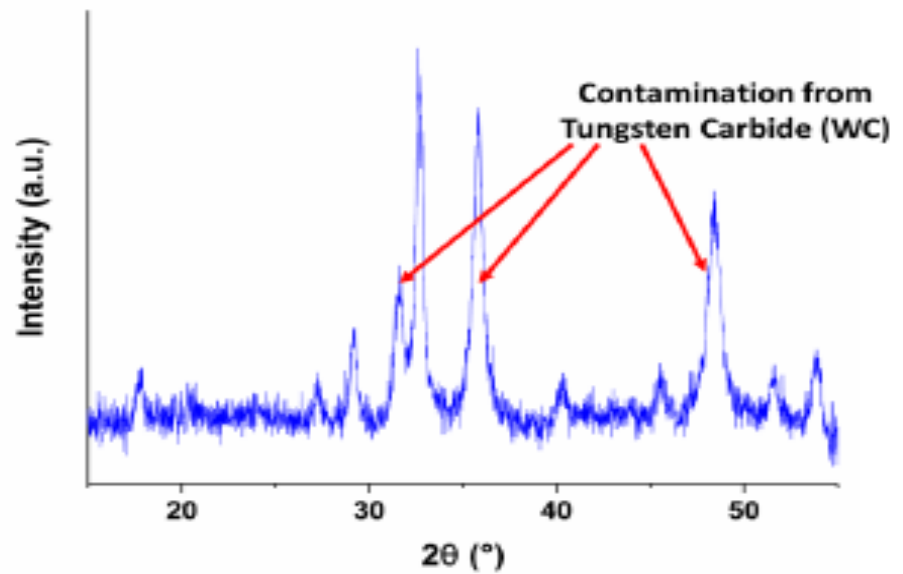
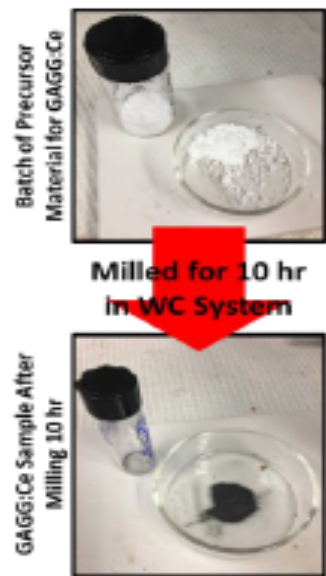


Figure 10 Degradation of tungsten carbide milling media results in stark black contamination of normally white-green GAGG powder after milling for 10 hours. Reprinted with permission.^[1]

material up and the ability to dissolve material away from the inorganic contaminants.^[94] For oxide materials being milled with either a nitride, oxide, or carbide, there are no simple ways to remove these from the powder. Because of these factors, ball milling was going to exceed budget and presented a much more significant challenge than originally thought and not pursued any further for the synthesis of nanoparticle oxides. An alternate method of synthesis was sought, ideally something simple in nature that would have limited chemical interaction to limit contamination. Our group settled on solution combustion synthesis, which will be described in more detail in the next section.

Solution Combustion, Template Assisted, and Microwave Assisted Combustion Synthesis of YAG

Introduction

This portion of work extended throughout 2016 and into 2017, performed concurrent to the ball milling studies. As previously mentioned in the Introduction, solution combustion is a method which uses a fuel to promote high temperature synthesis of materials. This paper's main focus is oxides, but it has been successfully used in the synthesis of sulfides^[95] and metals^[96]. Regarding oxides, numerous sources summarize the work performed by other groups, with the review by Varma, et al. (2016) being a particularly useful resource.^[37] Books by Patil, et al. (2008) and Rogachev & Mukasyan (2014) and a chapter by Aruna (2010) also aided greatly in the overview and understanding of the field and current state of research at the time this research was undertaken.^{[38][97][98]}

Similar to the traditional combustion synthesis is the use of a template to produce powders. The proposed mechanism taking advantage of the pores and pockets within a

sacrificial material to host the liquid and promote the formation of discrete particles. In these syntheses, polymers or another material that can be burnt off at elevated temperatures are employed as the sacrificial material.

Alternatively, the use of microwaves was explored to study the effects of its heating method on the powders developed.

This section will comprise traditional solution combustion synthesis, template assisted combustion synthesis, and microwave assisted solution combustion synthesis. For the reader's benefit it may be pertinent to note that solution combustion synthesis is arguably a subset of sol-gel combustion and similar to foaming techniques like steric entrapment and the well-known Pechini method. The commonality between these being a fuel or additive is used to assist in foaming and forming discrete nanoparticles. Hopefully this will assist others in their research if they choose to pursue one of the techniques.

Materials

Yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Strem Chemicals, 99.99%), aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Alfa Aesar, 99.999%), Cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Strem Chemicals, 99.99%), urea (Alfa Aesar, 98%), hexamethylene tetraamine (hexamine, Alfa Aesar, 99%), hydroxylamine sulfate salt ($\text{NH}_2\text{OH} \cdot \text{H}_2\text{SO}_4$, Eastman Kodak, 98%), and deionized water were all used in the synthesis of YAG from solution combustion.

Apparatus

Solutions were prepared in a CoorTek ceramic dish because of its high temperature stability and non-reactive glaze. Several MTI KSL-1100X furnaces were used to heat and perform the reactions.

Procedure – Solution Combustion

Nitrates of yttrium, aluminum, and cerium were individually weighed out while attempting to take into account for the water content and dissolved in water together to make the stoichiometric proportion of YAG. Enough of the solution was added into a CoorsTek ceramic dish to make 5 grams of powder and mixed with fuel right before being placed in the furnace. Fuels used were urea and hexamine because of their common use in the literature and hydroxylamine sulfate salt as a novel fuel for comparison to the two known and traditional fuels.

The furnace was preheated to 650°C, into which a ceramic bowl containing the homogenous mixed metal ions and fuel was placed to boil down and react. A portion of the resultant powder was then sintered in a microwave kiln for seven minutes to produce a crystalline material for XRD analysis and SEM imaging.

Procedure – Template Assisted Combustion Synthesis

An alternate templating method employed Grade 40 Whatman quantitative ashless filter paper and imbued it with a mixed solution of the metal nitrates and fuel and dried in an oven at 60°C overnight with constant air flow. The next day the filter paper was ignited and allowed to burn through to create the desired powder.

Procedure – Microwave Assisted Combustion Synthesis

Microwave assisted solution combustion was also attempted using a Panasonic NN-SN661SAZ 1200W microwave. Solutions were mixed as in the traditional method, but instead of being placed in a preheated furnace, the solutions were boiled down and

combusted in the microwave cavity. This usually took >30 minutes because of the water to be boiled off and heating up required for combustion to take place.

Results

Traditional synthesis was finished in the furnace in under ten minutes and the powder had cooled enough to be handled. A urea based combustion synthesis done outside of the furnace can be seen in Figure 11 to show the boiling and decomposition of the mixture over a Meker burner, resulting in a skeleton of the oxide powders. The XRD patterns of the traditional powder made with urea, hexamine, and hydroxylamine sulfate salt can be seen in Figure 12. These patterns matched the standard with no obvious secondary phases present.

The three syntheses may not differ much in XRD, but in the SEM images compiled in Figure 13 dramatic differences can be seen. The material from urea-based synthesis has the most sphere-like particles, but they are all necked to neighbors forming hard agglomerates. The hexamine sample has large particles with no distinguishable nanoparticles comprising the larger pieces. This may be due to the higher heat of combustion that hexamine is known to have per mole of material caused densification of the particles. Last, the hydroxylamine sample shows some porous material and thin flakes. These materials do not match the nanoparticles shown in the literature and deviate significantly from the promise of acceptable nanoparticles.

The shortcomings of the traditional method to produce viable product initially led to the use of a template method. The idea is that the filter paper provides a backbone and pockets for particles to form in during the reaction. Pictures from this synthesis can be seen

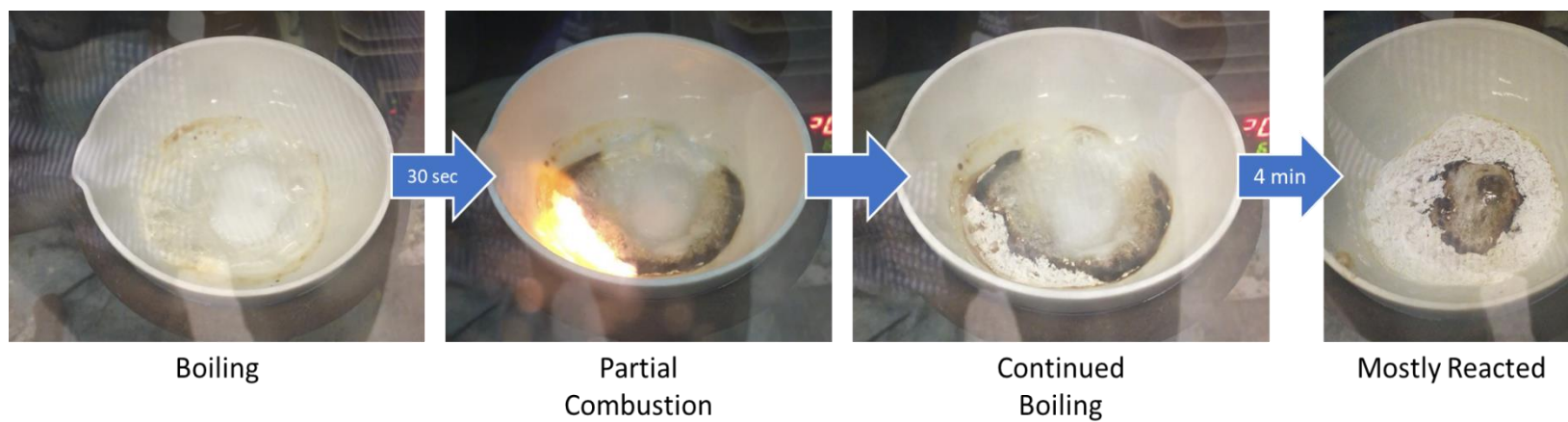


Figure 11 Traditional combustion synthesis performed over a Meker burner for easier viewing.

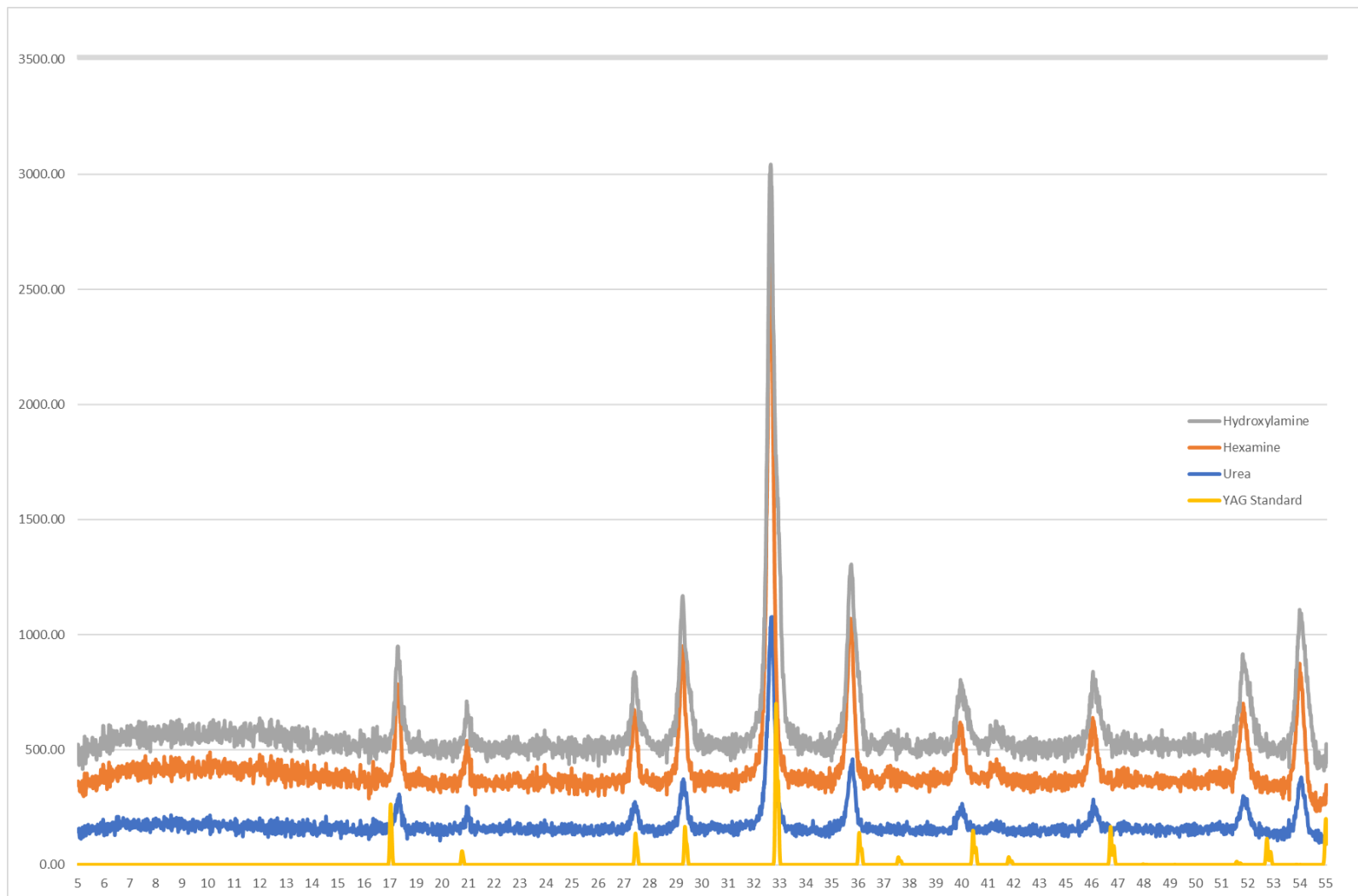


Figure 12 XRD pattern of the results from the combustion syntheses which have been sintered in a furnace at 900°C to obtain a crystalline pattern. A YAG standard from NIST is referenced for comparison.

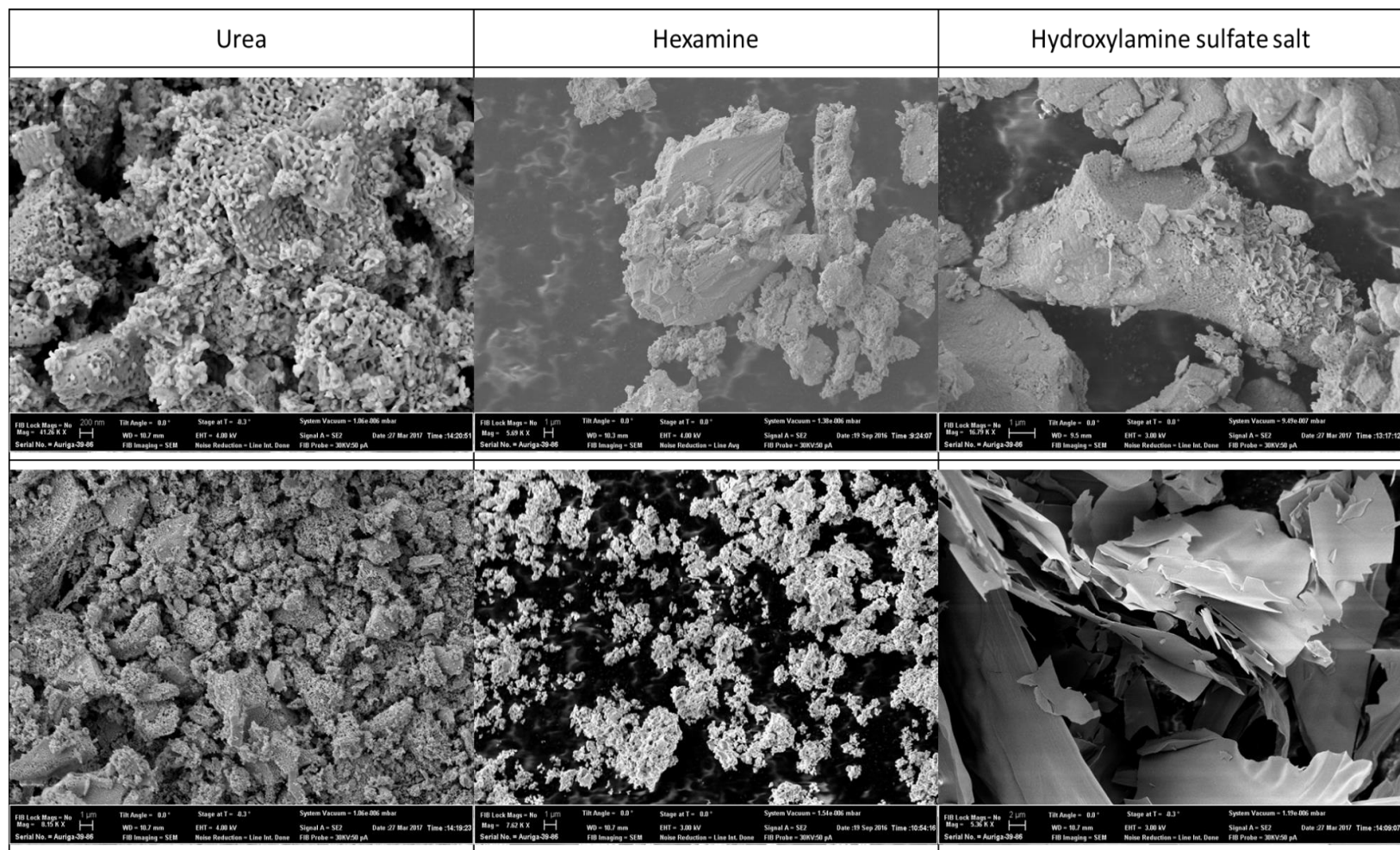


Figure 13 SEM images of the results from combustion syntheses. Only the top left urea image is a 200nm scale bar, the others are 1 or 2 μ m scale bars.

in Figure 14 showing the already ignited filter paper as the flame front travels across the paper. The unexpected resulting carbon left over was too difficult to remove from the powder, leading to the need for another method.

Microwave heating was suggested as an alternative to furnace heating because of its ability to heat more thoroughly. The synthesis mimicked the urea-YAG mixture from the furnaces and was heated in the microwave to drive off water and eventually lead to combustion. Resulting from this synthesis is a powder similar to that of the traditional synthesis and in Figure 15 is an XRD pattern which has significant presence of secondary phases. This represented a less than desirable outcome. Further, the use of a microwave did not reduce the effects of the corrosive gases, as shown in Figure 16 of the ejection of powder from a reaction, the high temperature breaking the floor of the microwave cavity and exposing the underlying microwave stirrer, and corrosion of the steel on the back wall of the cavity.

Also evident in Figure 16 is the colored powder ejected from the reaction, which demonstrates the high temperatures were capable of sintering the YAG:Ce. The high temperatures prevent phases from rectifying and sequester material from the desired phase and make it difficult to achieve a bulk material from phase-impure powders. Another difficulty is the batch-wise nature of this technique which limits production of larger quantities and requires larger apparatuses to produce material in amounts that can be used for studies of ceramics processing from a consistent source.

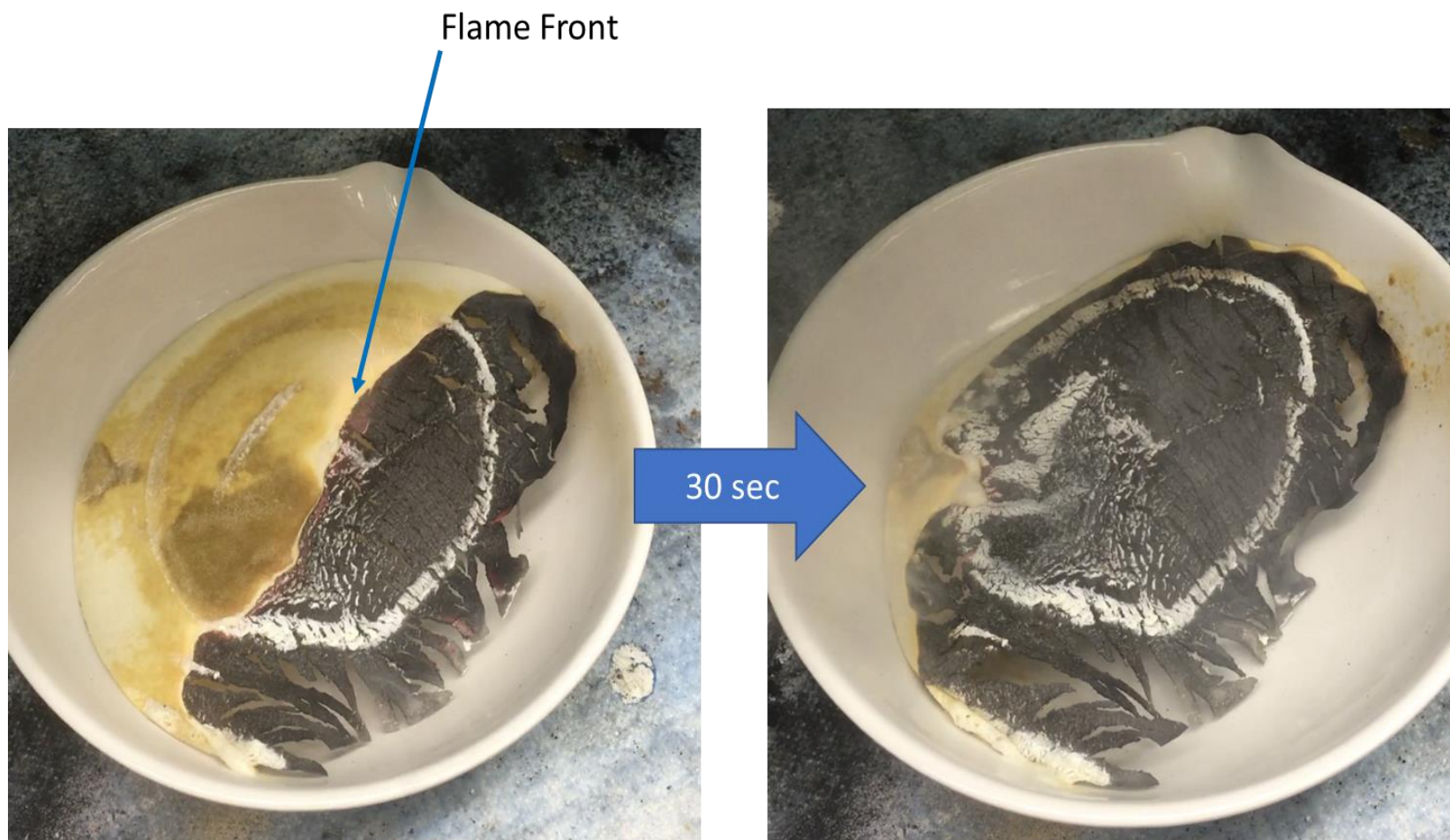


Figure 14 Pictures of a cellulose filter paper imbued with a metal nitrate and urea solution. The flame front can be seen travelling across the experiment.

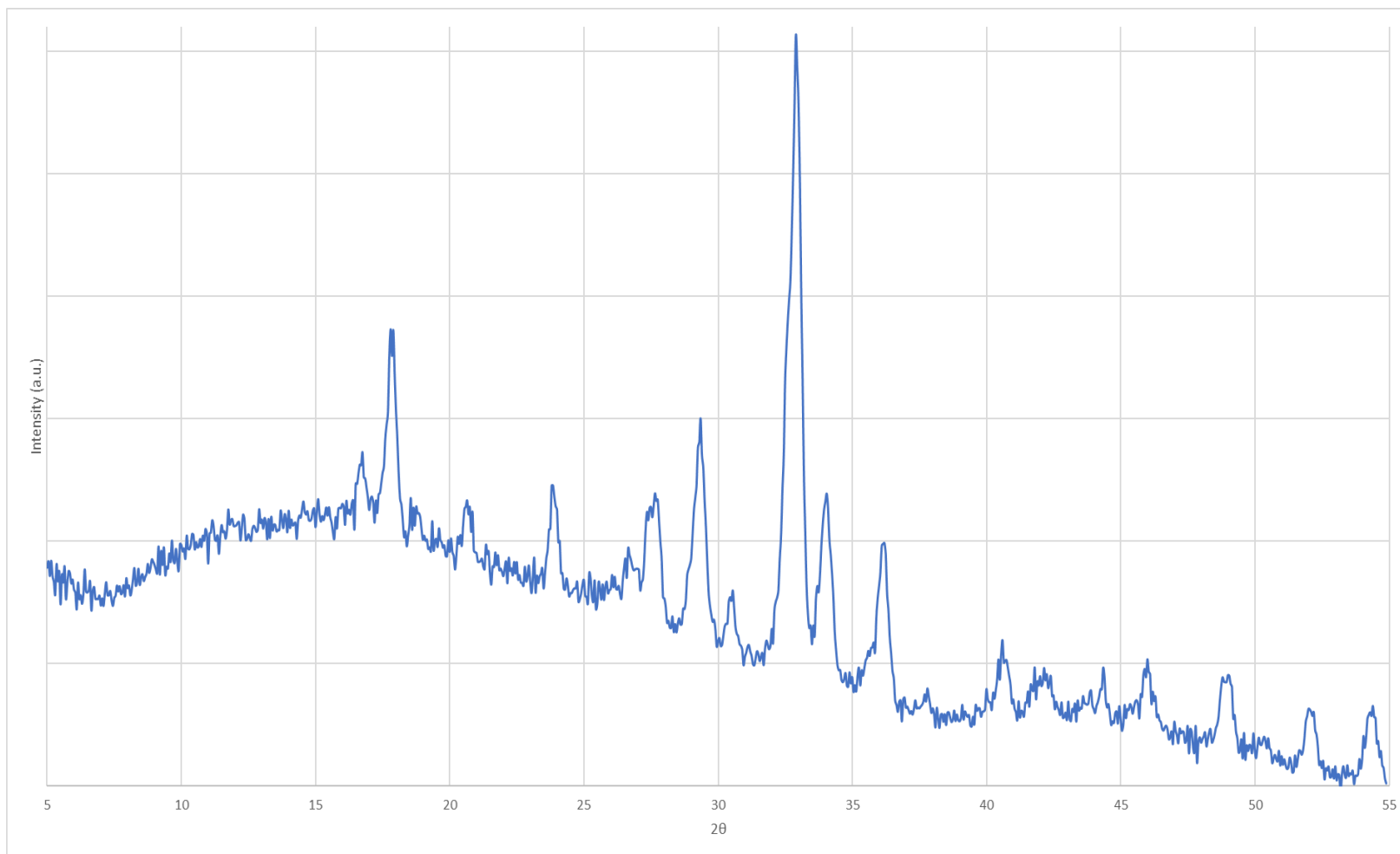


Figure 15 XRD pattern of the microwave assisted combustion synthesis using urea.



Figure 16 Example of the corrosion and wear from repeated use in microwave assisted solution combustion synthesis experiments.

Conclusion

In this section combustion synthesis was attempted using three different approaches, but ones that share the same basic methodology of using a fuel mixed in a metal ion solution to promote a vigorous reaction once boiled down and exposed to high temperatures or consistent heating. None of the methods attempted lived up the simplicity promoted in the literature and proved to be more laborious than expected.

Morphologies were not consistent among samples produced with different fuels in attempts to find an ideal additive that would work similar to literature. XRD patterns for those produced by microwaves were found to contain secondary phases that represent species segregation in the sample. Further, the noxious fumes from the reactions corroded several furnaces and two microwaves which represents a significant financial investment for most labs. These results are not useful for producing nanopowders which can be used in the densification of powders to make bulk ceramics. Because of this, these methods were no longer pursued, and resources were diverted to another technique that could potentially produce powders that are workable in a larger quantity.

Flame Spray Pyrolysis for the Synthesis of YAG

Introduction

Work performed in this section was undertaken in 2018 to 2019. A major portion of this work was done in a private lab which cannot be reported on because of a nondisclosure agreement. However, the work from this lab can be noted.

As mentioned in the introduction, flame spray pyrolysis (FSP) is one of the more well-known syntheses to produce simple and complex oxide nanopowders.^[53] Researchers tout its high throughput capacity and simple methodology as the key reasons it is applicable for larger scale applications.^[57] We had the good fortune of collaborating with notable researchers in the field and using a machine designed by them to produce some materials under more refined circumstances. From this experience we endeavored to explore FSP even in a rudimentary fashion, with off the shelf parts to cobble together a setup capable of mirroring the general approach noted in the literature.

Described here is the initial attempt to build a flame spray apparatus from off-the-shelf parts with minimal modifications and results compared to material produced by an industrial machine. Finally, a closer look at the powders produced and comparison of their morphologies to see how these results align with the expanded criteria were made.

Materials

Yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Strem Chemicals, 99.99%), aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Alfa Aesar, 99.999%), Cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Strem Chemicals, 99.99%), isopropanol (Fisher Scientific, HPLC grade), diethyleneglycol monobutylether (DEGMBE, Sigma Aldrich, 99%), 2-ethylhexanoic acid (2-EHA, Sigma Aldrich, 99%), n-xylene (Sigma Aldrich, 99%), and deionized water were used to make the component mixtures for the FSP stocks solutions.

Apparatus

A Meinhard Type-K ICP nozzle was setup to receive the liquid stream of the FSP precursor and mixed flow of gases to aspirate the liquid. Two centimeters away from the nozzle tip a Bunsen burner was positioned to provide a pilot light to help maintain a flame. Liquid is flowed to the nozzle by a Cole-Parmer peristaltic pump with LS 13 tubing.

Following the nozzle is a Pyrex glass tube which tapers to a 5cm opening to fit to a MetroVac Datovac vacuum cleaner with a linear flow body. A medical ankle wrap was affixed to flow cold water around the body of the vacuum cleaner to limit high temperature exposure of the vacuum motor. Cooling was done with an ActiveAqua water chiller and aquarium pump. The outflow of the vacuum cleaner is directed through a flexible steel wire wrapped tube to meet a trunk line of the fume hood system.

Material resulting from the pyrolysis was collected by a 0.2 μm paper vacuum bag stuffed with fiber glass for dispersing heat and to provide ample surface area for the capturing of particles which entered.

The general setup can be seen in Figure 17 showing the nozzle and burn area. The top portion of the picture concerns the testing of an isopropanol solution to modify flow rates and test burn safety. The lower picture is the nozzle in use attempting to make YAG. The need to aspirate to form the droplets of flammable precursor containing solution led to the use of a ICP nozzle. This nozzle's nebulization relies on gas flow to propel the droplets, and this gas can be made from a premixed fuel, like oxygen and hydrogen to make a highly exothermic flame. To keep the flame alight a pilot light of air/propane was used. For safety and containment of the flame, a long, wide Pyrex tube was used to direct the air flow and

shield surroundings from the fire. Produced gases were drawn towards a vacuum to capture the particles. Flow of the solution was moderated with a peristaltic pump using LS 13 tubing for a low flow so as not to overwhelm the nozzle.

Procedure

Following the solvent system defined by Strobel and Pratsinis (2015), metal nitrates of yttrium, aluminum, and cerium were individually dissolved in water and analyzed for concentration by ICP.^[54] These were then combined in the ratio for YAG ($\text{Y}_{2.98}\text{Al}_5\text{Ce}_{0.02}\text{O}_{12}$) intended to make a desired amount of powder and boiled down in a large boiling dish to create a viscous syrup and reduce water content. After cooling completely, ethyl alcohol was added while stirring the viscous metal nitrate syrup until the mixture was homogenous. Following this DEGMBE was added, followed by 2-EHA, and finally n-xylene in a 2:1:1:1 ratio of alcohol, ether, carboxylic acid, and xylene.

This was either used immediately or sprayed a month after the preparation. Phase separation was evident after sitting for the month, so extra alcohol was added to homogenize the solution and prolong the shelf life of ready-made solutions. After a long enough time, the total amount became a 3:1:1:1 ratio before it was used.

Results and Discussion

A ready-made flame spray apparatus costs as little as \$25,000, which is more than an exploratory investigation would like to commit. The apparatus used was modular in its setup due to the use of off-the-shelf parts. This setup did struggle with particle capture, which is not an unknown problem to the flame spray community. The dissertation of a N.

J. Taylor (2015) and their group's investigations of an electrostatic collector, "current [collector] design offers the collection efficiencies which peak at 70% and often dip below 50%."^[99] This corroborates the difficulty this field has with particle capture, coming from a student of one of the major research groups for FSP in the United States. Other researchers have also noted the difficulties with particle capture from this method, with optimal conditions also having 70% collection efficiency.^{[53][100][101]}

Dissolving of the metal nitrates and homogenization with alcohol presented an interesting problem if the solution was not cooled entirely. The alcohol was readily attacked by the nitrates to make nitrate esters in a runaway exothermic reaction that several precursors were lost to. As shown in Figure 18 is the result of one of these runaway reactions that was not cooled completely. Please note the drenched pig mat that was laid down in case of this event to absorb liquid and contain the spill and make clean up easier. Not shown in this picture, because of sudden reactivity, is the initial bubbling and evolution of brown NO_x gas which preempts this event. The stark yellow color of the solution is attributed to residual NO_x dissolved in the liquid. Chapter 5 of the book *Liquid Explosives* notes that this reaction is not unusual and common and wanted for other energetic applications.^[102] Analysis of the resulting product was never performed to determine if the product was the nitrate ester.

Another point of interest was the separation of the solution as it sat for any period of time, two layers could be seen. This might be due to a catalytic reaction of the alcohol and carboxylic acid with the cerium catalyzing an esterification.^[103] Addition of alcohol would merge these two layers temporarily, but as it continued to sit the layers would

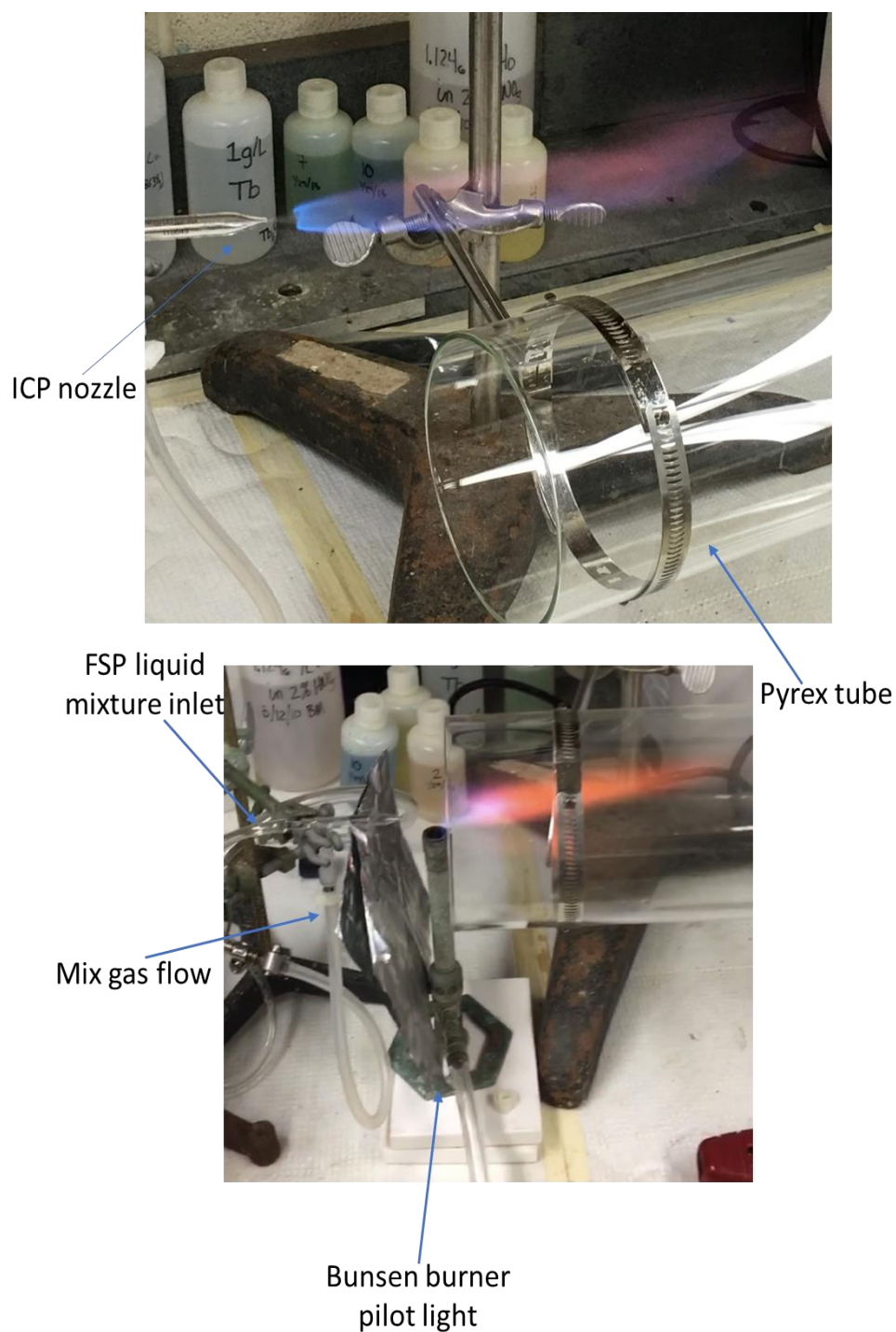


Figure 17 Top is a picture of testing the nozzle's flow with alcohol to simulate the FSP mixture. Bottom is the nozzle in position of the setup spraying the FSP mixture through the pilot light and down the tube to the filter

separate more distinctly than previous, and this would continue until used. No analysis was performed on the two layers except a crude evaporation to confirm that metals had migrated into both layers. It was determined that solutions should not sit and should be prepared immediately before use, so separation does not occur.

Regarding results from the spray pyrolysis, Figure 19 shows a compilation of SEM images from our lab's homemade apparatus. The materials, while nano in size were agglomerated and jagged. This is not ideal for the spherical material desired. Further, this material was recovered from the walls of the spray tube because little to no noticeable quantity was collected in the vacuum bag, likely due to how hot the particles were to melt through the bag, fused to the fiber glass, or their size limited the ability of the filter to capture them. Not enough material was obtained to get a discernable PXRD pattern.

For the professional, industrial grade apparatus, SEM images results can be seen in Figure 20. Many of the particles are spheres, but there are some which are not completely spherical in morphology. Also, the size distribution is not entirely consistent as can be seen by the larger spheres surrounded by smaller ones. Figure 20's upper left image shows a large cluster of spheres which makes the inconsistent size distribution more apparent.

Conclusion

This technique is quite simple in its approach and execution: dissolve metal ions in a flammable liquid, nebulize, and ignite to achieve discrete particles. The basics of this techniques have been well studied and groups continue to investigate improvements and variations of it to broaden its reach and applications. In our group's studies this technique fell short to meet an ideal method because of how dilute the solutions had to be to achieve

viable spray and the inconsistency in particle size. Industrially produced powders have limitations regarding homogenous size distributions, but they convey the promise of this technique better than our attempt.

Further, safety of the homemade apparatus left a lot to be desired and only a couple runs were performed because of fears involving the mostly contained flame, temperature of the vacuum cleaner used to promote air flow to the filter, and limitations of particle capture. Safety in the solution preparation was also a concern with the boil overs resulting from additions of alcohol. For these reasons, this method was not pursued much further. Ultimately, a method with a simpler preparation of materials, more uniform particle size, and higher concentration tolerance in the method would be extremely beneficial. These points will be explored by the classic method of precipitation.

Coprecipitation of YAG

Introduction

Work performed in this section took place over the course of 2019 into 2021. Inorganic precipitations are a conventional technique for the synthesis of materials using the combination of a metal ion and a specific anion to promote the formation of an insoluble salt. In the case of YAG and other oxides, these cannot be produced outright by precipitation, but intermediates for further treatment can be produced, unlike the previous sections which were capable of producing oxides but had limited control of particle sizes and morphologies.



Figure 18 An example of a boil over if the solution was not fully cooled and alcohol was added. The darker yellow color is attributed to dissolved NO_x.

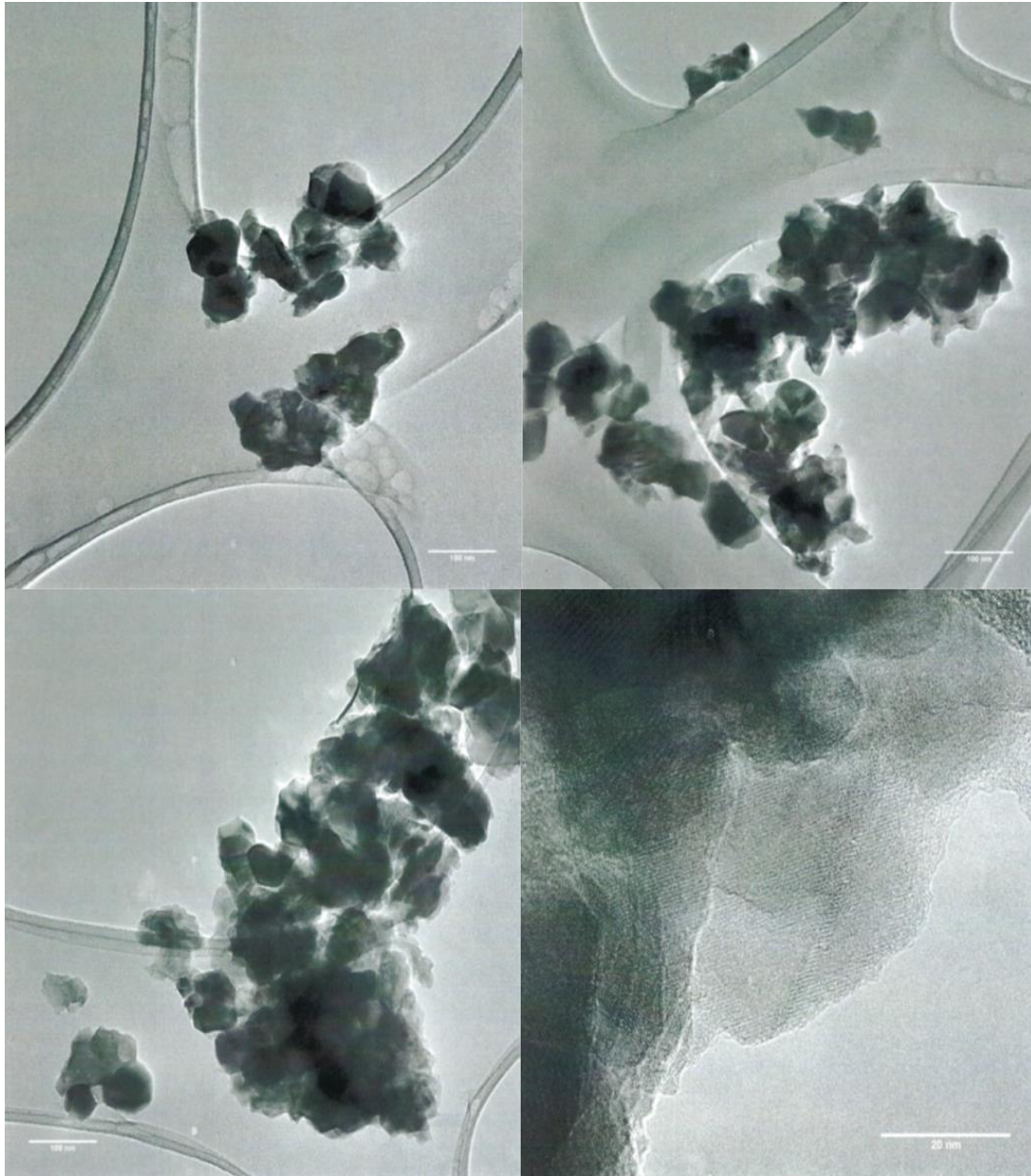


Figure 19 SEM images of the particles produced with the homemade setup. Note the jagged features and lack of any sphericity. This material was scraped from the walls of the tube, not captured in the filter which may contribute to their lack of sphericity.

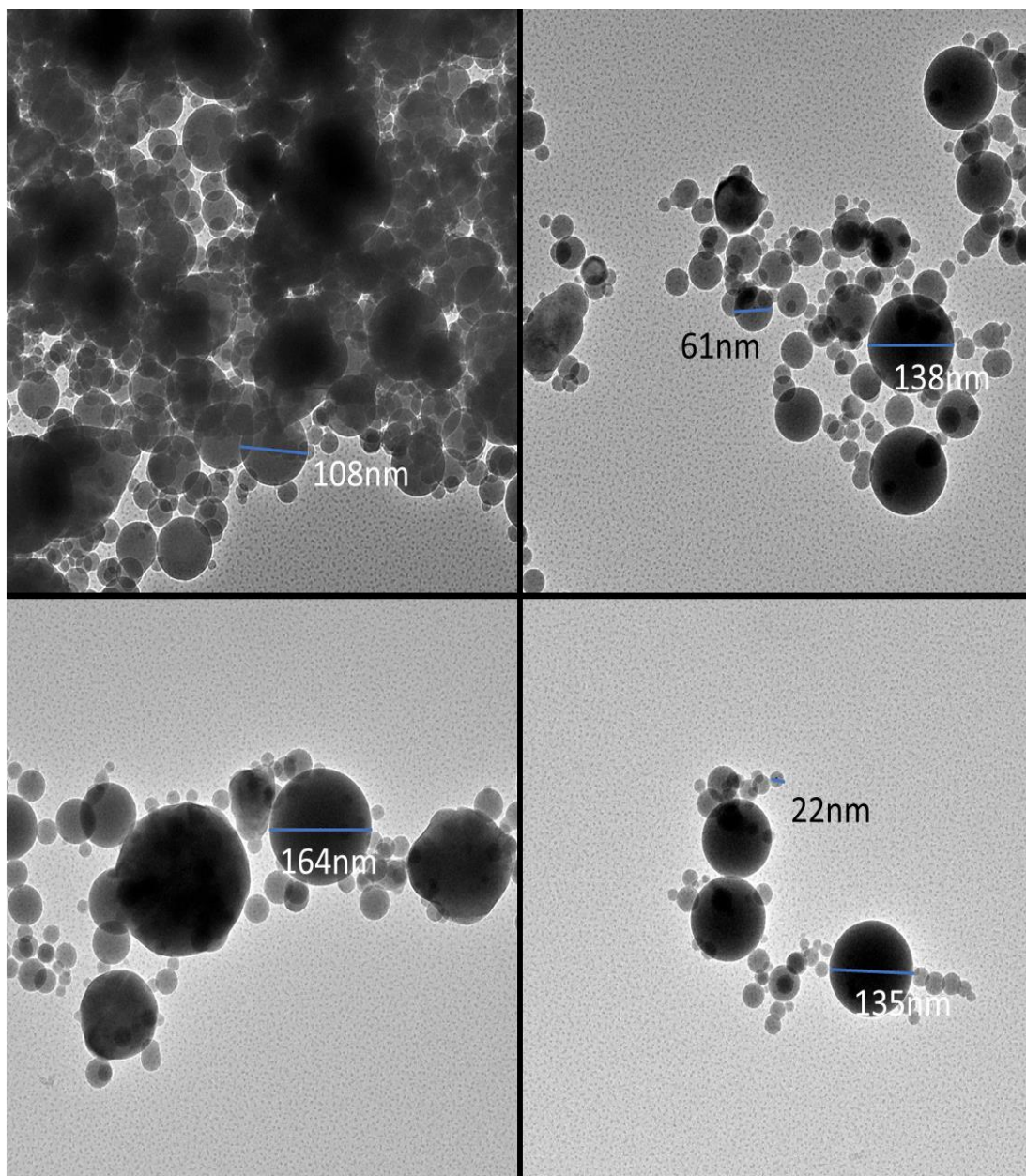


Figure 20 Particles prepared by a professional apparatus. These particles are more spherical with some morphological outliers. The size can vary drastically in these powders.

Precursors in precipitation of materials to eventually make oxides can range from oxalates^[104], carbonates^[105], and hydroxides^{[105][106]}. Some techniques will use soaps as well to take advantage of physical steric buffers to make nanoparticles.^[107] Hydroxides are not just limited to ammonium or sodium hydroxide, they can also be formed through by heating urea^[108] or amines^{[76][109]}. This is one of the benefits to precipitation, the varied approaches for precipitations of inorganic materials. For YAG specifically, ammonium bicarbonate has the strongest literature presence because of its ability to buffer at the ideal pH and low cost.^[110]

The method of combining solutions is also known to play a role in the formation of particles, with aluminum and yttrium have different insolubilities as pH increases. As such, the technique known as a ‘reverse strike’ was used where the metal ions solution is added to the precipitating solution.^[106] This ensures a constant pH is maintained, depositing the metal ions out of solution at the same time making them more homogenous.

Researchers have also improved precipitation’s yield by using alcohol, ethanol or isopropanol, which can broaden the window for complete precipitation by lowering the solubility of metal species more than is seen in water.^{[77][111][112]} Further, alcohols have also been investigated for their benefits in dispersing freshly precipitated material through an interaction with the surface hydroxides.^[113]

YAG has been made by several methods, as mentioned in the Introduction (Chapter 1), but here the exploration of alcohol’s influence on powder synthesis will be examined. This section will explore the basics of coprecipitation of YAG using

ammonium bicarbonate as the precipitant and ultimately evaluating how the product meets the criteria of the chart laid out in the introduction in a summary section.

Materials

Yttrium oxide (Strem, 99.99%), aluminum metal (Alfa Aesar, 99.999%), cerium nitrate (Strem, 99.99%), ammonium bicarbonate (Acros Organics, 99%), isopropanol (Fisher Scientific, HPLC grade), water (Fisher Scientific, 18M Ω) were used in the synthesis of carbonate precursors to YAG powders.

YAG precursor composed of metal nitrates was prepared by dissolving known quantities yttrium oxide and aluminum metal in nitric acid to give specific quantities. A solution of cerium nitrate was prepared previously and standardized via pyrolysis to get a g (CeO₂)/g (liquid) quantity to add the correct amount to the combined Y/Al solution. Usually, these solutions were prepared to make 500g of YAG:Ce total and portions to make 25g of oxide were taken to test larger quantity synthesis and know that all materials can from a single, homogenous source. Solutions were then diluted to a mix of 50/50 water and isopropanol.

Initial reports indicate that dropwise precipitation can be done with a sufficiently dilute solution, typically less than 0.1M, to make nanoparticles with the use of ammonium bicarbonate. Hydroxide precipitations were avoided due to the gelatinous nature of the hydroxides and not enough confidence that these would remain unagglomerated.^[114]

Apparatus

Figure 20 shows the precipitation setup. Overhead stirring by a PTFE agitator was maintained at 1000rpm in a 2000mL beaker. A Cole-Parmer peristaltic pump was used with LS13 tubing to draw solution through and to the precipitating solution at a rate of 10mL per minute.

Procedure

Two experiment types were conducted: one solely in water with the precipitant in a 3:1 molar ratio to total metal ion concentration, and a second experiment where the water was mixed with alcohol in a 50/50 ratio using the same excess of precipitant. All of these were conducted in a ‘reverse strike’ manner where the metal ion solution is added to the precipitant. This avoided segregation of insoluble species by preferential precipitation of the yttrium first, followed by the aluminum as the pH increased.

The setup was initially primed with a mix 1:1 water and isopropanol and following the conclusion of the metal solution, the lines were washed with the same mixture. The solutions were gravity filtered and calcined in a muffle furnace. Heating was done at a rate of 5°C/min to 650°C and held for 3 hours under air.

Results and Discussion

To test the effects of alcohol on the precipitation, samples were prepared both with and without alcohol to similar dilution levels. One sample was even washed with only alcohol. The samples which had alcohol showed no residual metal ions in the eluent, whereas those which had no alcohol showed some aluminum had been lost, and the

samples with no alcohol but washed with alcohol in the filter showed aluminum in the original eluent, but none in the wash liquid. This corroborates what was seen in other papers. Cerium was not recorded in this because its concentration would have been below detectable levels after dilution.

Ammonium bicarbonate was used to precipitate the powder in water under rapid stirring. SEM images of some of the samples can be seen in Figure 22. Because of the use of carbonate, yttrium carbonate flakes can be seen as a major component of the samples. This is likely due to the bulk addition of the metal ions via a drop which enable the nucleation and sequestering of yttrium.^[115]

The field of YAG syntheses has employed an alcohol-water mixture for precipitations because alcohol can yield a finer powder by interacting with the surface hydroxides. Particles in Figure 23 shows powder made by precipitation in a mixture of 1:1 alcohol to water. Compared to the previous water-only precipitation where large flakes and agglomerates can be seen, this powder is less agglomerated, but still has some large particles. These particles are mostly spherical in shape.

Conclusion

Dropwise precipitation has numerous variables to manipulate from the solvent composition, concentration, method of addition, and precipitant. The addition and influence of alcohol upon the synthesis of YAG was explored and demonstrated a stark influence, reducing agglomeration and making more fine powders, consistent with the literature. However, its need for low concentrations ($<0.1\text{M}$) of metal ions to make nanoparticles is not ideal because of large volume of liquid that need be used. Further, the

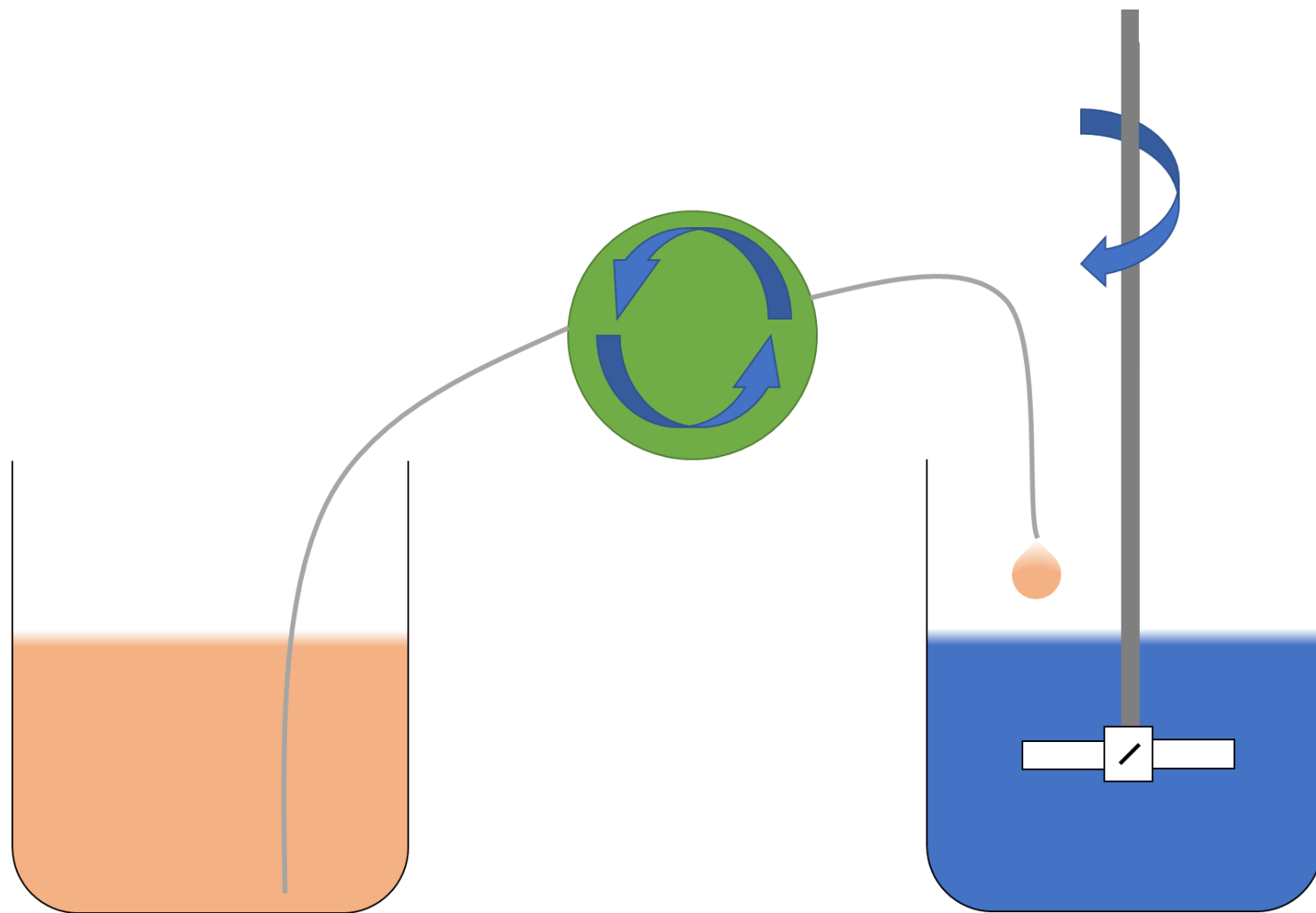


Figure 21 Diagram of the dropwise precipitation setup

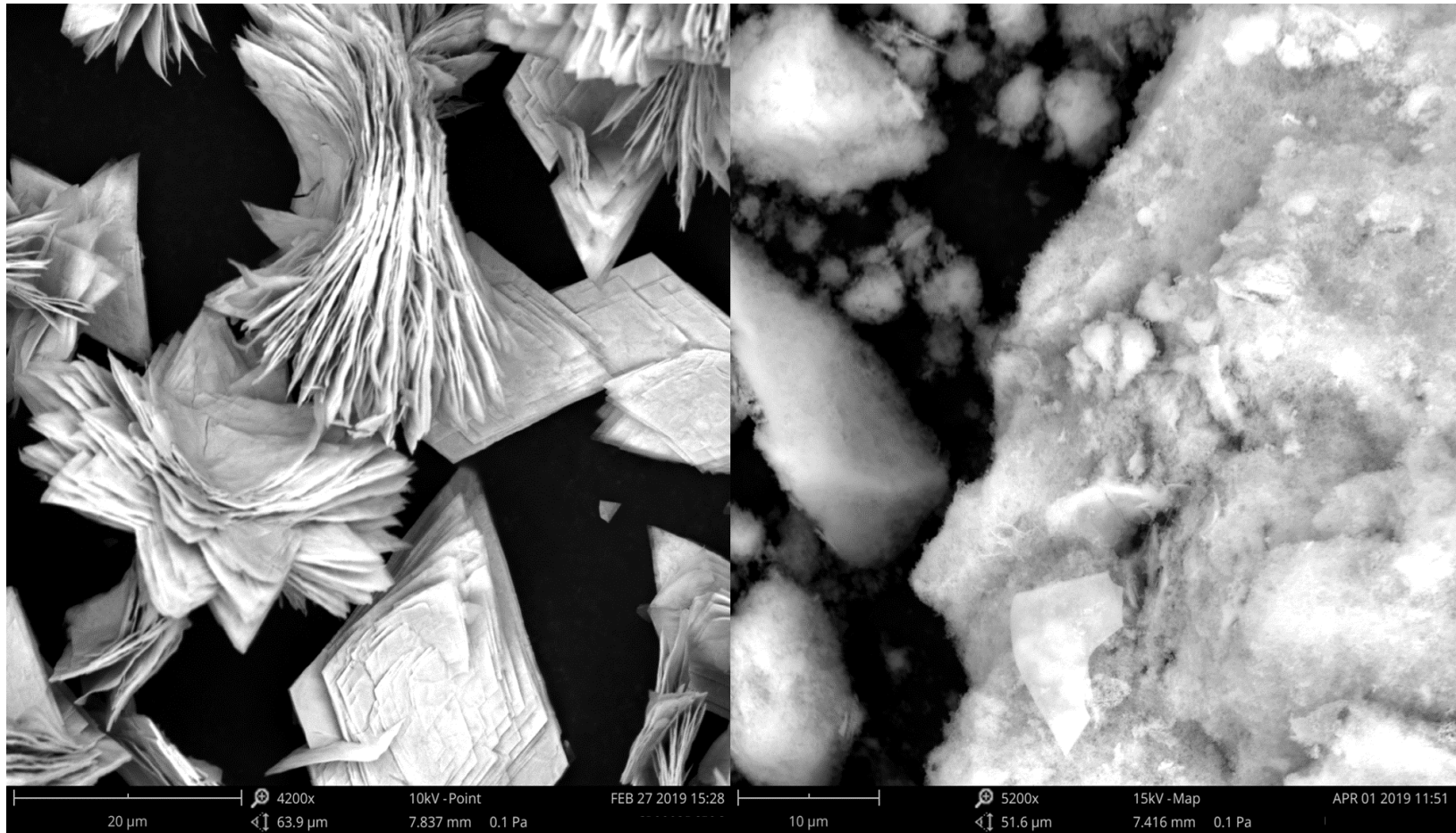


Figure 22 SEM images of precipitation of YAG in water with ammonium bicarbonate

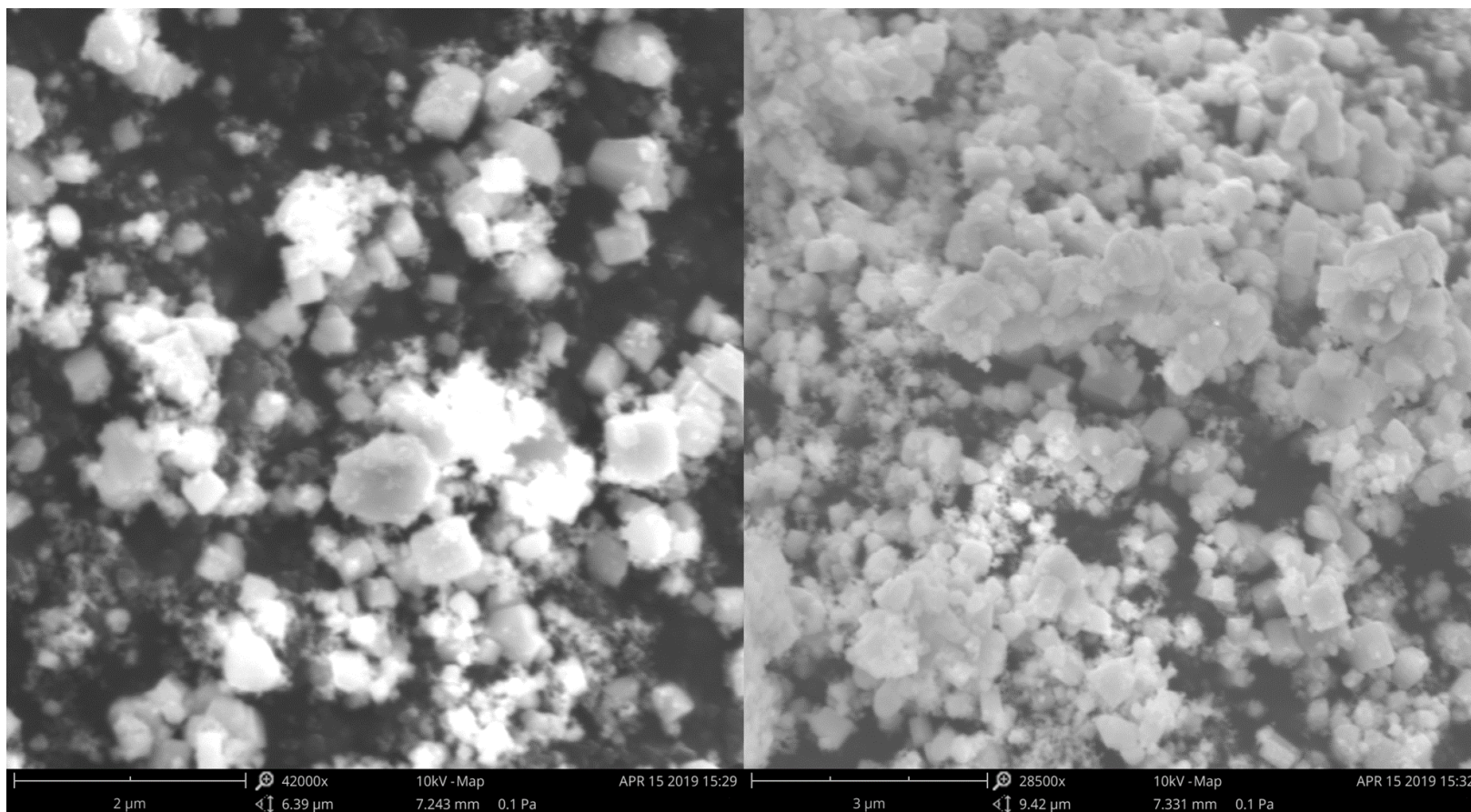


Figure 23 SEM images of the water/alcohol precipitation powders

need for further processing of the carbonate powder inputs another step that previous syntheses avoided. Ideally, there is a way to decompose the carbonate and process the material into a hydroxide or oxide without modifying it or sintering the powder. Hydrothermal will be explored in the next section to understand its influence over these powders by potentially decomposing the carbonate. syntheses avoided. Ideally, there is a way to decompose the carbonate and process the material into a hydroxide or oxide without modifying it or sintering the powder. Hydrothermal will be explored in the next section to understand its influence over these powders by potentially decomposing the carbonate.

Hydrothermal Synthesis of YAG

Introduction

This portion of work was performed in spring of 2021. Hydrothermal processing has developed into a common laboratory technique for the synthesis of powders and other novel materials.^[18] Mimicking geothermal processes, the high temperatures and pressures can encourage reactions that might otherwise be difficult under traditional standard temperatures and pressures. Subcritical processing is the most easily attainable, where the solvent has not reached its critical point, but temperatures and pressures are near it.^[116]

Under subcritical conditions, hydrothermal processing performs best as a supplemental technique modifying powders derived from another approach. This soft technique can be used as an intermediate step in the synthesis of a material by promoting decoration, chemical modification, or changes via aging like size or morphology.^{[78][79][81]}

This technique was investigated to understand the impact it has on powders taken from the previous section of precipitation and to address the carbonate residue that limits processing of the powder into a full oxide. Simplicity of the technique and the low cost of an apparatus made it an appealing technique and framed how useful this technique might be to future syntheses. This portion of experimentation hopes to demonstrate our current work on manipulation of powder with high temperature and pressure treatment.

Materials

Powders, which were prepared previously by coprecipitation, were treated in a PTFE reactor. Please see the previous section for the materials and methods used to synthesize the YAG powder treated herein. Powder was transferred to the reactor as produced with its 1:1 water and isopropanol mixture and residual ammonium bicarbonate to maintain pH. No washing or separation from the original solution was done.

Apparatus

A Baoshishan hydrothermal reactor with PTFE liner capable of holding 50mL of liquid was used for the treatment of the YAG precursor powder.

Procedure

The reactor was placed inside a furnace and heated at a rate of 5°C/min to 240°C and held for up to 24 hours. The reactor is rated for 6 MPa of pressure. Materials from these reactions were calcined at 650°C for six hours or sintered at 1000°C for six hours under oxygen. Heating rates were consistent between samples at a rate of 5°C/min.

Results and Discussion

An initial test was performed for six hours on a sample of YAG prepared with ammonium bicarbonate. A sample of 25mL of the precipitation suspension was taken and added to the reactor. Below is the FTIR spectrum of the sample in Figure 23. The stretches are labelled using literature sources.^[117-119] The biggest difference between the precursor (blue) and high temperature and high pressure treated sample (orange) is the development of distinct carbonate stretches at 1500 and 1390 cm^{-1} , the loss of solvent stretches in the 2800-3350 cm^{-1} region, and the presence of more metal-oxygen stretches and bends in the $<1050 \text{ cm}^{-1}$ portion of the graph. This shows that the reactor promotes decomposition of NH_4HCO_3 , which is not surprising given that it decomposes at 42°C at atmospheric pressure. The reactor also induces a change in the material by making more metal-oxygen bonds and strong stretches of residual carbonate, indicating yttrium and aluminum carbonates remain.

Another sample from another newly precipitated sample was treated in the same manner for 24 hours to see how the material is affected by more time. Figure 24 shows the precursor with expected stretches and bends of untreated powder with water, alcohol, unreacted bicarbonate and nitrate species evident in it. After treatment the powder was centrifuged to separate it from the liquid and noticed to have split into two forms: one was a translucent powder and the other was a dense white powder, these can be seen in separate vials in Figure 25. The FTIR spectrum shows these two powders chemically different. The translucent powder shows signs of being unreacted with evidence of nitrates, carbonates and ammonium still present, meanwhile the more dense powder bears little to no resemblance to the original precursor lacking any distinct stretches or bends.

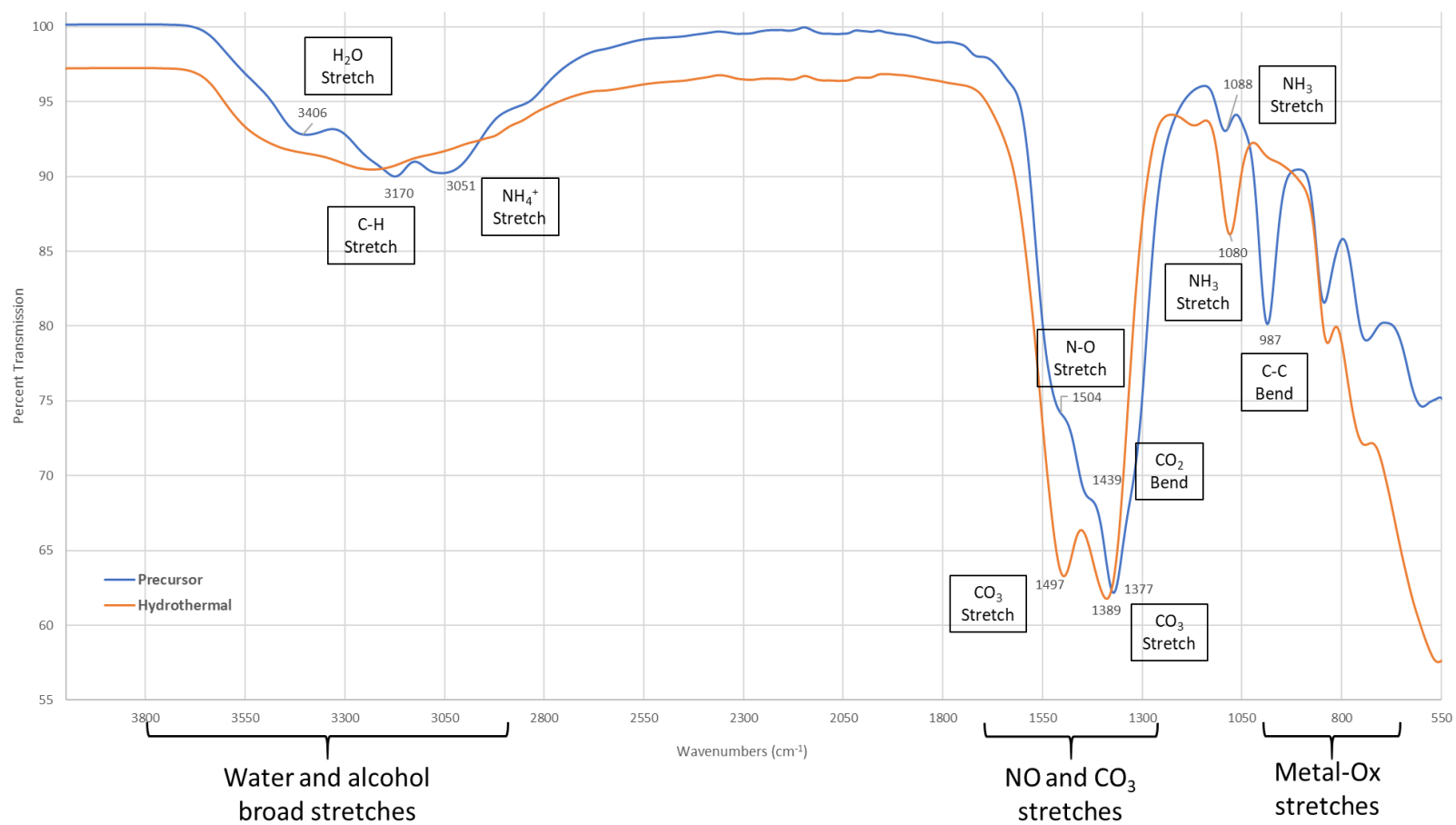


Figure 24 FTIR Stretches and bend of the hydrothermally treated powder

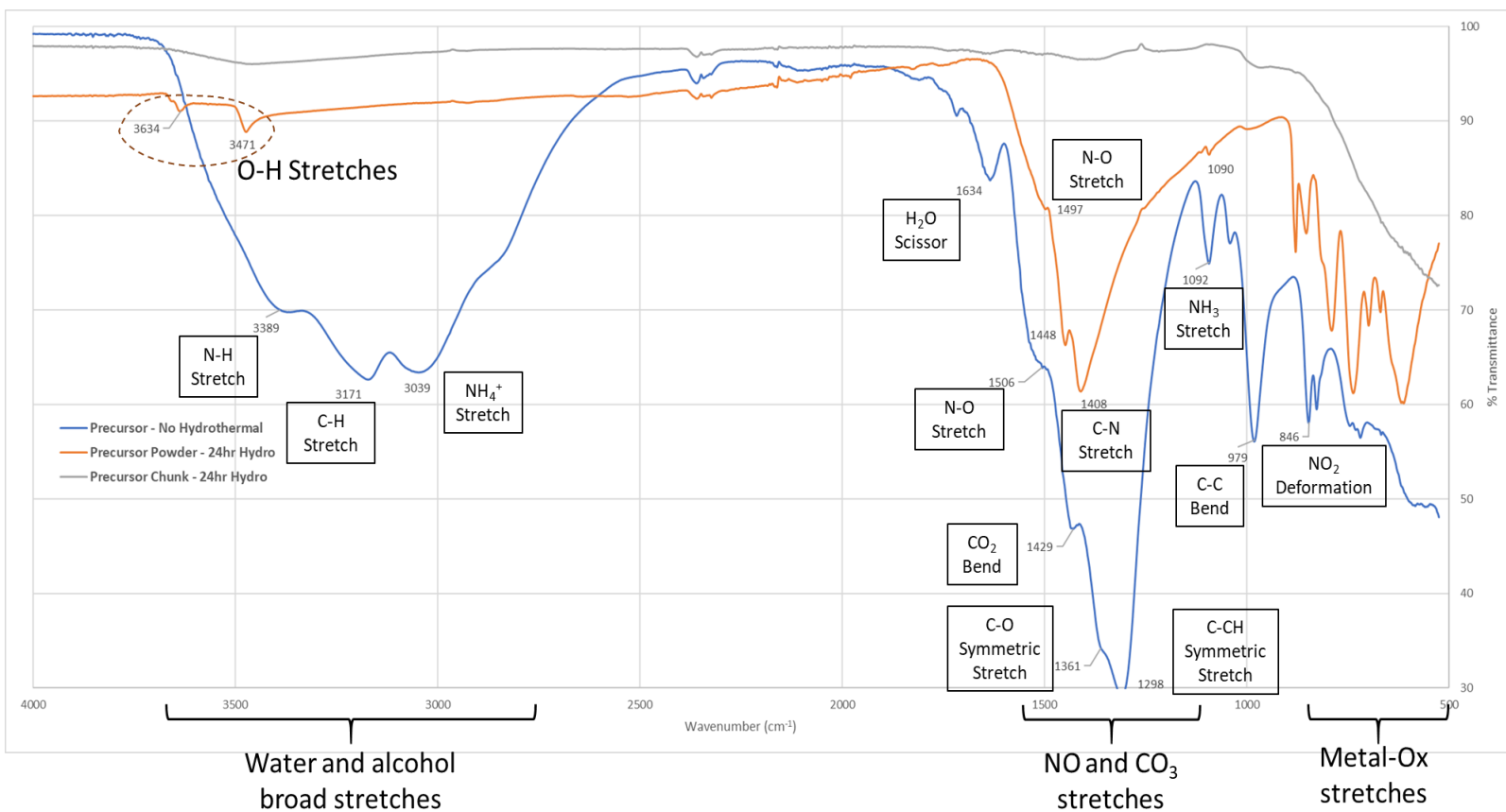


Figure 25 Comparison of the precursor and hydrothermal powders which had segregated.

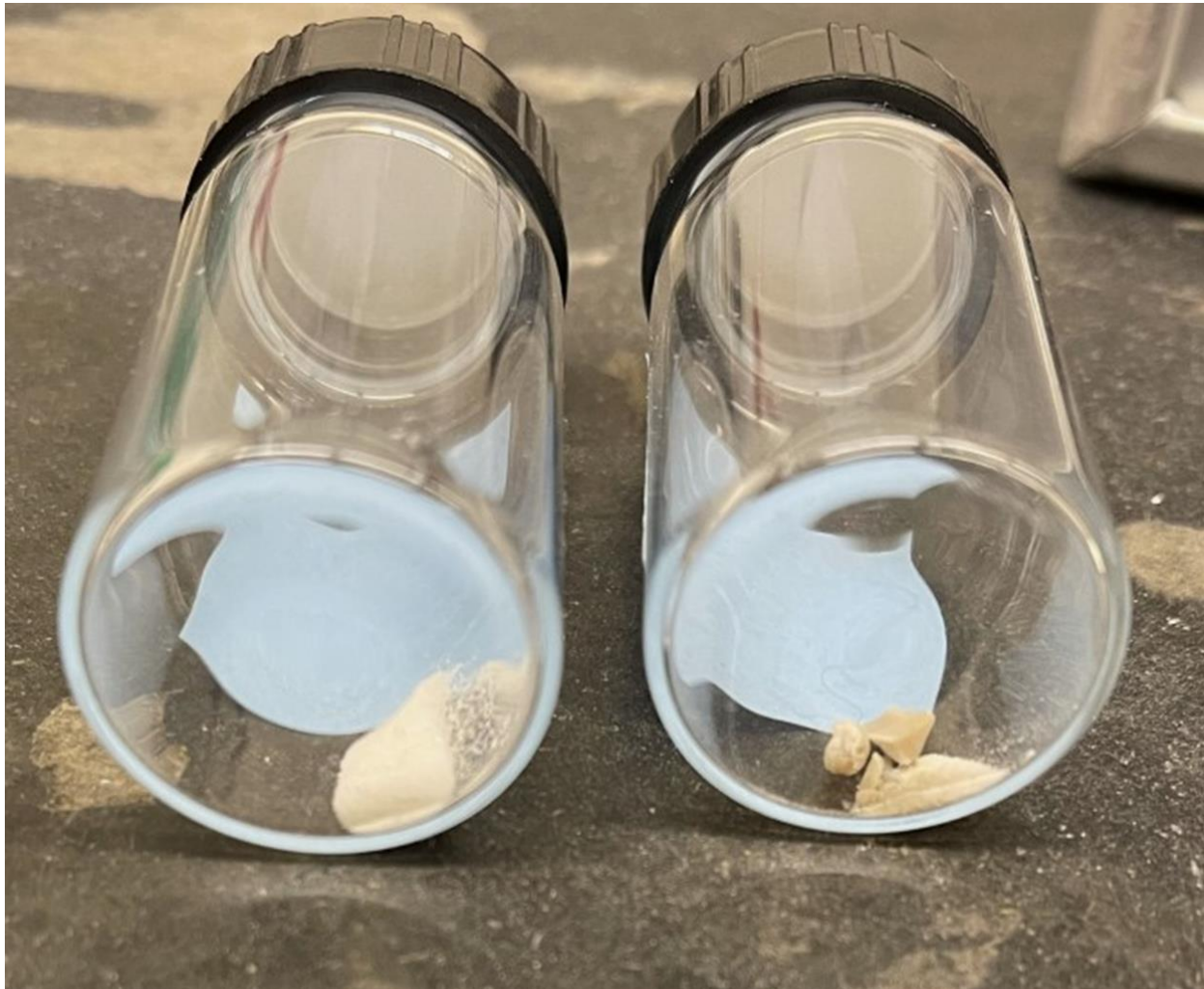


Figure 26 Picture of the segregated powder.

Continuing the study of this bisected powder derived from a singular precursor, XRD analysis was used to look for signs of a crystal structure after it was calcined at 650°C and after sintering at 1000°C. The XRD patterns of these two materials, calcined at 650°C can be seen in Figure 27. In the powder pattern (orange) the peaks correlate to a mixture of alpha and gamma phases of aluminum oxide. The yttrium species was not seen in the pattern because it likely did not form a crystalline phase, but aluminum oxide is capable of many different phases depending on synthesis conditions.^[120] This might mean the material has segregated and aluminum oxide has crystallized. The chunk material's pattern (blue) shows the same peaks, but with significantly less intensity, indicating it is more amorphous. The XRD pattern of these two calcined 1000°C for six hours under air samples can be seen in Figure 28. The resulting XRD patterns differ between the two pieces, but the phases present are not known at this time, with only small portions of yttrium oxide and aluminum oxide phases being present among the larger unknown peaks.

Because of the temperature range of this reactor, it is unlikely that the setup benefited from supercritical fluids, which are known to decompose carbonates and calcine materials in the case of supercritical water.^[121] Further, supercritical alcohol is not known to react with the reactants. Speculatively, residual nitrate may have played a role creating an autogenous reaction and making some intermediary nitrates (NO_x) which decompose the carbonates to interact with the metal ion and then decompose themselves to leave the oxyhydroxides behind.^{[119][122]} Nitrates are known to decompose at 200-230°C at atmospheric pressure and this reaction can be used for the promotion of autogenous

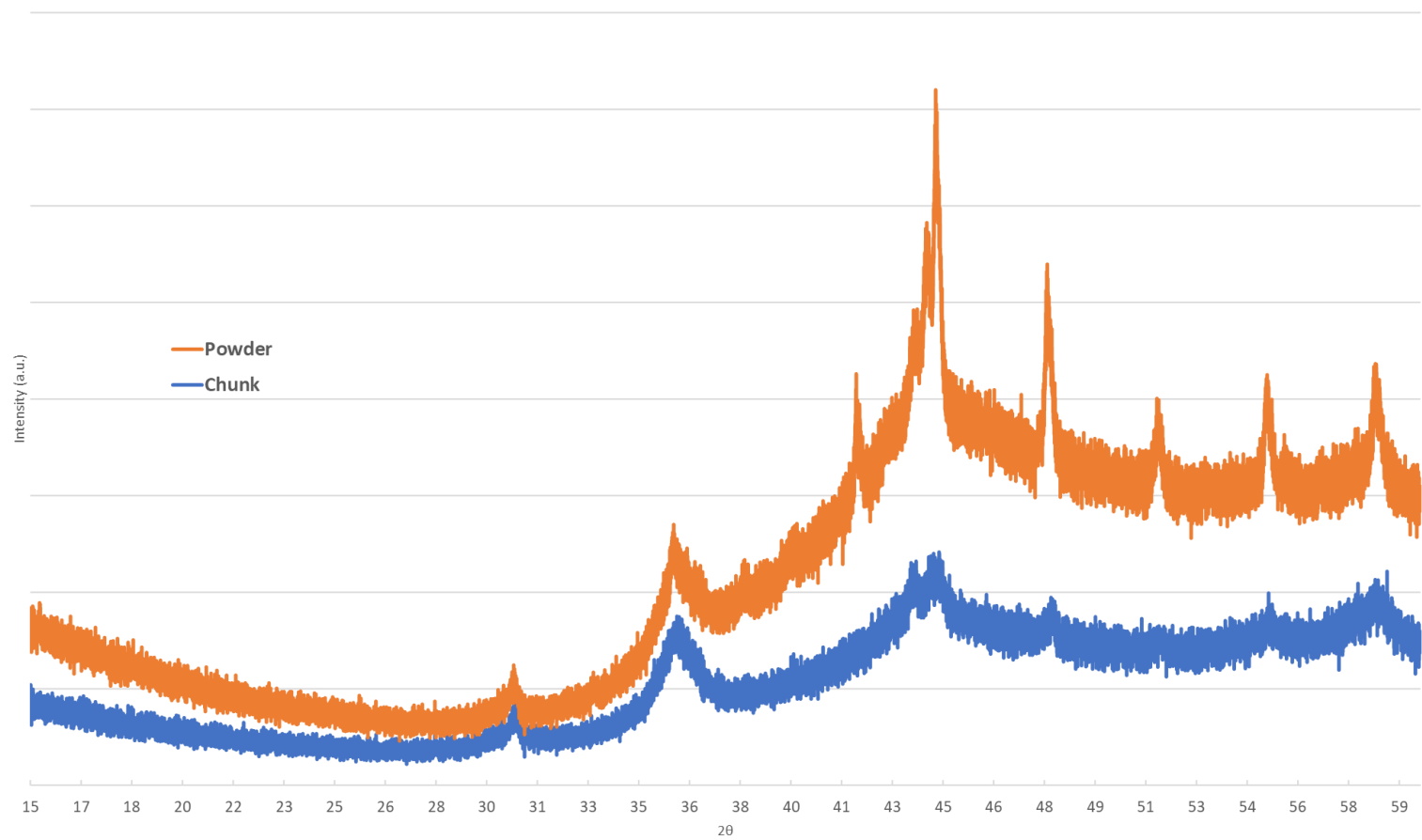


Figure 27 XRD of the segregated powders calcined at 650°C

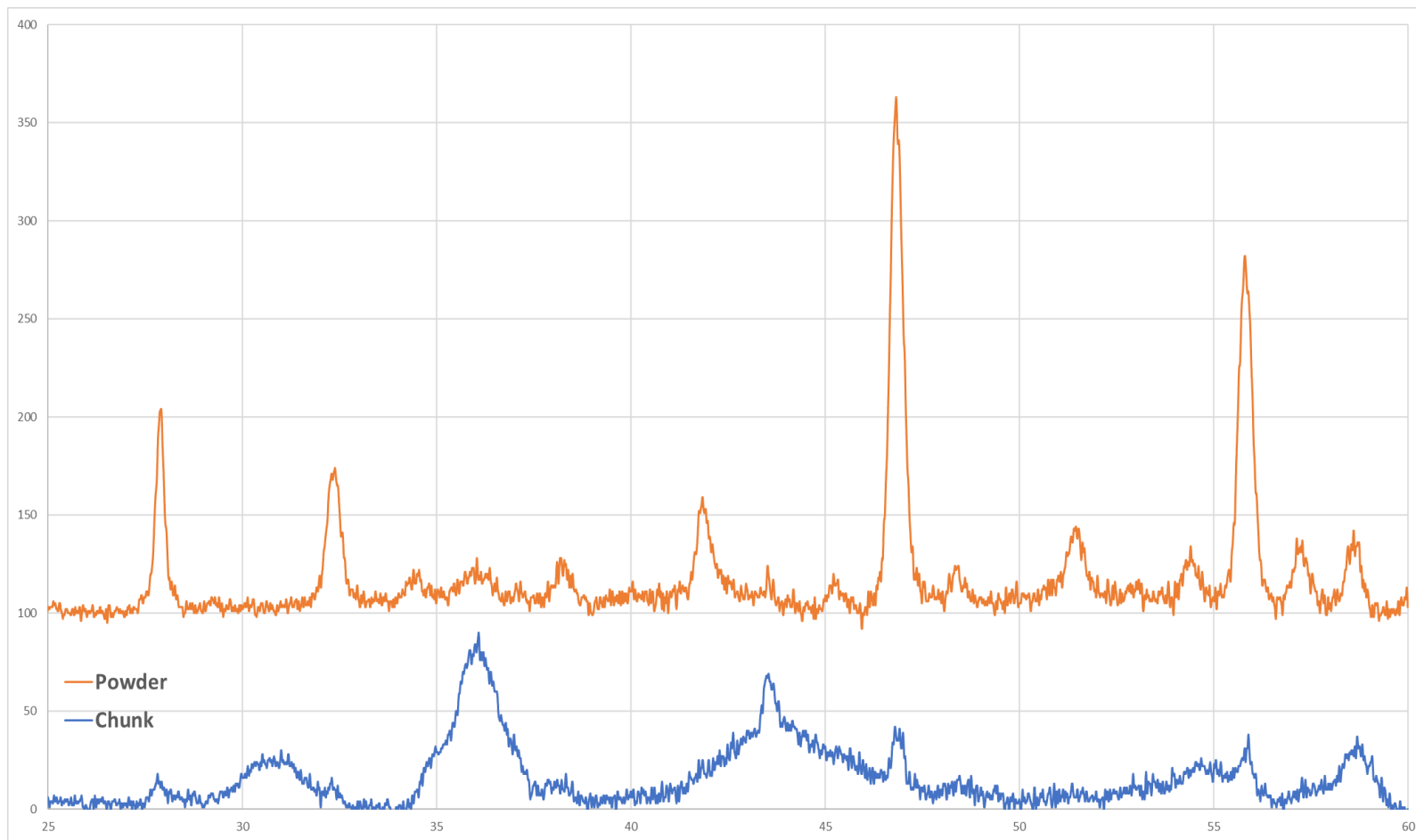


Figure 28 Comparison of the hydrothermally treated YAG precipitants sintered at 1000°C for 6 hours

autogenous reactions^[120], but the mechanism under these conditions has not been studied in much detail, likely because of the difficulty analyzing the reaction.

Conclusion

Hydrothermal treatments were chosen because they have been shown to promote significant change in carbonate material and decompose carbonate more easily at lower temperatures than traditional heating. This series of experiments was unable to meet the basic conditions for hydrothermal or solvothermal treatments, so an alternate explanation was put forth to explain the results. Regardless, this portion of syntheses has shown that treatment via subcritical processing in a hydro/solvothermal setup has the potential to decompose the carbonate at temperatures lower than that of traditional processing.

Experimental Chronology Conclusion

Experimental Summary

Initially ball milling was investigated because of our group's familiarity with the technique and the desire for a simple, fast, and concise technique that could yield highly dispersed and uniform powders. Through experiments performed by lab mates and investigations of energy imparted during milling it was found that the grinding media would eventually contaminate the powder. This was so pronounced that it could be seen with XRD analysis Figure 10 and could not be removed through some chemical processing without degrading the powder. Degradation limits the working life of the grinding cups and media and was shorter than is feasible for continued use.

In the updated chart in Table 1 ball milling was evaluated generally poorly in most of the criteria. Taking what was learned from ball milling and sticking to a simple approach with minimal interaction with a container, limited chemical input, and a rapid synthesis time. Solution combustion synthesis seemed like an ideal candidate, hopefully bypassing the need for further processing that similar methods like the sol-gel combustion or steric entrapment need.

The literature portrayed solution combustion synthesis as a simple approach where the fuel and metal ions would react vigorously and leave you with a powder of discrete nanoparticles and little to no residue if your fuel choice was proper. What was left out of the literature was how aggressive these techniques were to any furnace or microwave as they evolved off hot fumes that corroded heating wires, thermocouple, and the internal cavity (Figure 16). Attempts to control the combustion by a templating method left too much residue behind to make the powder viable. It was found to be a simple approach, but after several furnaces and two microwaves were destroyed this was deemed too hazardous and uncontrollable to continue.

In Table 3, the section for combustion synthesis and microwave are evaluated about the same with some differences being about waste disposal since microwave struggle to promote a total reaction, whereas a furnace can push the system to completeness. This also influenced the yield efficiency since the microwave could not form a complete product. Further, the rapidness of the reaction gave little ability for control since the conflagration would overwhelm the whole reaction and leave one powder behind when finished. These two sections were also considered separately because of their distinct differences in heating

and the effects that it had were noticable. The shortcomings of these showed that something with more control and less damaging to the apparatus would be good for the next technique.

Flame spray is a more complex method involving the mixed solvents, but the concept is simple of spray mixture of metal salts dissolved in a flammable liquid through oxidizing flame and end up with oxides in the outflow. Lots of work has gone into developing this technique, so there is a solid foundation of research and it is currently a standard method for the synthesis of nanomaterials. There were issues preparing soluble nitrates in organic liquids with a minimal amount of water and how dilute the solutions had to be for adequate spraying. In our setup we found that flame spray pyrolysis was simple in execution, however, capturing the particles was very difficult. Even material from an industrial apparatus showed a lack of uniformity in particle size.

These issues made flame spray pyrolysis less ideal and a method that can offer more control over particle sizes, operate at a higher concentration, limit the hazards of both preparation and processing of the precursor, and enable easier particle capture. Table 1 reflects the opinion developed of this method and how it compares to the other methods.

The requirements have been getting more and more refined and defined as these methods have been explored. Up to this point precipitation had been avoided because of what the literature portrayed as a daunting amount of liquid needed to get this technique to work, but it seemed to be one of the best to offer some control over the reaction and product. Precipitation for inorganic syntheses is simple using some combination of salts to form an insoluble product containing the desired product. There is no immediate pathway to the oxide as there was with the previous methods, the products need some further treatment to

change into the oxide. The experiments conducted investigated the influence alcohol would have over the powders precipitated and agreed with the literature that the addition of alcohol creates a more even distribution. Experiments of only water showed some other distinct features, like flakes, which were lacking in the alcohol/water mixture influenced powders. Size was lacking as was the necessary amount of liquid to dilute the solution for nanoparticle production. In contrast to flame spray pyrolysis, the particles from precipitation are significantly easier to recover by filtration, sedimentation, or centrifugation.

Another problem arose with these powders made with bicarbonate where the carbonate species persisted after calcination and might hinder the full development into a dense material. Table 1 summarizes the precipitation method noting the large amount of liquid needed to make any portion of powder.

To overcome this persistence of carbonate and, based on literature surveys, manipulate particle size led to hydrothermal synthesis because of its known properties where the higher temperatures and pressures can induce novel reactions. Liquid suspensions of powder from the precipitations were taken and put into the reactor and results were recorded with FTIR analysis to document the changes regarding carbonate. This experiment was fruitful in showing the modest decomposition of carbonate in samples but was limited by the physical constraints of the reactor's pressure rating and temperature limit. To pursue studies into the realm of supercritical solvents a much more robust and costly reactor would be needed.

Reflected in Table 1 is the summary of hydrothermal synthesis. This batchwise reactor had its limitations, but the method is unique from the other methods and how it causes a reaction. Changing to a continuous method would make hydrothermal more appealing, the general cost is not conducive to broad exploratory studies and the cheaper reactors do not seem to be capable of the reactions from the literature. Solutions also must be relatively dilute to prevent agglomeration, which limits the quantity of oxide that can be produced.

These broad experimental investigations were performed to choose one method which seemed the most promising based on its results. From the impressions of these precipitation was selected because the major hinderance it has was concentration related and ways to overcome that will be investigated further. The issues with the indirect synthesis of YAG by way of an alternate material to decompose can also be mitigated by higher temperature processing under air, but that is energy intensive. An appreciation was gained for the smaller steps precipitation forces an experimenter to take instead of jumping immediately to an oxide. Further, the other variables left to manipulate, like solvents, precipitants, and methods of addition represent other avenues of discovery that fit the initial preferences laid out by Darr, et al. (2017) and have room for improvement.

Table 3 Expanded Darr criteria applied to the grading of the techniques after experimental experience with each.

<i>(In regard to oxide syntheses)</i>	Ball Milling	Solution Combustion Synthesis	Microwave	Flame Spray Pyrolysis	Precipitation	Hydro-thermal
Product meets desired composition	C	A	A	A	A	A
Product meets desired characteristics	D	B	B	C	B	A
Process is Energy Efficient	D	C	B	C	A	B
Process is Cost Efficient	C	B	C	C	A	B
Process is Yield Efficient	A	A	B	D	C	B
Process is Flexible	D	D	C	C	A	A
Process has a Minimum of Steps	A	C	C	C	B	C
Product is Reproducible	C	A	A	B	A	A
Residual Contamination Elimination	D	C	C	B	B	A
Capable of Continuous Operation	D	D	D	B	A	B
Process can be Monitored In-Line	D	D	D	C	A	A
Process has Minimal Hazards	A	C	C	C	B	B
Waste and Disposal are Manageable	A	A	B	A	B	B
Excellent	Good	Poor	Unsatisfactory			
A	B	C	D			

CHAPTER 4

CONTINUED EXAMINATIONS OF THE COPRECIPITATION OF YAG

Introduction

Work in this portion of the dissertation was conducted from 2018-2020. This work continues the investigations of precipitation as a synthesis method. Precipitation was selected from the other syntheses because of its low cost, simple method, and fast results. Further, it has lots of independent variable to manipulate and is a soft approach, which makes a material that is an intermediate on the way to the final product. Soft approaches may not be ideal for some researchers, but they have the potential to reclaim material for recycling from the resulting hydroxides or carbonates.

Precipitation was also selected because its faults were not as daunting, primarily regarding concentration, which if able to be overcome would make this a significantly more appealing approach for materials synthesis. The normal operating concentration of 0.1 molar for nanoparticle synthesis is a limitation that some researchers have partially surpassed by using capping agents to deter particle interactions and reduce agglomeration.^[123-126] Ideally, capping agents should be avoided because carbonates will not agglomerate, and some capping agents persist beyond calcinations of 600-800°C and can contaminate the product.^[127]

Dropwise precipitation is the traditional approach that was tested previously where a precursor metal ion solution is dripped into a rapid stirred precipitant. This method's setup was straightforward using only a pump to draw liquid through tubing to deliver it to

a beaker stirred with an overhead stirrer containing the precipitant. Immediate results can be seen as the drops interact with the precipitating solution. As covered in the previous section, there are some independent variables which can be manipulated, like strike direction^[106] and alcohol^[77] to favor certain reactions, namely a homogenous precipitation and to reduce metal ion solubility, respectively. These method ultimately failed to meet the goal of nanoparticles with its large, hard agglomerates seen in the SEM images and volume of liquid that had to be handled to make small amounts of product. The volume of liquid point is belabored in other publications as the major shortcoming for precipitation.^{[57][58]} To make nanoparticles from this method using a concentrated precursor metal ion solution, something needs to happen which can divide the precipitated powder either in situ or preemptively break up the precursor.

Sonication is a common technique for the suspending and fragmenting of material.^[128] Researchers have taken powder and shown that these can be broken up into smaller particles than what originally started.^[129] Some researchers have also employed focused ultrasound to concentrate the cavitation energy and break apart material more efficiently than bulk sonication.^[130] Applying this in situ would break up precipitated material and give finer powders.

Instead of breaking particles apart, the concept of dividing the precursor metal ion solution into droplets by modifying the traditional precipitation setup is another approach that has been shown to produce nanoparticles. Researchers use a carrier gas to aspirate droplets into a precipitating solution, limiting the amount of material present to nucleate and form a precipitate.^[131] Researchers in a few case have been able to push to a

concentration of 0.2 molar, doubling a typical concentration for coprecipitation.^[132-134] One group reports a spray precipitation of up to 0.4 molar, which is a significant step.^[135] These papers demonstrate the viability of this method to broaden the working range of concentrations for coprecipitation.

Similar to aerosolized droplets, ultrasonic nebulization can produce more consistent and smaller sized micron-sized droplets without the need for a carrier gas. Compared to aerosol atomization with droplets ranging from 10-50 μm ^[136], ultrasonic nebulization can reduce the size of the droplets to 5-22 μm using high frequency ultrasound (>100 kHz).^[137] Researchers have taken advantage of this as an alternative approach to spray precipitation, but have not pushed the boundaries of concentration.^{[138][139]} This method could help eliminate a variable of airflow while taking advantage of small droplets to produce nanoparticles.

Literature is rather sparse on electrospray ionization for precipitations. This method is well known for its use in analytical methods which benefit from the micro- and nanodroplets that it can produce.^[140] Some researchers have taken advantage of these droplets to produce nanoparticles of polymers.^[141] This is a novel route that could explore the application of electrospray to inorganic precipitations.

To refine the methods of coprecipitation and improve the traditional technique, the four approaches were tested to gauge which could produce nanoparticles suitable for further testing. Concentration limitations will also be manipulated to define the capabilities of the worthwhile methods. If the primary limitation of coprecipitation is concentration, then methods using dispersion and division will result in finer particles than previous

attempts. The four proposed methods will be evaluated following the criteria used to find a suitable method for general production.

Experimental

Materials

Yttrium oxide (Strem, 99.99%), aluminum metal (Alfa Aesar, 99.999%), cerium nitrate (Strem, 99.99%), ammonium hydrogen carbonate (Acros Organics, 99%), polyethylene glycol 4000 (PEG-4000, Alfa Aesar), ammonium bisulfate (NH_4HSO_4 , Acros Organics, 90%), isopropanol (Fisher Scientific, HPLC grade), water (Fisher Scientific, 18M Ω) were used in the syntheses of metal carbonate precursors to YAG powders.

3-Aminophthalhydrazide (Luminol, Alfa Aesar, 99%), sodium hydroxide (Alfa Aesar, 99%), sodium carbonate (Baker Reagents, 99%), ethylenediamine tetraacetic acid (EDTA, Fisher Scientific, 99%), hydrogen peroxide (Fischer Chemicals, 30%) were used in the luminol testing of the ultrasound apparatus.

Apparatus

To conduct the ultrasonic influence experiment an ultrasonic bath was made consisting of twenty-three 100W 25kHz transducers powered by a 2500W Beijing Ultrasonic generator. The bottom of the basin had nine transducers affixed to it, the sides had two sets of four and two sets of three for the broad and short sides respectively. Transducers of similar frequencies were chosen to match with another transducer across the body of the basin. The transducers were affixed to an 8-liter stainless steel basin with a high vibration resistant epoxy. Each of the transducers were wired in series so the current

stayed the same across each component. Testing of ultrasonic intensity was done with luminol to demonstrate cavitation activity. Please see figure 29 for a diagram and pictures of the assembled apparatus.

For spray coprecipitation a pneumatic aerosolizer was used, repurposed from the flame spray pyrolysis experiments. This was a Meinhard Type A ICP nozzle, capable of high flow and high-pressure gas flow. The pneumatic spray gas flow was supplied by an oxygen concentrator capable of a 10 liter per minute flow rate at 20 pounds per square inch, within the nozzle's specifications. Flow rate for the nozzle was controlled by a Cole Parmer peristaltic pump which used L/S 13 tubing and compatible pump head at a rate of 10 milliliters per minute. The spray was direct down towards the middle of the vessel, orthogonal to the surface of the precipitant solution. Stirring was provided by a Fisherbrand overhead stirrer at a rate of 1000 RPM with a Chemglass 45° blade angle, 110 mm PTFE agitator mounted on a Chemglass glass stirring rod. These precipitations were performed in a 2000 mL beaker for ease of setup and modification above. Please see Figure 30 for a general diagram of the setup.

Similarly, the ultrasonic nebulized spray was performed using a SonoTek 130kHz ultrasonic nebulizer. A flow rate of 3 milliliters per minute for the nozzle was controlled by a Cole Parmer peristaltic pump which used L/S 13 tubing and compatible pump head. The setup and ultrasonic nebulization spray orientation was the same as the aerosol spray setup and a diagram can be seen in Figure 31.

Electrospray ionization was done using an Information Unlimited high voltage 5-35kV DC variable power supply to provide the voltage potential bias. An initial setup using

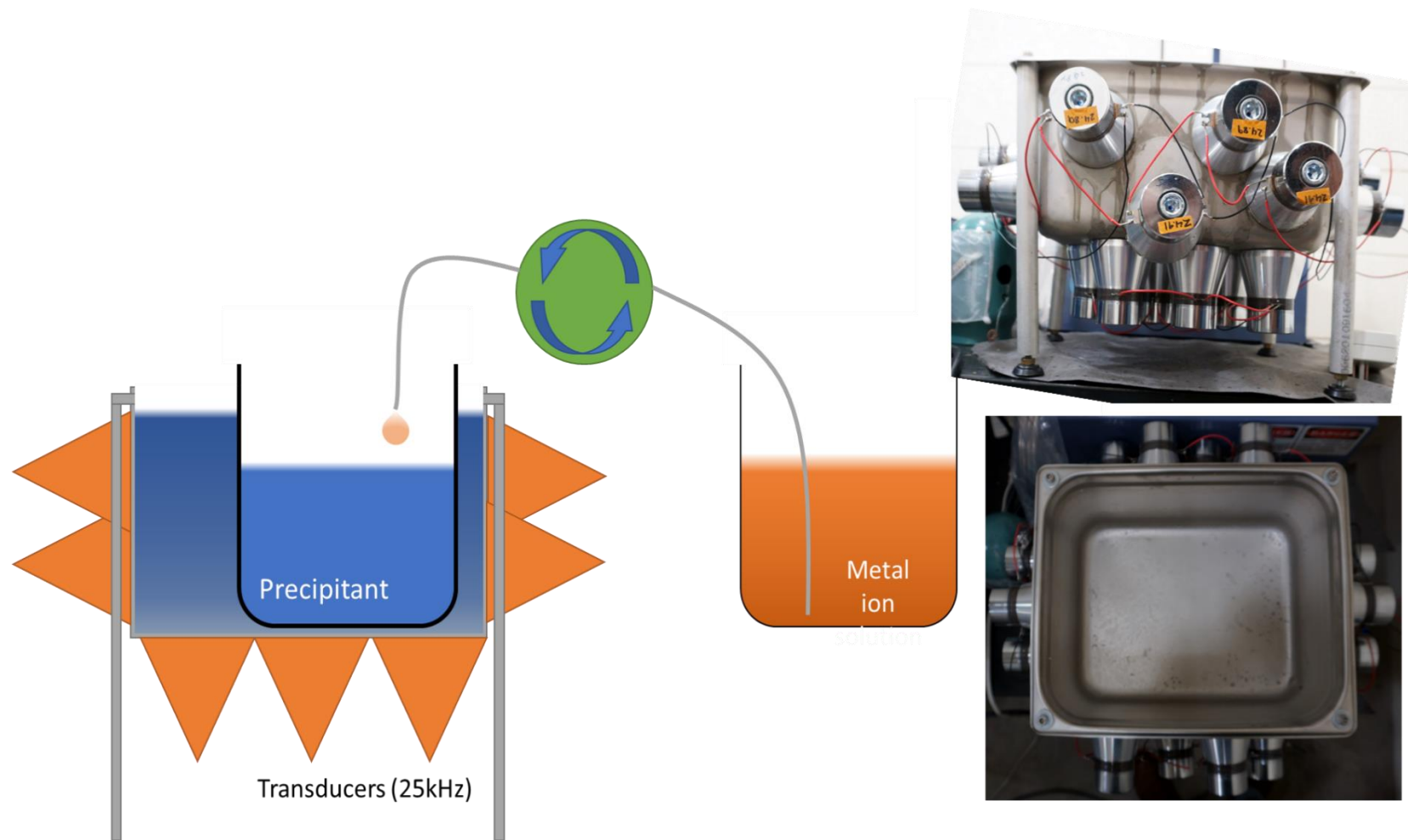


Figure 29 Ultrasonic diagram and pictures of the setup from the side and top-down view.

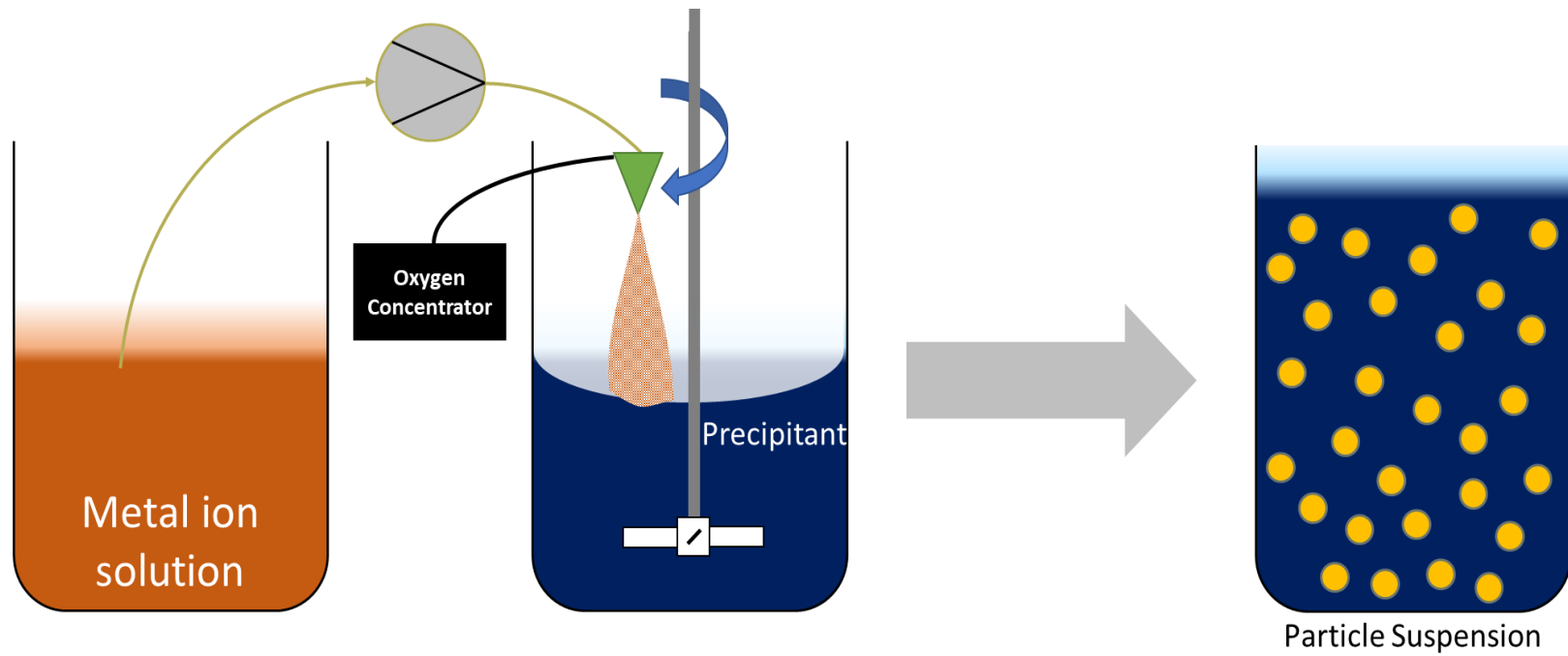


Figure 30 Spray precipitation setup diagram showing the flow of materials and resultant particle suspension.

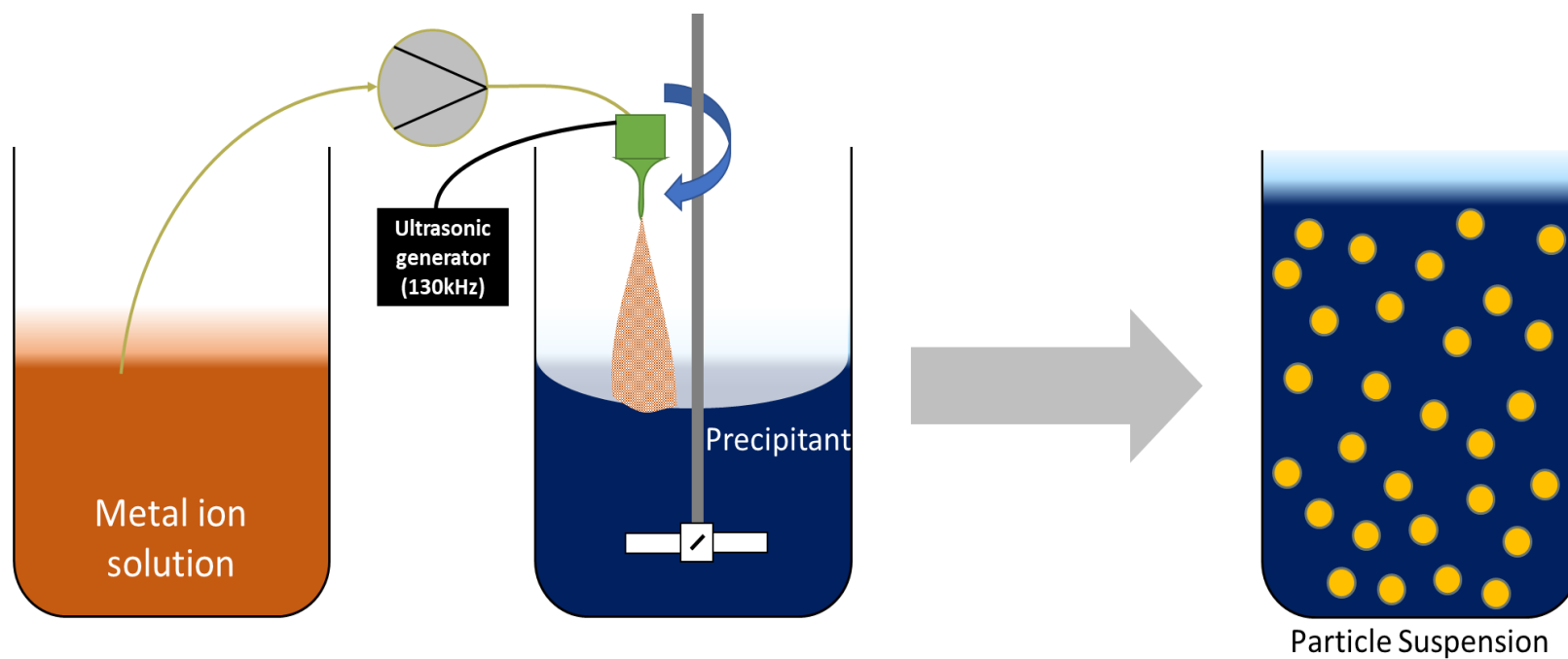


Figure 31 Ultrasonic nebulization spray setup diagram. Compared to the previous setup, the oxygen concentrator has been replaced by the ultrasonic generator.

an inverted fritted filter support so the tube would be used as a liquid reservoir and a stainless steel wire could be inserted easily. A wire connected to ground was inserted into a beaker below to direct the droplets into the container. The voltage was varied to above 10,000V to manipulate both the flow and resulting sprays. A diagram of the setup can be seen in Figure 32.

Procedure

YAG:Ce precursor composed of metal nitrates were prepared by dissolving known quantities yttrium oxide and aluminum metal in nitric acid to give specific combined stoichiometry, 2.97 parts yttrium and 5 parts aluminum. A solution of cerium nitrate was prepared previously and standardized via pyrolysis. A portion of this solution was added to the yttrium/aluminum solution in a 1% molar ratio of total rare earth content, or 0.03 parts cerium for a total of 3.00 parts rare earth content. Usually, these solutions were prepared to make 500 grams of YAG:Ce total and the concentration was standardized by pyrolysis. Portions to make 10 grams of oxide were taken from this standard body of solution to test syntheses. Solutions were then diluted with a mixture of 50/50 water and isopropanol to make a final concentration of 0.1 molar. Some samples were diluted less to test more concentrated solutions, usually up to 0.4 molar

In some solutions for ultrasonic spraying, capping agents were added to the precursor metal ion solution so that the capping agent was consistent in relative concentration to the metals. PEG was dissolved into the metal solution as a 0.1-0.2% relative to the total metal ion concentration. Ammonium bisulfate was added following papers using sulfate as a capping agent, which meant equivalent to the aluminum content.^[125]

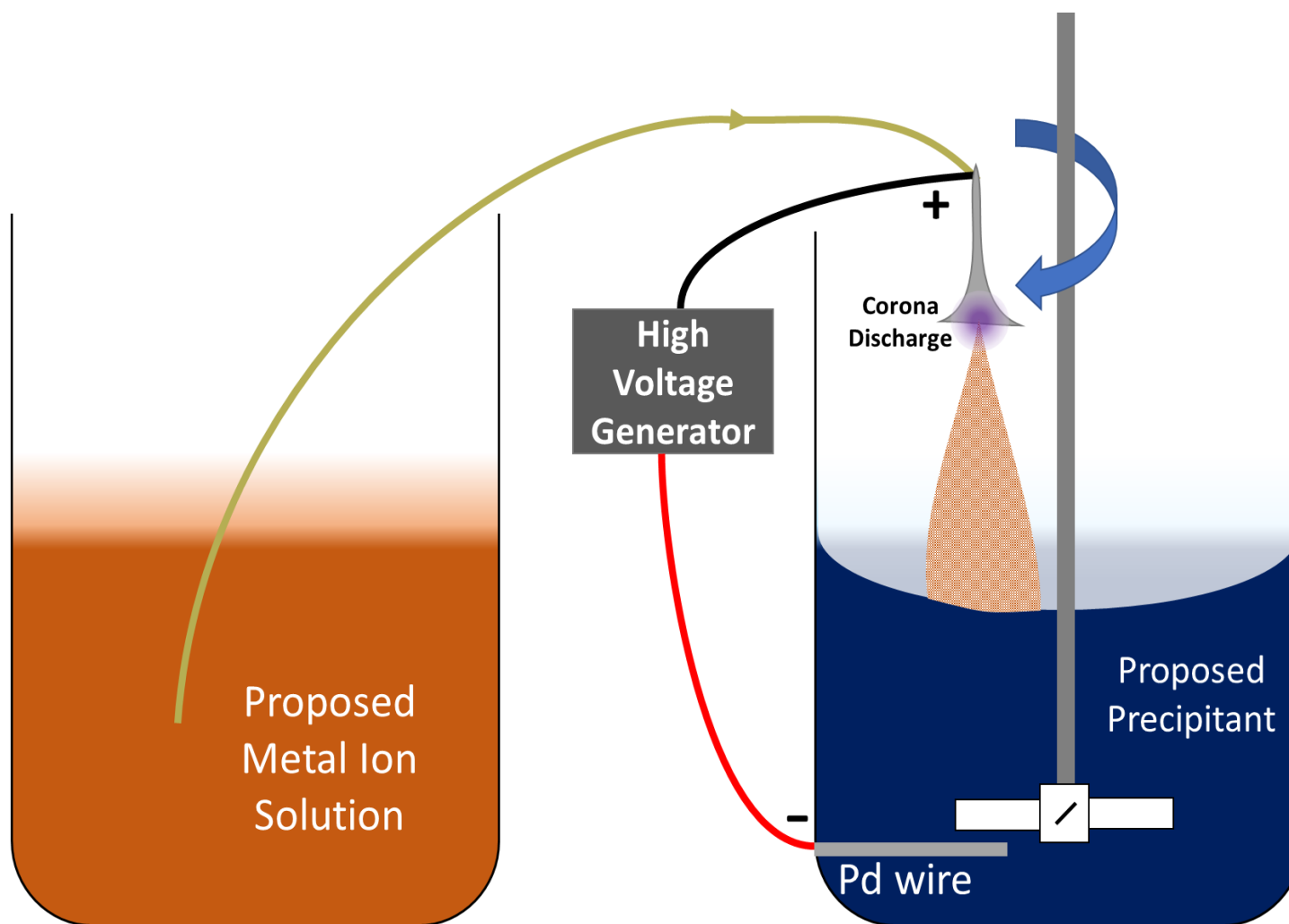


Figure 32 Proposed setup for an electrospray precipitation using an overhead stirrer.

Luminol testing was done using a buffer solution of sodium hydroxide, sodium carbonate, ethylenediamine tetraacetic acid (EDTA), and luminol.^[142] This was added to a container and placed in the ultrasonic field to document visually where the active spots in the sonicator were. Pictures were taken with a Sony α -6500 on a tripod with an ISO of 32000 for low light conditions using a 16-50 millimeter lens triggered by a remote to take pictures.

Results

Sonication identification by luminol showed high activity by the walls of the glass vessels. This helped guide the ideal setup for where to drip solution in for the precipitation. Figure 33 show the blue active areas of luminol chemiluminescence. These active spots were found to be brightest near the wall as opposed to the center of the container indicating areas of greater activity. The whole column of luminol in the bottle was noted as being active, showing a lack of focused ultrasound, but a thorough cavitating field. Using this as an indicator the precipitation was positioned near the wall of the vessel for the best attempt of fragmentation.

Precipitation SEM images can be seen in figure 34 of two different attempts. These attempts used the same liquid precursor and only altered position in the bath to match the center and wall locations shown in Figure 33 of the luminol sonic activity characterization. Both show lackluster results and that the material is lacking consistency in size and morphology. XRD studies were considered but not pursued because the primary goal became particle characteristics, not composition. This expedited the research and as such, the majority of results here will be reported as solely SEM images.

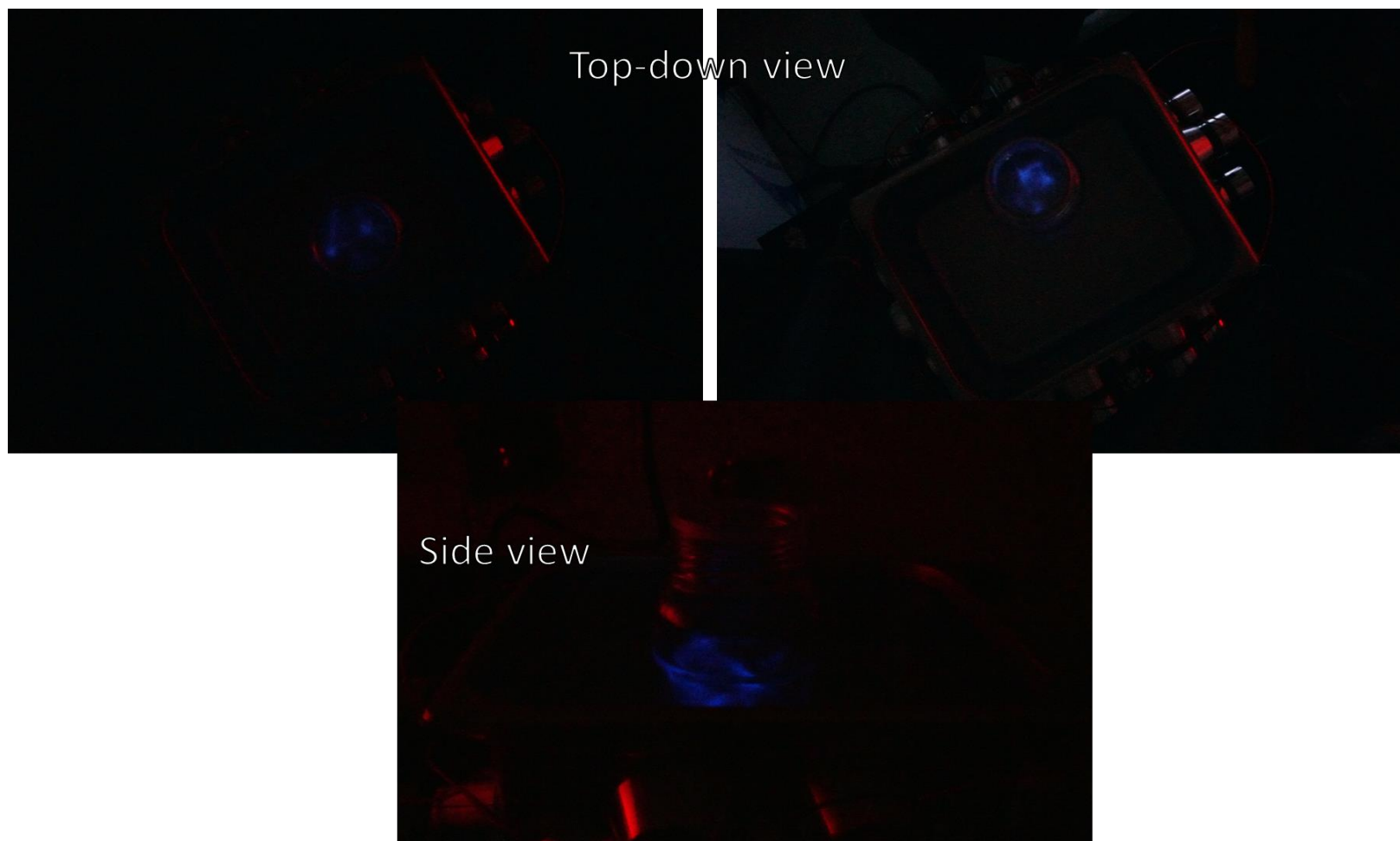


Figure 33 Sonochemiluminescence from luminol excitation in the bath reactor. The bottle has drifted towards the wall in the second top-down picture and shows significantly more activity. The bottom picture is of a bottle near the side showing activity only in the area below the waterline of the bath.

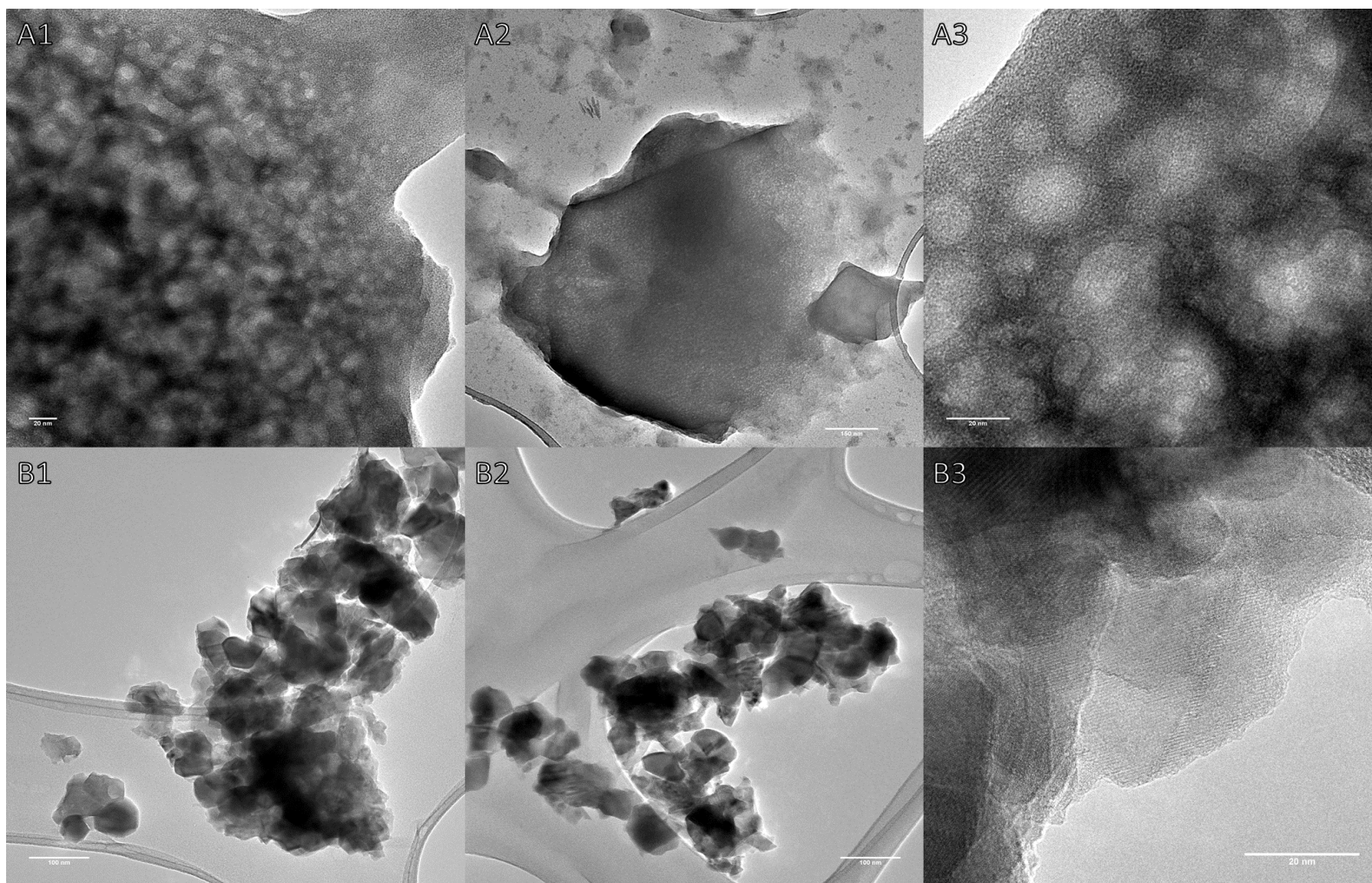


Figure 34 SEM images of powder precipitated from the ultrasonic bath reactor. The top is an initial sample, and the bottom is another sample attempt with the same chemicals.

The failures of the ultrasonic powder likely come from the fact that the metal solution dripped into the acoustically agitated solution formed a ‘raft’ of precipitant which floated on top of the solution and failed to mix in well. Stirring was not recommended because acoustics would be hindered by the mixing. This severely limited the viability of this technique because transducer sonication has limitations on how well they can transmit energy^[143], unlike a probe sonicator, but those are known to degrade over the course of use and were avoided.

The modification of a traditional precipitation made spray precipitation an enticing approach because it added one minor step in the delivery of the metal-ion precursor solution. The nozzle was repurposed from the flame spray pyrolysis experiment and in conjunction with the nozzle an oxygen concentrator was capable of a strong aspiration of liquid. The oxygen concentrator was used specifically because it pre-filtered the air and offered a significant flow rate over lab nitrogen lines and cost less than buying gas cylinders. This ensured no clogged nozzles and adequate, adjustable airflow. Sprays were vigorous and simple to direct. The fast airflow could be seen diverting the rapidly stirred solution as the nozzle got closer and injected aerosolized droplets.

Results from the spray precipitation can be seen in Figure 35 which shows a few images resulting from the atomized spray. Of note here is the loosely agglomerate powder which is comprised of mostly spherical nanoparticles. Some platelet-like particles can be seen, likely the concentration of yttrium carbonate, which are known to make these types of precipitates.^[144] To overcome these platelets an experiment was setup with a reduced flow rate of precursor metal ion solution to give more ability for atomization.

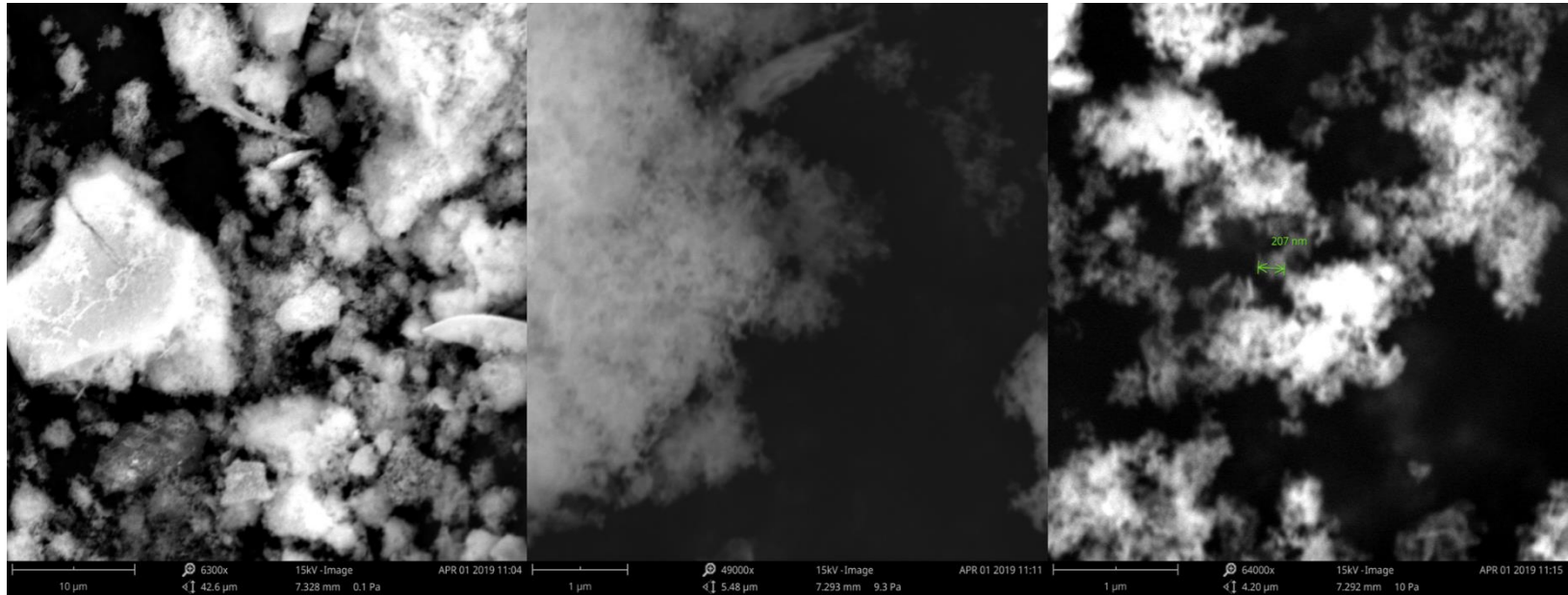


Figure 35 SEM images from the spray precipitation of YAG. The left most picture has a scale bar of 10 micrometers, the middle and right pictures are 1 micrometer.

Figure 36 shows the synthesis of powder at a slower flow rate of 1 milliliter per minute with a gas flow of 10 liters per minute at 20 pounds per square inch. Small nanoparticles have resulted, not within the size regime desired, but spherical in morphology. Of note are the agglomerates, some very large. These look to be loosely interacting, soft agglomerates, not hard where necking and bridging occur between particles. The slow flow rate does hinder this method as making 10 grams of product took nearly eight hours from setup prep to filtration. Also of note was an odd phenomenon not totally unexpected because of the gas flow: droplet ejection and liquid accumulation on the beaker and surrounding area.

Spray precipitation was a promising technique, but it suffered from the issue of droplet ejection with the gas flow resulting in either loss of product or accumulation of larger droplets which would make larger particles. When this setup was covered, the droplets collected on the lid of the container and formed droplets which would drip in and results from that can be seen in Figure 37 and the middle image of Figure 36. Because of these issues the need for a method which could break up droplets without the aid of a carrier gas was needed to limit the ability of droplets to leave the system.

The loss of material from droplet ejection and the potential resulting large particles from accumulation of droplets limited the usefulness of this technique and highlighted a shortcoming of other gas-powered techniques. A method which could aspirate liquid without the need of flowing gas was the next modification to be made in the setup. Some other researchers had already attempted this using ultrasonic nebulizers which take advantage of an ultrasonic tip ejecting material from it as it vibrates rapidly.

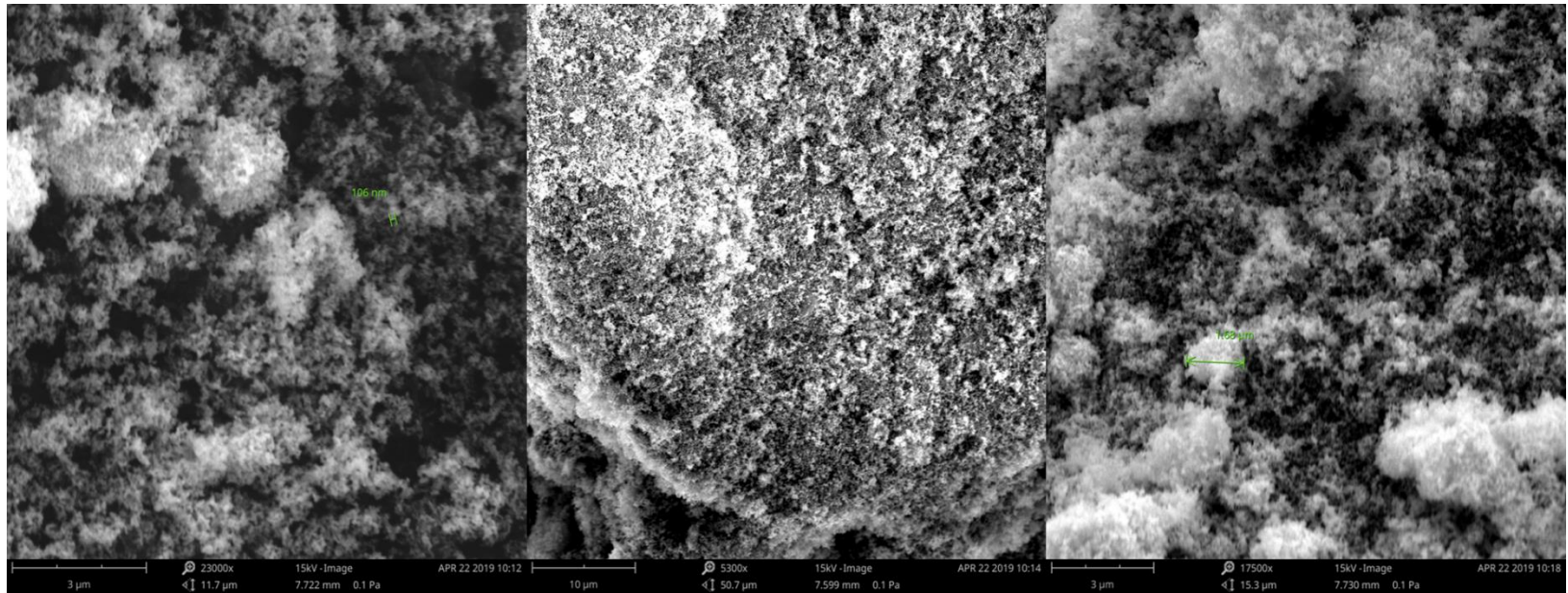


Figure 36 Precipitation of Al at a slower flow rate via spray pyrolysis



Figure 37 Powder resulting from the dripping of solution into the spray co-precipitated setup when a lid was put on to catch the ejected liquid.

SEM images of the powders resulting from ultrasonic nebulization can be seen in Figure 38. These powders are significantly more agglomerated than those from an aerosolized system. This is likely due to a phenomenon seen in Figure 39 which shows the turbulence from the stirred solution causing accumulation of large piles of material on the lip of the beaker which then fall in and constitute a significant portion of the material seen in the SEM images.

This is similar to the droplet ejection, not due to gas flow, but turbulent air in the setup. Two other issues arose from ultrasonic nebulization regarding viscosity and flow rate. At higher concentrations the ultrasonic nozzle was not capable of nebulizing efficiently and would result in drips into the solution. Limitations of flow also would overwhelm the nozzle and cause dripping to take over the ultrasonic nebulization, rendering it ineffective.

Attempts to limit the turbulence by removing the overhead stirrer and use a magnetic stirrer were also attempted as shown in Figure 40 but failed to produce viable results because of the nozzle becoming overwhelmed by the liquid flow rate. Flow rates that looked adequate would eventually become unstable overtime, so constant monitoring was needed to ensure this was limited. Retrospectively, this may be due to the pulsing of the pulsing from the peristaltic pump.

Attempts to try and augment the synthesis using capping agents was considered next. When PEG was used it made the solutions more viscous cause more dripping than solutions without. Alternate capping agents like ammonium sulfate were attempted, but the use of isopropanol limited the amount of ammonium salts that could be dissolved.

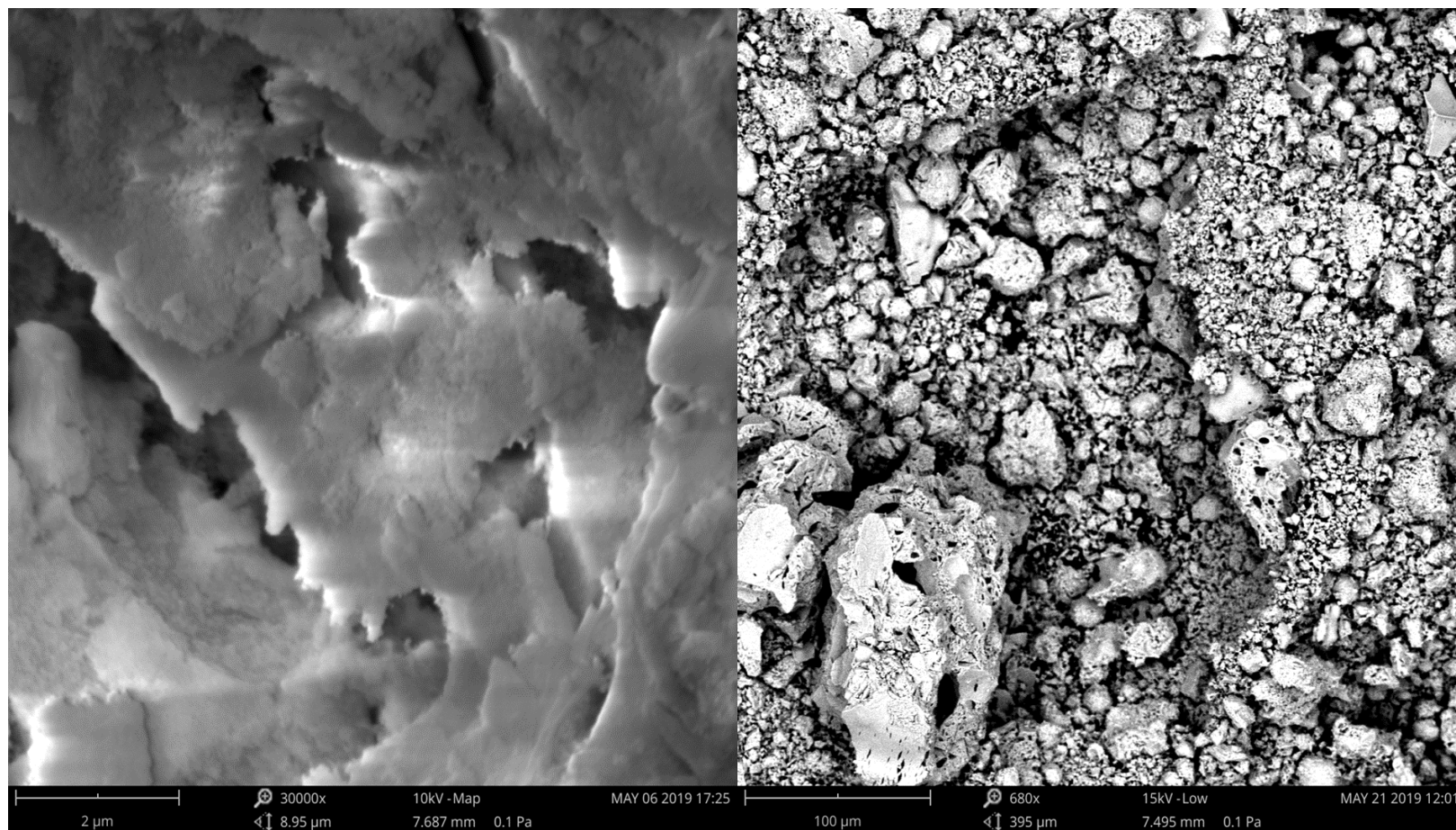


Figure 38 Powder resulting from ultrasonic nebulization spray at 130kHz.



Figure 39 Precipitated spray powder collecting on the lip of the beaker from the turbulent air ejecting the ultrasonic spray.



Figure 40 Alternative setup of the ultrasonic spraying to try and limit turbulence from overhead stirring by using magnetic stirring.

An experiment was attempted where the metal precursor solution was mixed thoroughly with ammonium sulfate and filtered off the remaining salt. This eventually led to clogging of the capillary in the ultrasonic nozzle as the salt crystallized out of the saturated solution. In retrospect this was a poor experiment because the salt likely exchanged anions with the metals preferentially and would have eventually caused a stoichiometric disproportionation if it had worked because of the poor solubility aluminum sulfate has in alcohol.^[145]

Issues regarding the flow and droplet management from the aerosolizer and ultrasonic nebulizer meant an alternative that could propel a droplet to limit effects by turbulence was desirable. Electrospray was considered because of the electromotive forces which cause ionized droplets to flow towards the opposite charge. In the travel from cathode to ground it is known that as the droplet tries to reach an equilibrium, the droplet will shed smaller droplets, sometimes in the nano-regime. Further, the liquid can flow on its own as the electromotive forces induce flow through the nozzle. As seen in Figure 41 are a few pictures of a test setup using an inverted portion of a fritted filter to act as a reservoir for the water. The general setup for this can be seen in Figure 32 with the cathode portion suspended over the anode. Both solutions were made of deionized water for testing. The Taylor cones can be seen in several pictures in Figure 41 indicating the solution is ionizing adequately. Flow rates were low, less than a milliliter per minute, and upon increasing the voltage past 10,000 volts the solution began to act erratically, and hissing was apparent as the air began to ionize. Because of the slow flow rate and the potential degradation of the steel electrodes, which would contaminate the system, this setup was

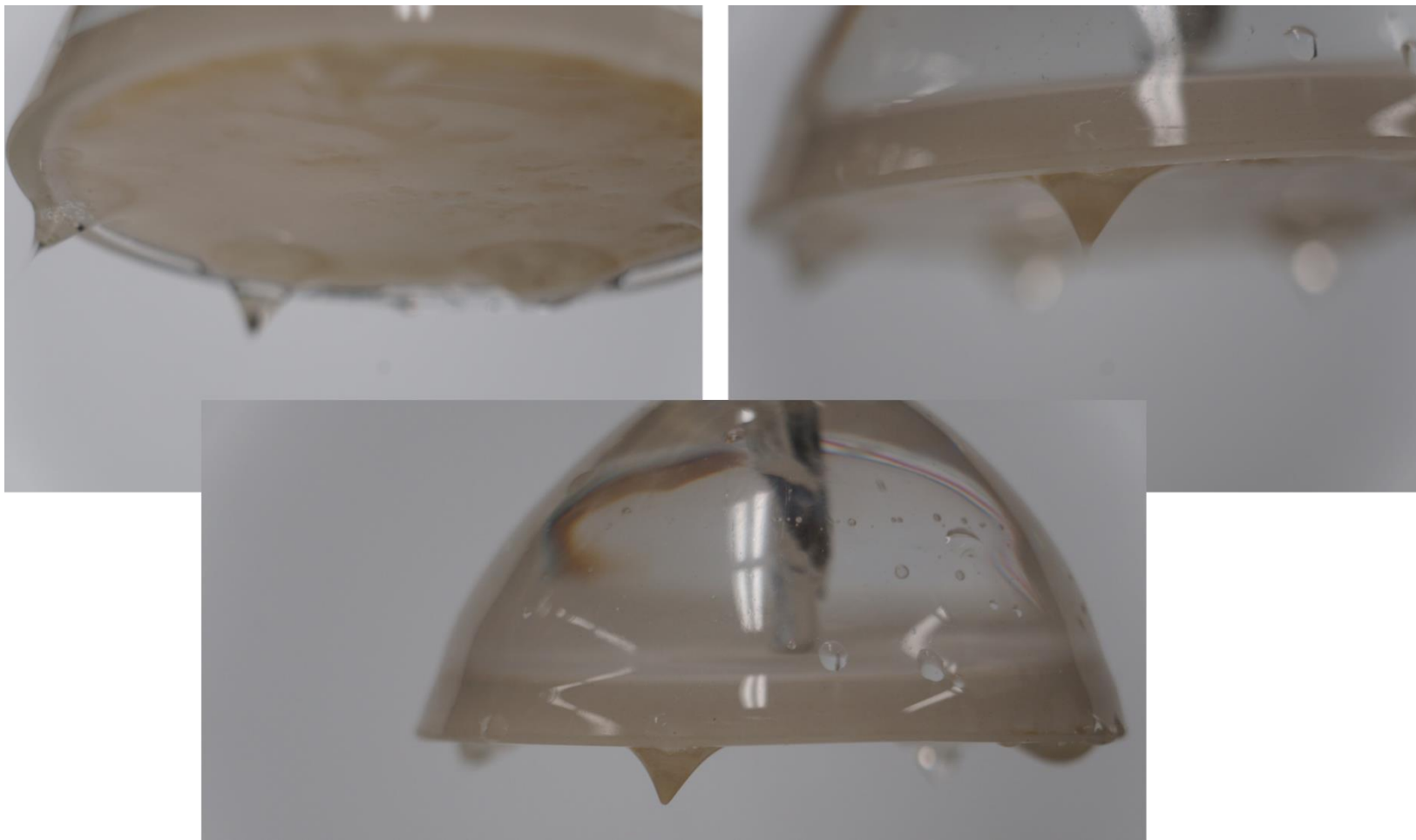


Figure 41 Different angles of the electrospray setup with Taylor cones formed in each picture.

not tested any further. The addition of high voltage in an open setup was also disconcerting and not recommended to be tried again.

Conclusion

This section tested a few approaches to influence a precipitation by limiting the amount of material present to react. By limiting this, the reaction would inherently make smaller particles. A few methods were tried to break the droplets up as they interacted with the precipitating solution by ultrasonication, or break droplets up before they arrived at the precipitating solution as with the various spray precipitation attempted. Of these attempts, traditional aerosolization by a repurposed ICP nozzle made the best particles, but it suffered from droplet ejection which coated surrounding area or condensed on a lid and made large agglomerates because of these dripping in.

Evaluation of these method can be seen in Table 1, where these methods are compared to the traditional drop-wise precipitation. The two processes attempting to employ ultrasound were evaluated worse because of the system requirement limit continuous flow, as with the ultrasonic bath reactor, and the finicky nature of the ultrasonic spray nozzle which greatly affect the product. The aerosol spray precipitation showcased a good approach, but its waste with regard to droplet ejection and the drips from attempts to cover it were an improvement over traditional dropwise. It was overall a marginal improvement to traditional precipitations. Disappointingly, none of these methods were able to operate at higher concentrations and only the spray precipitation could produce a promising precipitate.

Table 4 Judging the broader precipitation processes based on the expanded Darr criteria.

<i>(In regard to oxide syntheses)</i>	Dropwise Precipitation	Ultrasonic- Influenced Precipitation	Aerosol Spray Precipitation	Ultrasonic Nebulization Precipitation
Product meets desired composition	A	A	A	A
Product meets desired characteristics	B	B	A	C
Process is Energy Efficient	A	A	A	A
Process is Cost Efficient	A	A	A	A
Process is Yield Efficient	C	C	B	B
Process is Flexible	A	C	B	B
Process has a Minimum of Steps	B	C	C	C
Product is Reproducible	A	A	A	A
Residual Contamination Elimination	B	B	B	B
Capable of Continuous Operation	A	C	A	A
Process can be Monitored In- Line	A	A	A	A
Process has Minimal Hazards	B	B	B	B
Waste and Disposal are Manageable	B	B	B	B
Excellent	Good	Poor	Unsatisfactory	
A	B	C	D	

CHAPTER 5

FRIT-ASSISTED PRECIPITATION

Introduction

This section of experiments were performed in 2020-present. Unfortunately, the previous approaches and confounding variables of droplet ejection and coalescence limited the effectiveness of the spray methods. Further, the poor performance with more concentrated solutions did not meet the goal which would make precipitation a more appealing technique. The experimenting with electrospray did offer a unique moment of inspiration.

In the previous section, a filter frit base had been chosen to initially setup some experiments because it could be easily manipulated with wires to accommodate electrospray. The base when inverted acted as its own reservoir of liquid, and the free flow from this reservoir motivated by the high voltage led to multiple Taylor cones which were ejecting droplets. This increased the flow through the fine pore frit and would have been an improvement, but the corona discharge from the high voltage made this less than desirable. Spray was also susceptible to turbulence in the air. However, if this airgap could be closer or have the liquid directly injected, then these influences might be reduced or eliminated.

Glass frits are a porous material made of ground borosilicate glass that is pressed and fused together for a duration of time to produce average pore sizes. What was striking about a frit was this notion of pore size. An idea arose around liquid coming out of these pores and how these droplets emerging from the frit would be close to the characteristic

pore sizes immediately after exiting the frit. Under influence of a vigorously stirred solution these droplets would be sliced off and whipped away in the current, taking advantage of the limited droplet size. This would encourage both mixing and promote diffusion in the small droplets.

To support this idea, literature was searched regarding liquid flowing through porous materials or sparging with gases to make nanoparticles. Some oddities involving eggshell membranes to make nanoparticles^{[146][147]} were found, but more appropriate were a few papers about sparging a calcium hydroxide solution with carbon dioxide to make calcium carbonate nanoparticles for CO₂ sequestering. Xiang, et al. (2004) correlated the bubble size with the particle size by comparing SEM images and noted that as the bubble size decreases, so does the size of the resulting particles.^[148] A second paper by Feng, et al. (2007) also investigated the bubble size and its influence on particle size but failed to find a distinct difference in dynamic light scattering (DLS) measurements.^[149] DLS struggles to differentiate agglomerates, so true particle sizes are not known. A third paper by Fuchise-Fukuoka, et al. (2020) showed that direct injection of fine bubbles into a calcium hydroxide solution, mixed with a wood pulp additive as a host material, resulted in particle sizes which were highly dependent on the flow rate of carbon dioxide. There was an ideal flow rate for a constant calcium concentration, too high or low and the particles were larger than those at a moderate gas flow rate.^[150]

These papers give some initial hope that bubble size does influence particle sizes and that an ideal flow rate may play a significant role in final particle sizes. Stirring is also shown to have an effect on particle size, noting that as the stirrer speed increased, the

particle size decreased.^[148] Those researchers attribute it to increased mixing and increased mass transfer. Variations on concentration were also demonstrated in the papers, but the system differentiated too much from the concept of a liquid-liquid mixing setup to give much confidence.

Microfluidics was also looked to as an analogous field, but these researchers are more adept at precise additions and mixtures. The closest to a frit-aided addition was what is known as a T-cell where two reactants are added together from the top arms of the T and flow out the long portion. Some of these have been performed in small capillaries, but the reported studies require 0.2 to 0.3 molar metal ion concentrations to make nanoparticles.^{[151][152]} The slightly increased solution concentration (over 0.1 molar) lends credence to the idea of using small droplets to limit the nucleation and growth potential of particles.

These loose concepts support the idea that small droplets or bubbles leading to smaller particles. Therefore, a setup involving an immersed frit, turbulent stirring, a mixed metal ion solution being delivered to a precipitant, and the effects of concentration and precipitant on nanoparticle syntheses are proposed to be studied. If the concentrated (greater than 0.1 molar) precursor solution is divided up by pores of a frit, then the resulting particles from the direct introduction into a turbulent precipitating solution will make suitable nanoparticles. Further studies about how the pores size of the frits and effects of organic modifiers will be investigated as well.

Experimental

Materials

Yttrium oxide (Strem, 99.99%), aluminum metal (Alfa Aesar, 99.999%), cerium nitrate (Strem, 99.99%), ammonium hydrogen carbonate (Acros Organics, 99%), ammonium carbonate (Acros Organics, 99%), ammonium hydroxide (Fisher Scientific, 32%), ethylenediamine (EDA, Sigma Aldrich, 99%), isopropanol (Fisher Scientific, HPLC grade), water (Fisher Scientific, 18M Ω) were used in the syntheses of precursors to YAG powders. For the capping agent and organic modifier studies *p*-toluenesulfonic acid (*p*TSA, Sigma Aldrich, 99%), stearic acid (Sigma Aldrich, 99%), 2-ethylhexanoic acid (2EHA, Sigma Aldrich 98%), and acetylacetone (acac, Sigma Aldrich, 99%) were used.

Apparatus

A setup using a 2000 milliliter Pyrex beaker, a Fisherbrand overhead stirrer with a Chemglass PTFE agitator on a Chemglass stir rod with ground section for the agitator locking screw, and Cole-Parmer peristaltic pump with pump dampener used in the previous syntheses was arranged as shown in Figure 42. A 12-millimeter diameter fine pore frit from ChemGlass (item number: CGB-201-05) was encased in compatible 1/4-inch glass tubing and bent 180° from normal to have the frit facing upwards. LS 14 tubing was friction fit around the top of the glass tubing leading to the frit and clamped in place by two hose clamps. This setup was held firmly in place in the beaker by a three-finger clamp and the head of the frit was adjusted so it resided within a couple millimeters below the agitator blades and the glass tubing was clear of the blades.

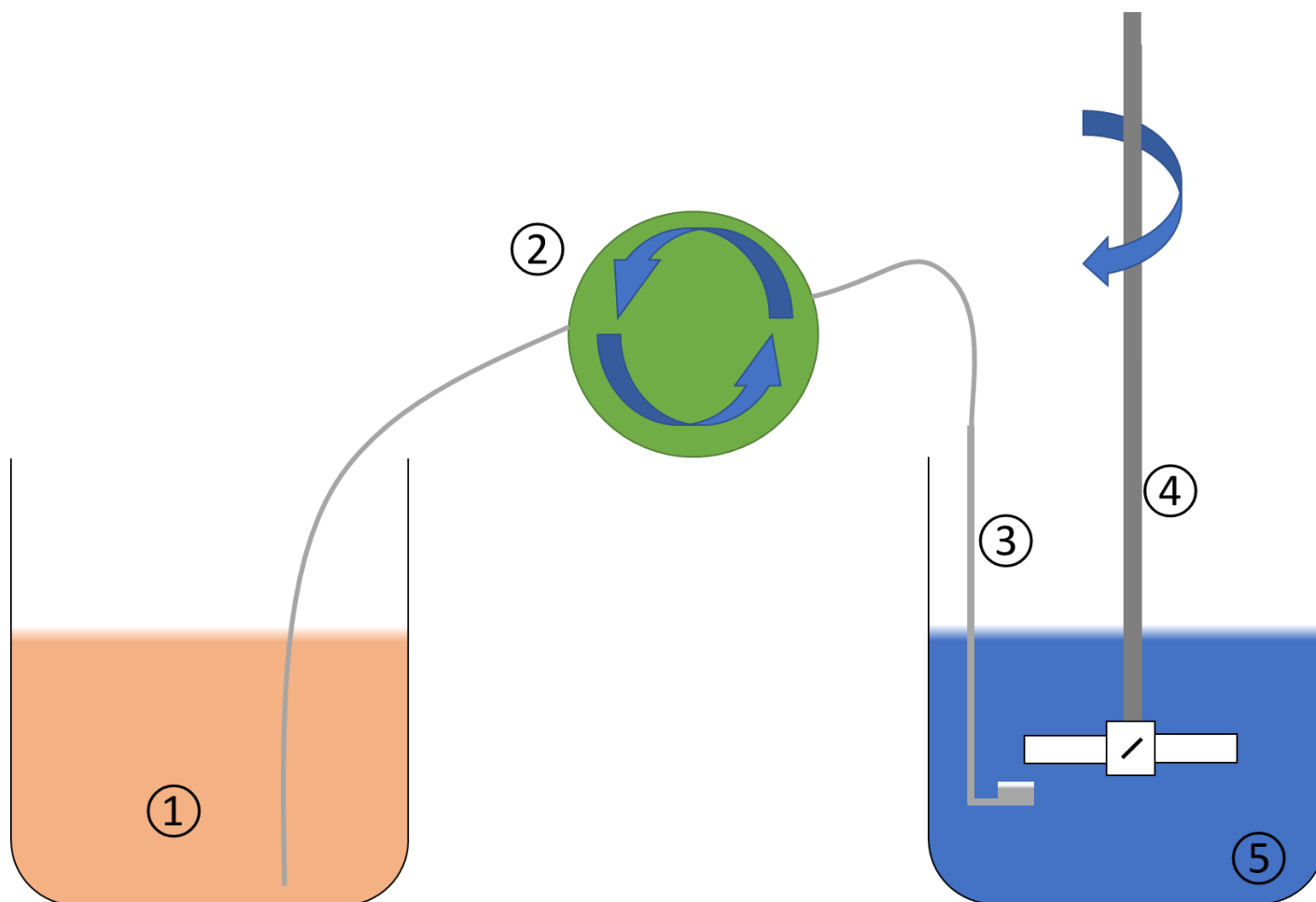


Figure 42 Diagram of the frit-assisted precipitation setup. Item ① is the metal ion precursor solution, item ② is the pump, item ③ is the frit, item ④ is the overhead stirrer, and item ⑤ is the precipitating solution.

A second frit would be made to have the head extended 5 centimeters from the tubing so the frit can be more easily positioned below the agitator and the glass tubing it is attached to can clear the full sweep of the blades. This frit also used the same ChemGlass part number mentioned previously. Two more fine frits of an inch in diameter were made from vintage ChemGlass parts provided by the glass blower.

A modular and more durable frit holder was made out of titanium rod stock, plate, screws, and ¼-inch tubing. A computer-generated illustration of this can be seen in Figure 43 of only the holder portion. This holder is intended to hold a titanium ultrafiltration chromatography frit. This frit will be compression fit against an o-ring within the holder to prevent leaking and the screw plug in the front allows ease of cleaning. A picture of all the frits and the frit holder can be seen in Figure 44 to show the evolution of design.

Procedure

YAG:Ce precursor composed of metal nitrates was prepared by dissolving known quantities yttrium oxide and aluminum metal in nitric acid to give specific combined stoichiometry, 2.97 molar parts yttrium and 5 molar parts aluminum. A solution of cerium nitrate was prepared and standardized via pyrolysis. A portion of this solution was added to the yttrium/aluminum solution in a 1% molar ratio of total rare earth content, or 0.03 molar parts cerium for a total of 3.00 moles of rare earth content relative to aluminum. Usually, these solutions were prepared to make 500 grams of YAG:Ce total and the concentration was standardized by pyrolysis. Portions to make 10 grams of oxide were taken from this standard body of solution to test syntheses. This was diluted by half (1:1

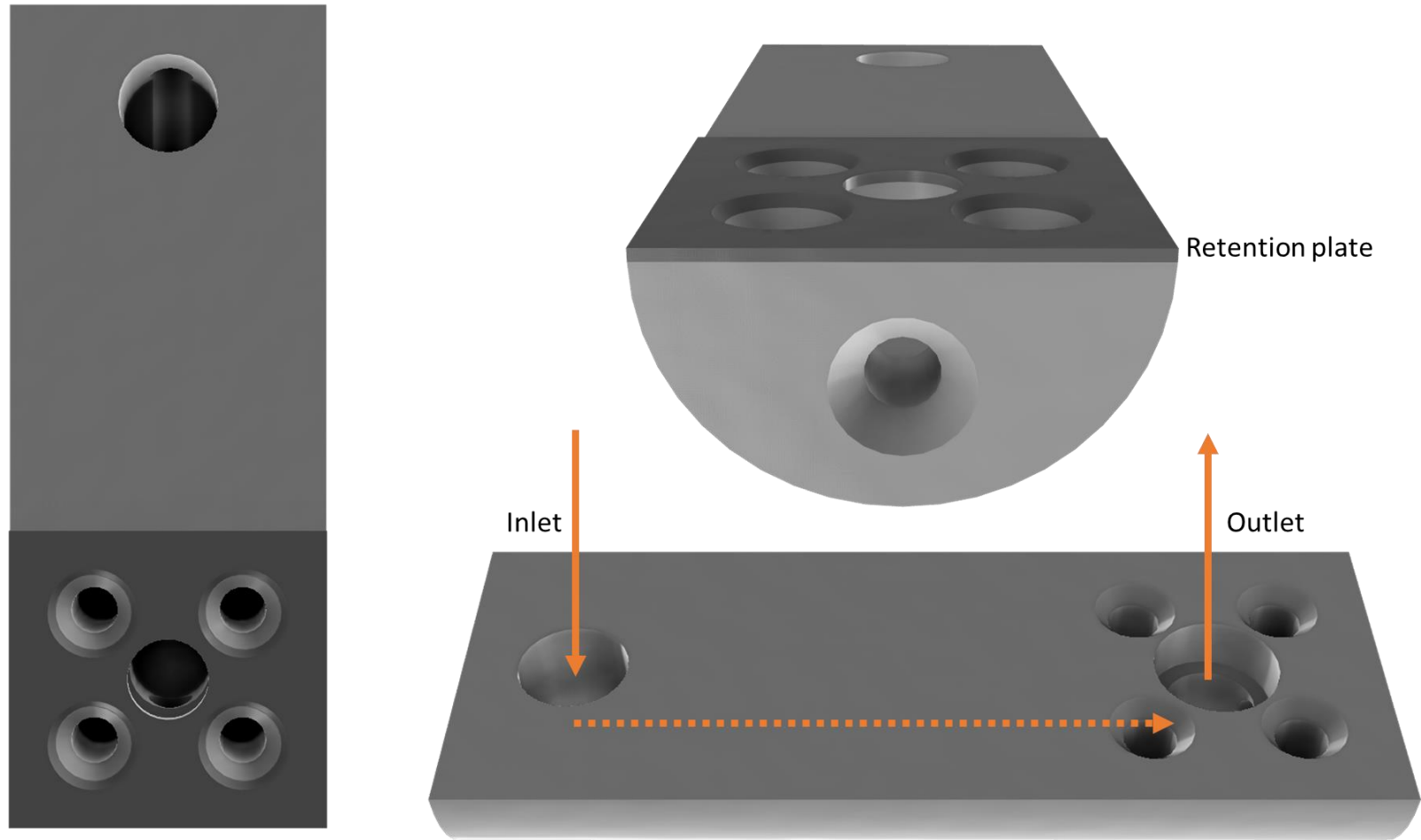


Figure 43 Computer generated rendition of the titanium frit holder (light grey) and retention plate (dark gray) and lines to demonstrate the route liquid will take through the holder when setup.

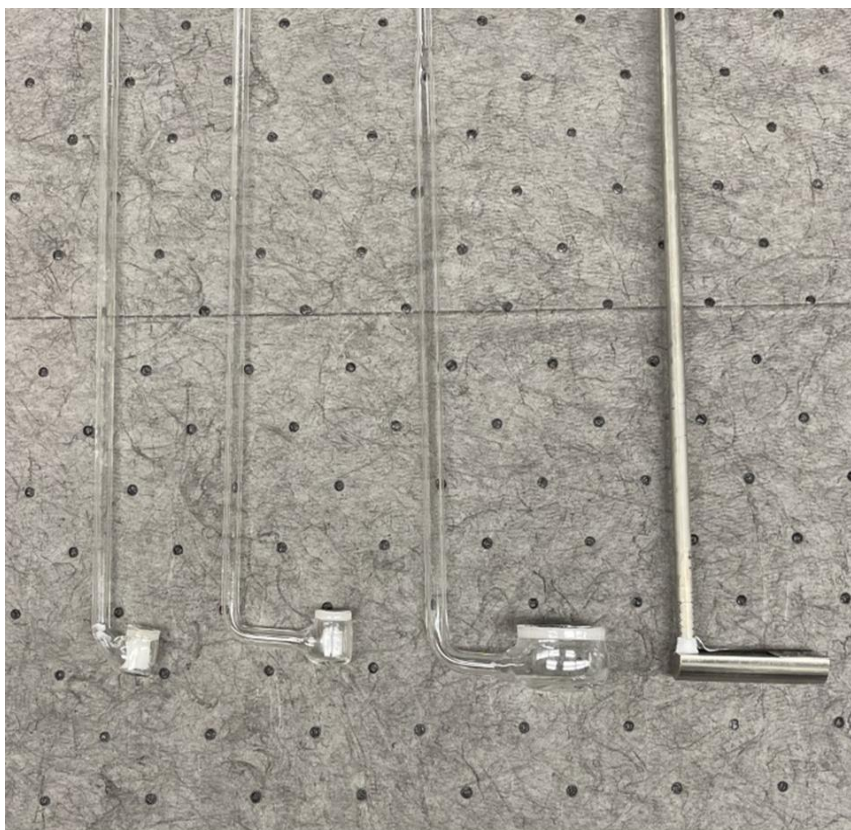


Figure 44 Side profile (left) and front profile (right) of the evolution of frits designed and improved for these studies.

ratio) from its original concentration of 1.6 molar to 0.8 molar for use in the frits. In the concentration study further dilutions of 0.53 (2:1 ratio) and 0.4 (3:1 ratio) molar were.

Precipitating solutions were comprised a balanced ratio of precipitant to metals (2:3) and then an additional 3 moles excess of precipitant. The excess precipitant accounted for the residual nitric acid from dissolving the oxide and metal, as well as acting as a buffer for the pH. This is following the procedures of other researchers in which an excess of precipitant is desirable for a complete reaction.^{[75][132][153][154]}

In the case of solid precipitants, like the ammonium carbonate and ammonium bicarbonate, all of the solid was added to the beaker containing a 50-50 mixture of isopropanol and water right before the precipitation. Stirring by the overhead stirrer would ensure dissolving and the excess of precipitant ensured a concentrated solution for the metal ion precursor solution to react with. The liquid precipitants, ammonium hydroxide and ethylenediamine, were mixed with the 50-50 mixed isopropanol and water solution right before the reaction to limit how much ammonia was lost over time as it sat. For the ethylenediamine, the solution was heated in a water bath to 50°C, consistent with the literature to promote the reaction of the amine with water and create an alkaline solution.^[75]

Experiments with the organic modifiers or capping agents, like the 2-ethylhexanoic acid (2-EHA), acetylacetone (ACAC), *para*-toluene sulfonic acid (*p*-TSA), or stearic acid, had these added directly to the metal ion precursor solution so there was a consistent amount present during the precipitation. These materials were added in an equivalence to

the aluminum content, following previous syntheses which required that for the sulfate and similar to the previous sections.^[125]

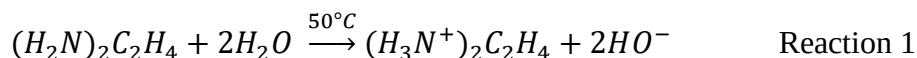
Separation of the precipitated material was done by gravity filtering through Whatman 42 filter paper in a 1-liter ribbed filter funnel and covered with aluminum foil to limit dust contamination. Filtration was left overnight to then be transferred to a crucible for calcination at 650°C for 3 hours. These powders were then analyzed by SEM, XRD, FTIR, and TGA. Liquid from the filtration was analyzed by ICP-OES.

Results

It was initially proposed to begin with a high concentration to limit time spent on studying this method, should it not have worthwhile results. The solution of yttrium, aluminum, and cerium nitrates was taken from its 1.6 molar total metal ion concentration and diluted to 0.8 molar. The use of a fine frit was chosen because of its 4 to 5 micrometer pore size and abundance from glass suppliers. Based on the previous precipitations attempted, a reverse strike (metals added into the precipitant) and concentrated solution of ammonium hydroxide (excess of 3 molar to metal ion ratio) were chosen as the conditions. Rapid stirring of 1000 RPMs by the overhead stirrer would mix the solution inside a 2000 milliliter beaker. A pump rate of 10 milliliters per minute was originally set but reduced to 3 because of the pressure the pump lines were under and a fear it might burst. Two experiments were performed with the frit using ammonium hydroxide or ammonium bicarbonate as two different precipitants. As a comparative, ultrasonic nebulization from the previous section was used to demonstrate any potential improvement over spray precipitation the frit might have.

SEM images from the ammonium hydroxide precipitation through the frit can be seen in Figure 45. While particle sizes are not initially within the sub-100 nanometer dimension, they are consistently sub-micron size and seem to be mostly around 200nm in size. The second experiment using ammonium bicarbonate as the precipitant had some initial issues with leaking from the interface of the pump tubing and glass tubing to the frit. This resulted in drips down to the body of the tubing to the precipitating solution but was rectified with hose clamps. In figure 46 some smaller particles from this bicarbonate precipitation can be seen coating the surface of the large chunks, but overall, this synthesis failed to yield a nanopowder. Of the two ammonium hydroxide precipitations using the external ultrasonic nebulized spray or the immersed frit, Figure 47 shows a stark difference where the ultrasonic nebulized spray precipitation produced only large, jagged chunks of material whereas the frit made an adequate dispersion of particles. This was a promising route from such a simple, direct injection approach, so the investigations continued.

Following this set of experiments another series was conducted to explore the effect of an amine on precipitation and concentration. Other amines have been reported, but ethylenediamine was the simplest and has a significant history in the literature as a ligand. Heating to 50°C promotes the reaction of the amine with water to form ethylenediammonium hydroxide through the reaction in Reaction (1)^[75]



Care was taken because without proper ventilation the ammonia-like fumes would overwhelm the immediate vicinity. Solutions of YAG were diluted from pyrolysis standardized YAG solution in ratios of 1:1, 2:1, and 3:1 dilution resulting in concentrations

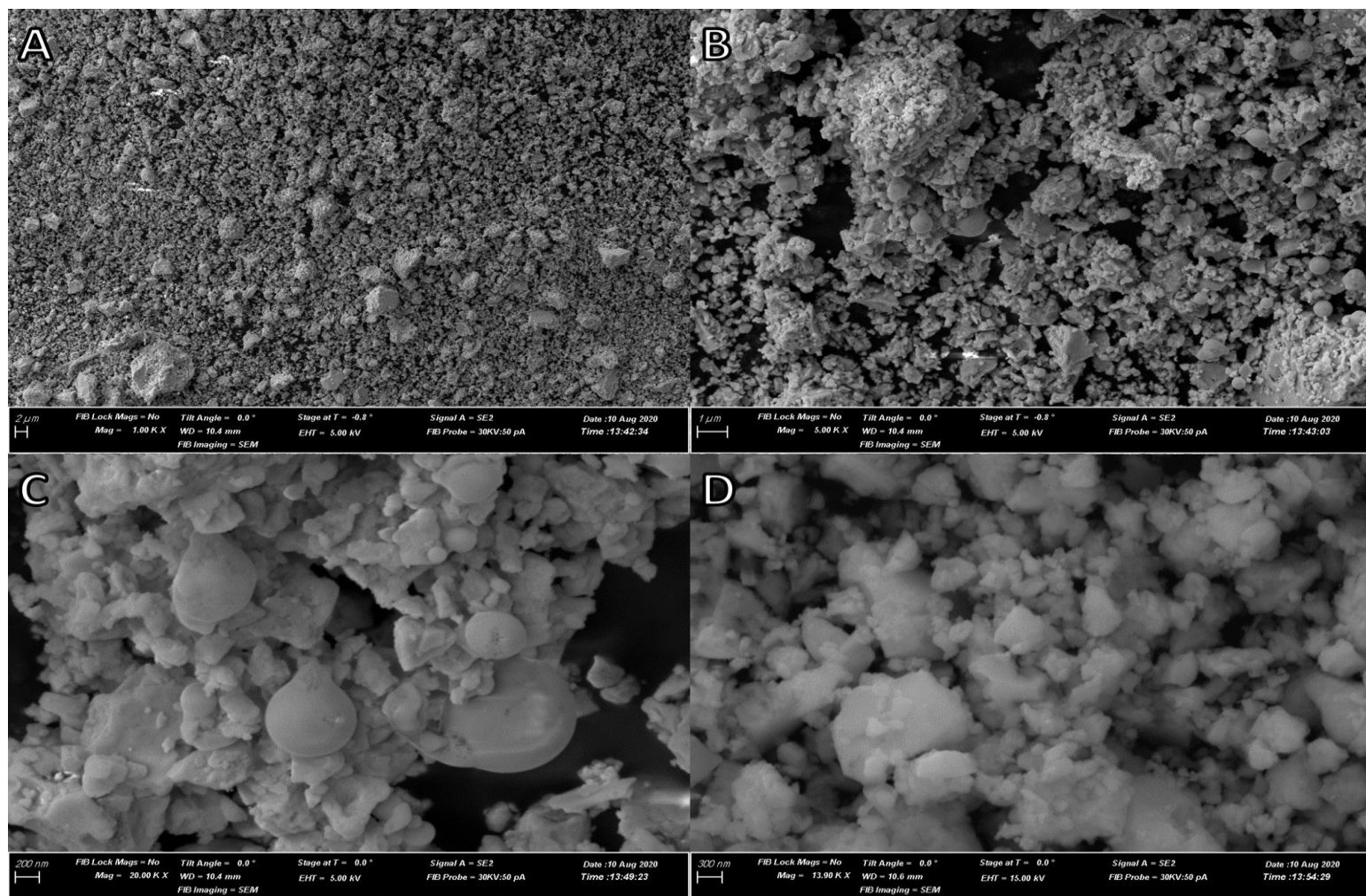


Figure 45 SEM images of powders precipitated with NH_4OH through a fine glass frit. Image bars are A) 2 μm , B) 1 μm , C) 200 nm, and D) 300 nm.

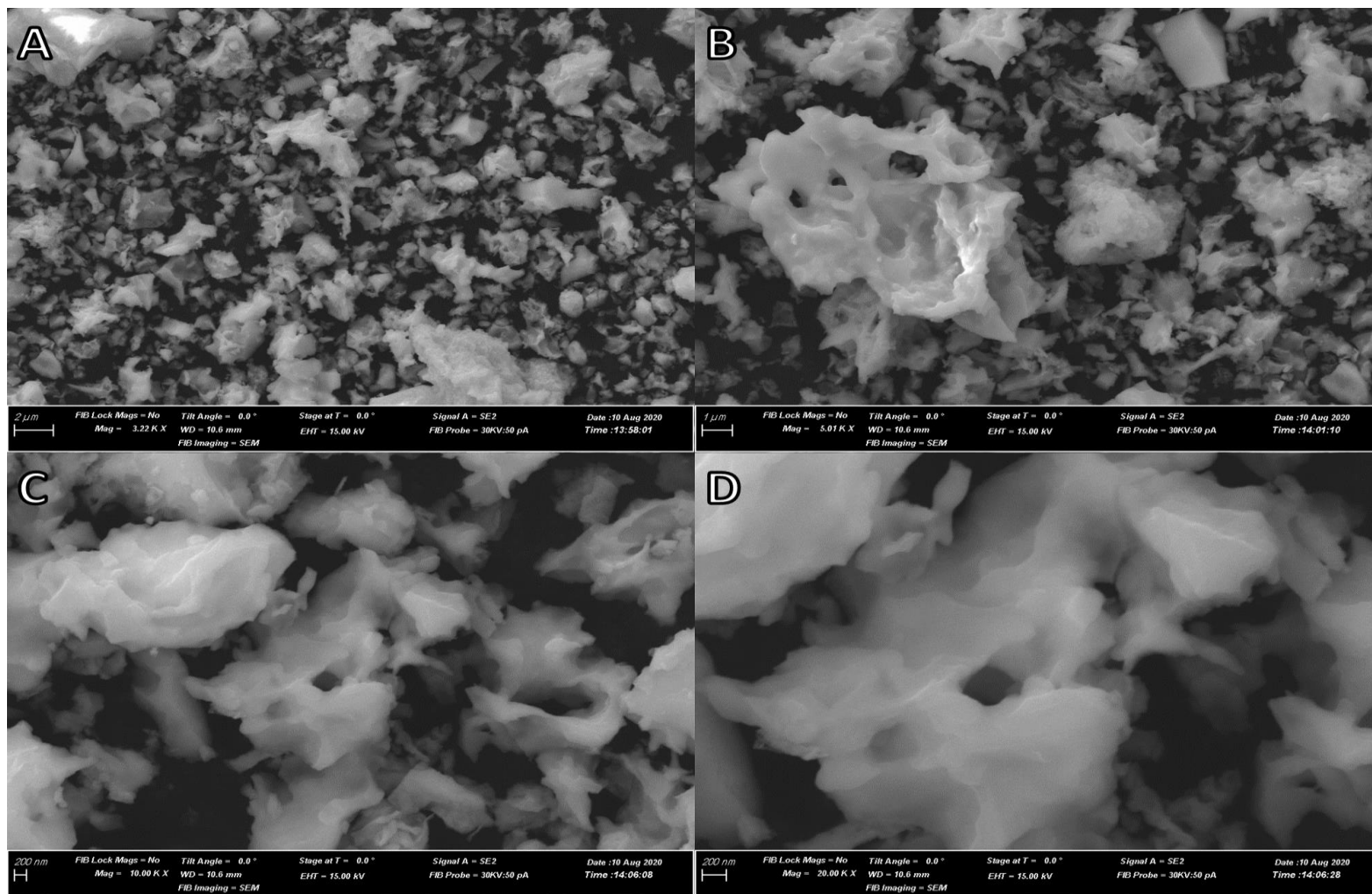


Figure 46 SEM images of powders precipitated with NH_4OH while being sprayed into the solution. Image bars are A) 2 μm , B) 1 μm , C) 200 nm, and D) 200 nm.

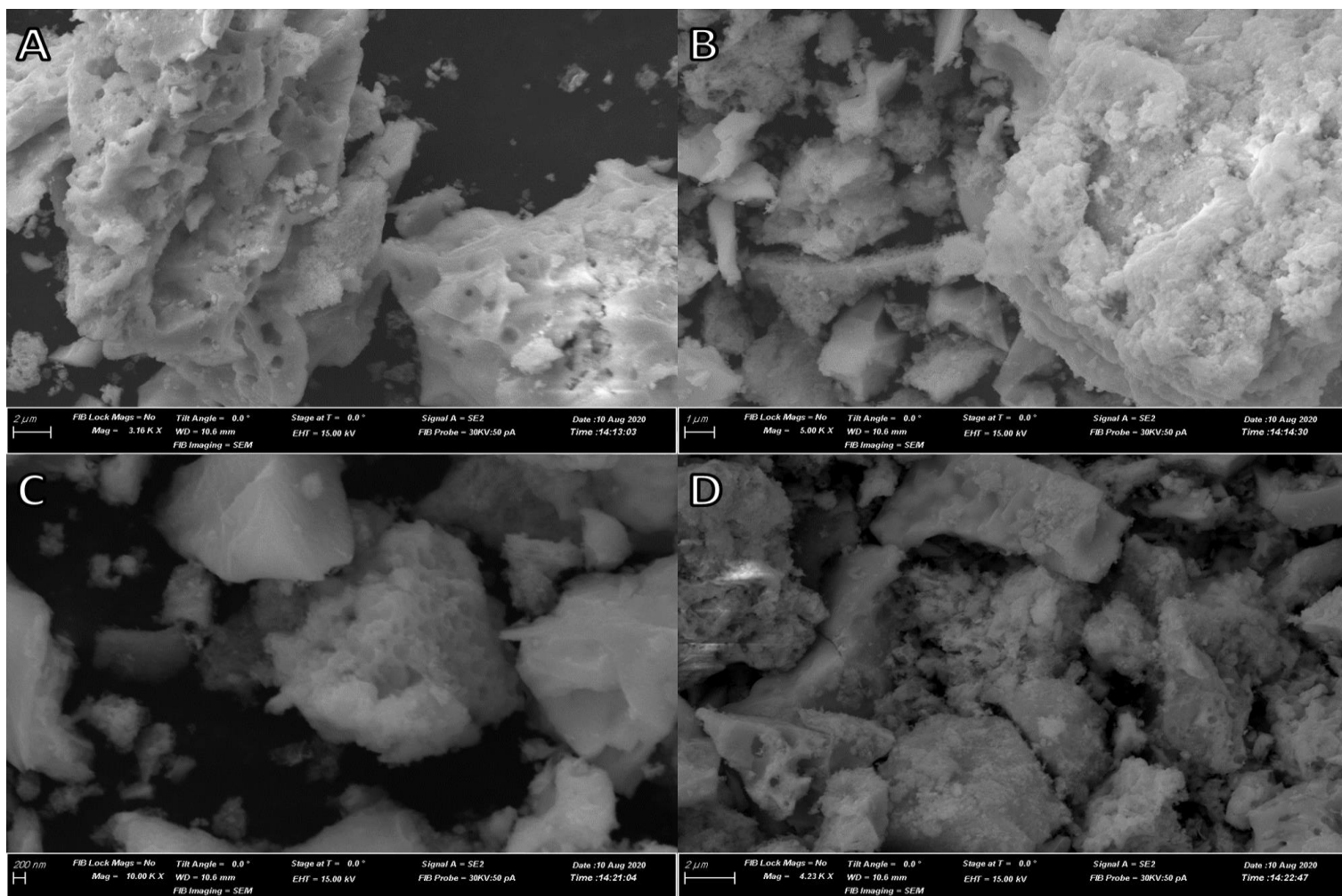


Figure 47 SEM images of powders precipitated with NH_4HCO_3 through a fine glass frit. Image bars are A) 2 μm , B) 1 μm , C) 200 nm, and D) 2 μm .

of 0.85, 0.56, and 0.42 molar. These dilutions were chosen because they fit within the beaker and didn't modify the setup since a more dilute solution would have necessitated a larger container. This would affect how the stirrer mixed the solution and the general flow; this was an attempt to limit that variable. These were also compared to a dropwise precipitation as a control.

SEM images of the resulting concentration study can be seen in Figures 48 through 50 comprised of collages of each dilution to give a broad overview. Figure 48 has the smallest particles resulting from the most concentrated solution of 0.85 molar. Some flakes are apparent in Figure 48B, but these are limited and small, as shown by Figure 48A. Figure 49 has the sample diluted in a 2:1 ratio resulting in a 0.56 molar solution. It has the most uniform powder results with chunks, not spherical particles. Figure 50 is the most dilute in a 3:1 ratio giving a concentration of 0.42 molar. Oddly enough, the particles here show a similar trend of large chunks, but these are much larger than the 2:1 dilution's pieces. The Figure 50A shows a wide view and makes it apparent that there are some significantly large pieces in this powder. For comparison, a dropwise 3:1 dilution was done, and its powder can be seen in Figure 51. The morphology here resembles the material passed through the frit.

In this system the more dilute solutions made larger particles, counterintuitive to what would be expected. After months of deliberation, it was hypothesized the mechanism here focuses on diffusion of precipitant into the metal ion extrusions. The more metal ions present, the more material there is to immediately precipitate and form a thick skin which prevents agglomeration of particles resulting from collisions. The less concentrated a

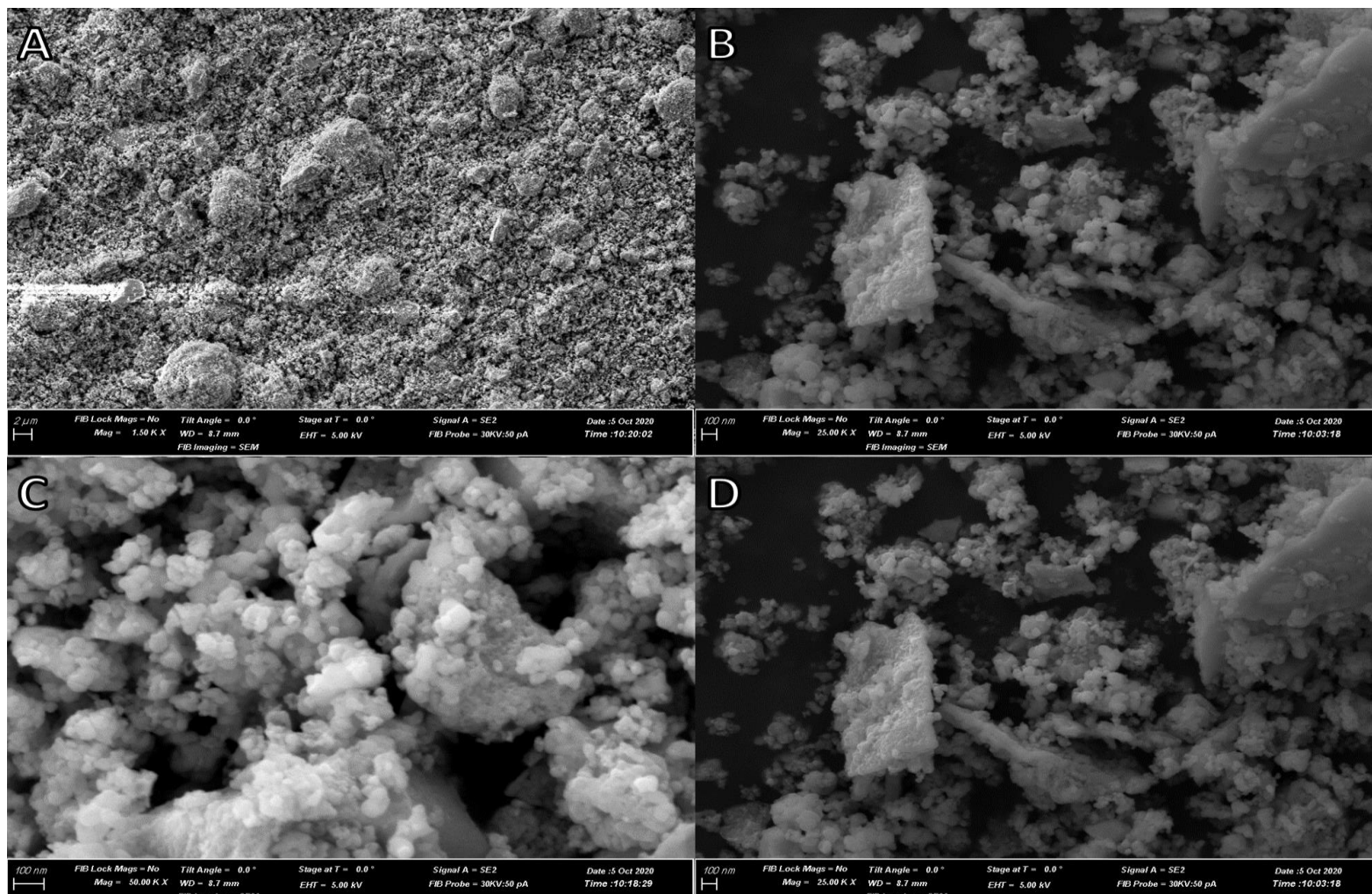


Figure 48 SEM images of YAG powders from a 1:1 diluted precursor solution passed through a fine glass frit and precipitated with ethylenediamine heated to 50°C. Image bars are A) 2 μm , B) 100 nm, C) 100 nm, and D) 100 nm.

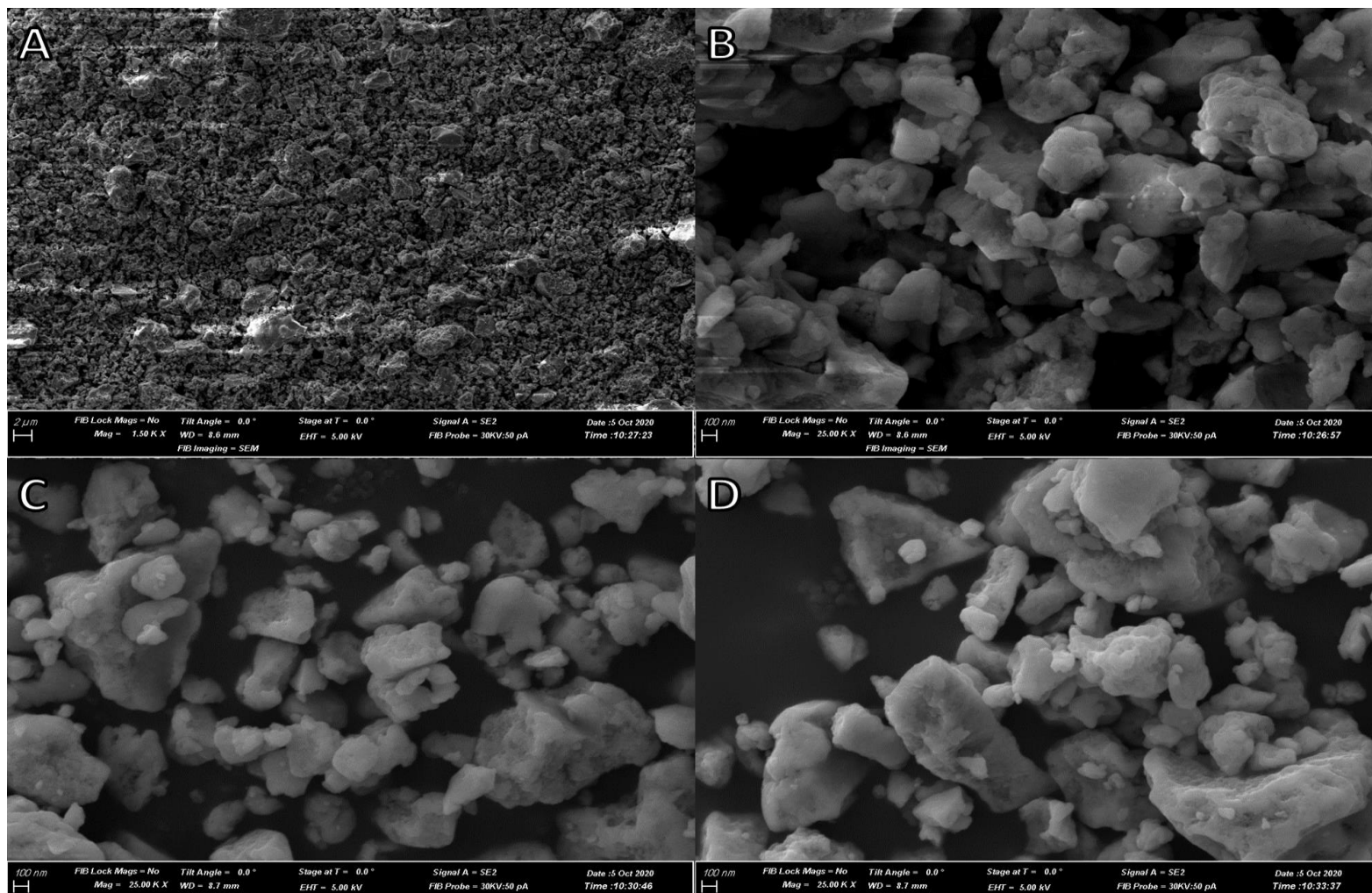


Figure 49 SEM images of YAG powders from a 2:1 diluted precursor solution passed through a fine glass frit and precipitated with ethylenediamine heated to 50°C. Image bars are A) 2 μ m, B) 100 nm, C) 100 nm, and D) 100 nm.

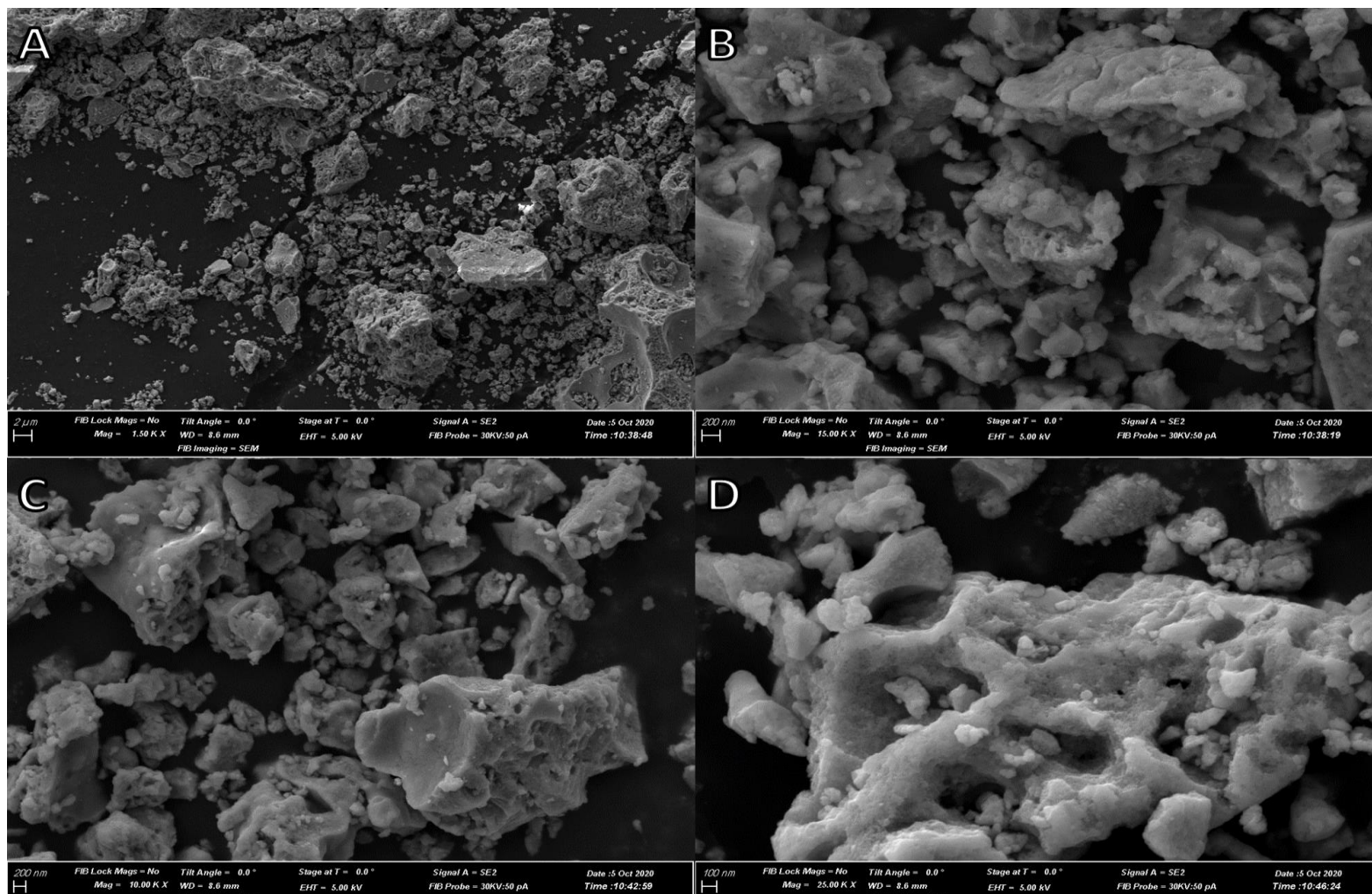


Figure 50 SEM images of YAG powders from a 3:1 diluted precursor solution passed through a fine glass frit and precipitated with ethylenediamine heated to 50°C. Image bars are A) 2 μ m, B) 200 nm, C) 100 nm, and D) 100 nm.

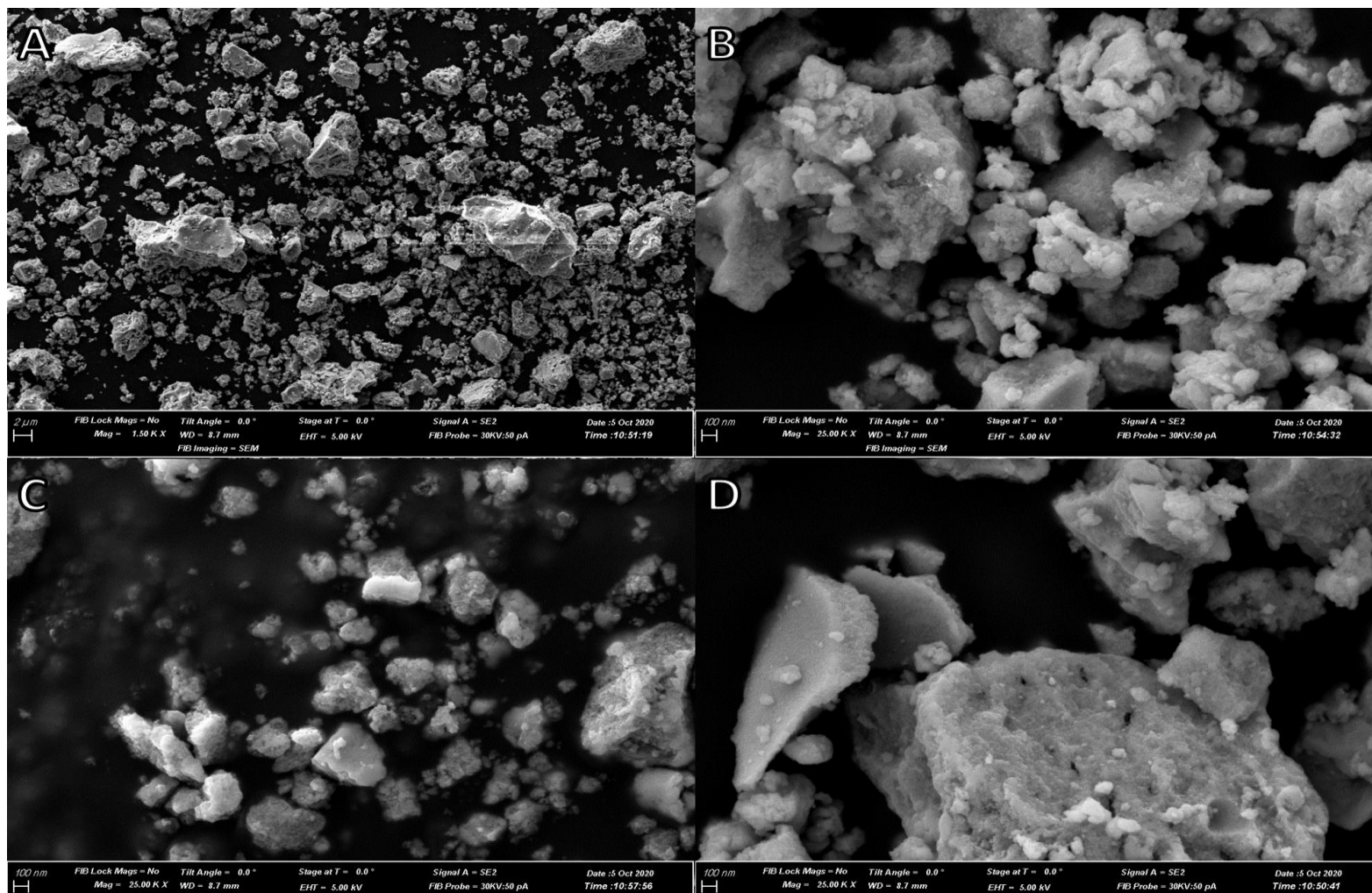


Figure 51 SEM images of YAG powders from a 3:1 diluted precursor solution dripped into an ethylenediamine solution heated to 50°C. Image bars are A) 2 μm, B) 100 nm, C) 100 nm, and D) 100 nm.

solution, the thinner a skin and longer it takes for a robust skin to form and more likely a collision with another droplet causes breakthrough of the skin and results in agglomeration. This would explain the larger particles in each scenario as being derived from impacts and the robustness of the skin as based on the diffusion rate of the precipitant into a droplet to continue the reaction and thicken the skin.

Regarding the ethylenediamine used as the precipitant, since success was had with the morphology of small particles from a concentrated solution, ICP was used to analyze the filtered effluent. It was found that in all of the samples that aluminum remained in solution, typically 200 parts per million. No yttrium or cerium was found with it in relative ratios, eliminating the idea that some precipitant had made it through. This could have been due to the chelating property of ethylenediamine, since aluminum and rare earths are complexed similarly^[155], therefore yttrium and cerium would be expected in the samples as well. pH is the only major factor that could have selectively drawn aluminum back into solution. Because of this consistent result, ethylenediamine was not pursued any further since it risked the stoichiometry of the final product.

At the same time as the concentration studies were conducted, experiments exploring capping agents was undertaken to compare unmodified material of YAG to that of YAG synthesized with capping agents in an ammonium carbonate precipitation. *p*-TSA and stearic acid were chosen as capping agents. The sulfonic acid group on *p*-TSA was expected to behave like sulfate has been shown to behave from other researchers^[125] and the organic bulk of the material might help sterically hinder particle agglomeration. Stearic acid was chosen because of its long chains for more steric bulk and researchers have

previously shown that it is capable of producing nanoparticles from yttrium stearate.^[107] Both of these were soluble in the 0.8 M precursor mix and needed no other additives, but the stearic acid did need heat to melt and homogenize in the solution and required heating during the precipitation to flow through the frit. Precipitation was conducted with ammonium carbonate.

The SEM images in Figure 52 show the *p*-TSA samples which look the best of any sample so far with consistently small nanoparticles below 50nm in size in every picture. The samples with stearic acid shown in Figure 53 have a significant presence of flakes, as discussed previously these flakes are attributable to rare earth carbonates. Compared to a control that was made without a capping agent, the resulting powders seen in Figure 54 are very coarse but show some loose powder that might be liberated if milled or broken up by ultrasonication. This study highlights the benefits of sulfate and shows that in this system where ammonium sulfate is insoluble in the solvent mixture, but organic sulfates may be used in a similar manner to make discrete nanoparticles.

The promising small particles from the *p*-TSA sample were processed by an outside group and when returned it was found that there was too much residual carbon residue and the sulfate's high temperature residence on powders prevented total consolidation. The sample can be seen in Figure 55 compared to a properly made cerium-doped transparent standard. More research would be needed to understand this carbon residue and the sulfate's influence.

Due to the lack of understanding about the influence of organic compounds resulting in residue, a series of experiments was proposed to study the effects of some

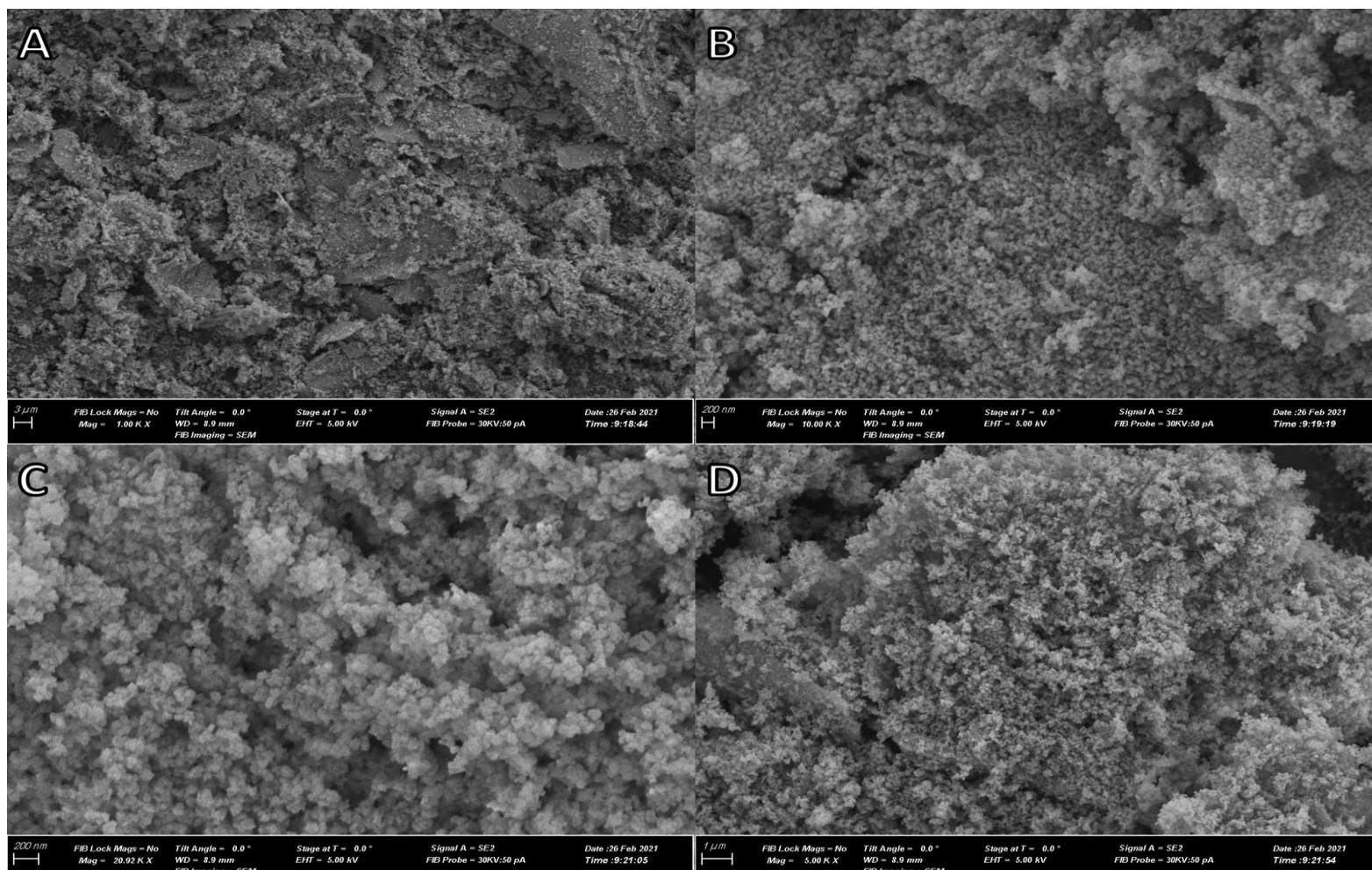


Figure 52 SEM images of YAG powders diluted 1:1 and mixed with p-TSA as a capping agent. These were precipitated with ammonium carbonate by passing the precursor YAG solution through a fine glass frit. Image bars are A) 3 μm, B) 200 nm, C) 200 nm, and D) 1 μm.

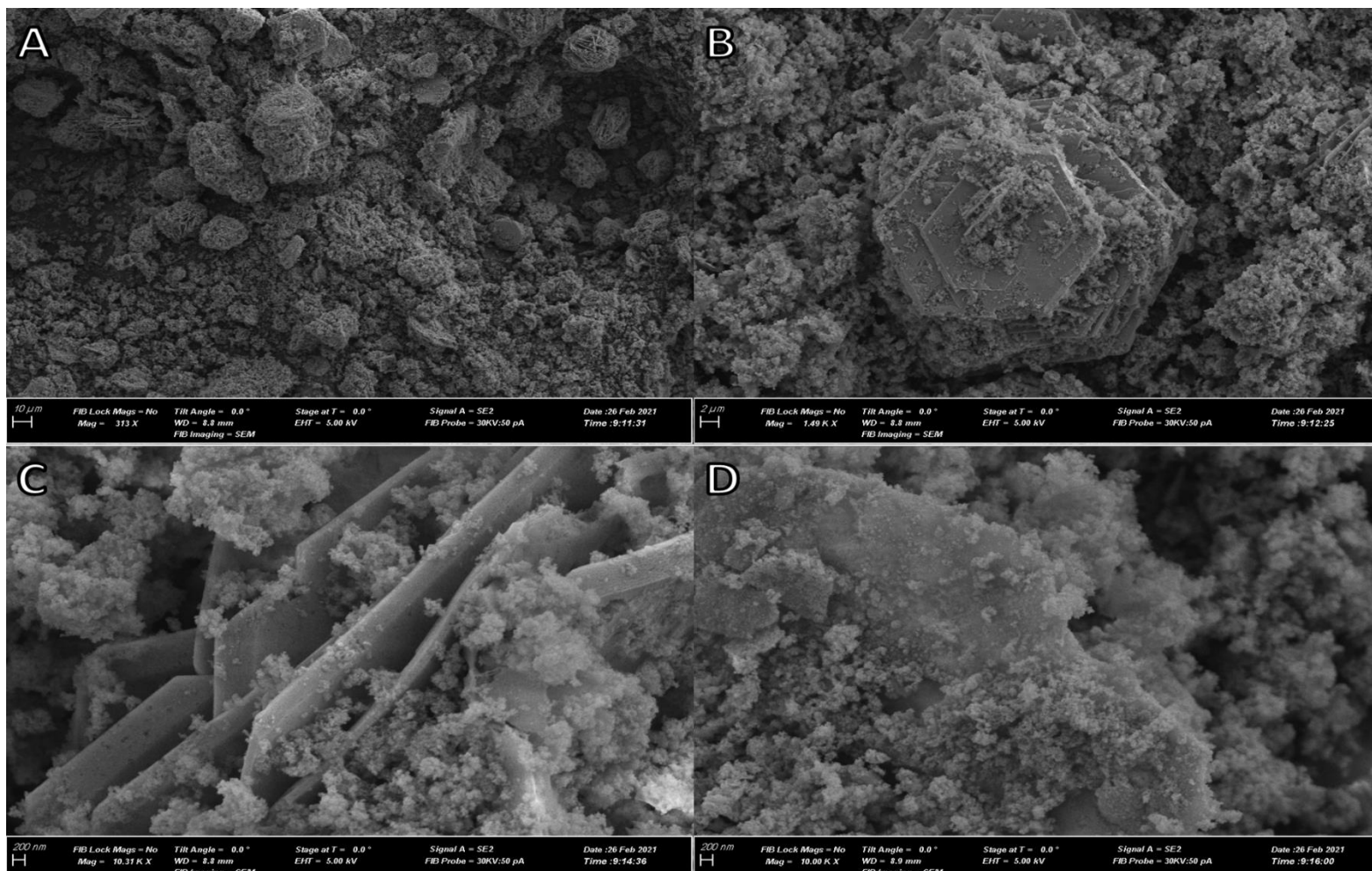


Figure 53 SEM images of YAG powders diluted 1:1 and mixed with stearic acid as a capping agent. These were precipitated with ammonium carbonate by passing the precursor YAG solution through a fine glass frit. Image bars are A) 10 µm, B) 2 µm, C) 200 nm, and D) 200 nm.

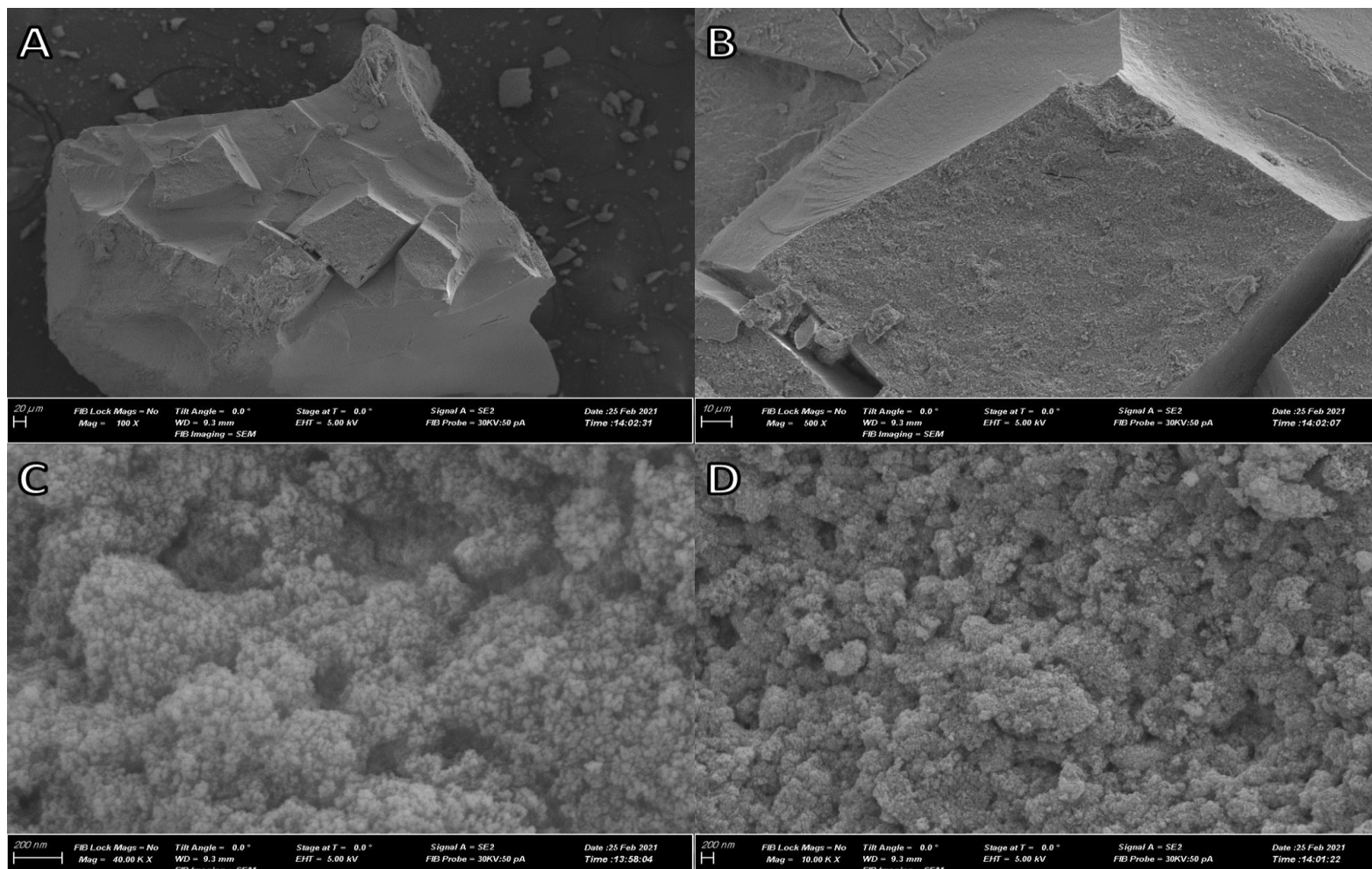


Figure 54 SEM images of YAG powders diluted 1:1 and no capping agent. These were precipitated with ammonium carbonate by passing the precursor YAG solution through a fine glass frit. Image bars are A) 20 μ m, B) 10 μ m, C) 200 nm, and D) 200 nm.

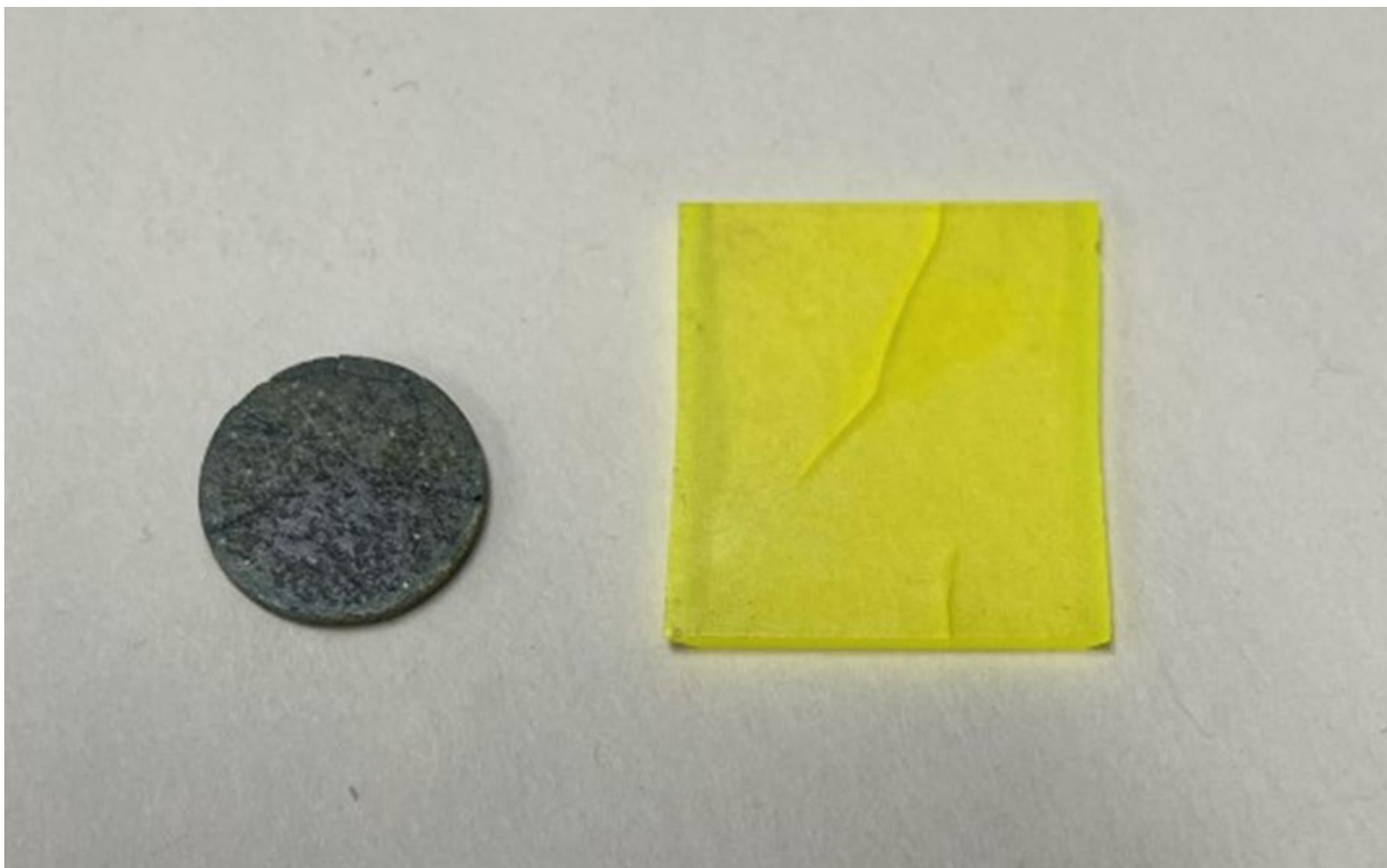


Figure 55 Pressed sample of the p-TSA capped powder (left) and a transparent standard (right) processed by an outside group.

simple organic modifiers on the powder, as well as the most basic approaches that could be taken to make a powder. These approaches were simply the control experiments for this study, consisting of precipitation using either ammonium hydroxide, ammonium bicarbonate, or ammonium carbonate as the precipitant. Two organic modifiers were chosen ACAC or 2EHA because these were leftovers from the FSP experiments and ACACs are known to readily decompose to the oxide.^{[156][157]} Fortunately, the mixture of isopropanol and water made it easy to homogenize the metal ion precursor solutions. Care was taken to calculate and add equal proportions of modifier and solutions were diluted to equal volumes with a total metal ion concentration of 0.8 molar. In all, nine experiments were performed to try and outline the best approach for the frit and future experiments. Because of the successes and frustrations so far, these experiments were investigated a little further than just SEM images.

Powder X-ray diffraction was used to characterize the phase purity of the samples. The samples which were sintered at 1000°C for six hours under air show the crystallinity of the product, and in several samples yttrium and aluminum monoclinic phase and yttrium oxide phases appear. Other researches have noticed monoclinic^[158] and perovskite^[153] phases arising from experiments to precipitate YAG. The samples in Figure 56 show that the garnet phase was consistent among all samples.

Characterization of the precipitated material composition by thermogravimetric analysis (TGA) was conducted to measure the weight loss as a function of temperature. Figure 57(Top) shows the decomposition of comparable hydroxide precipitated material, the only difference being the presence or lack of an organic modifier. An initial loss of

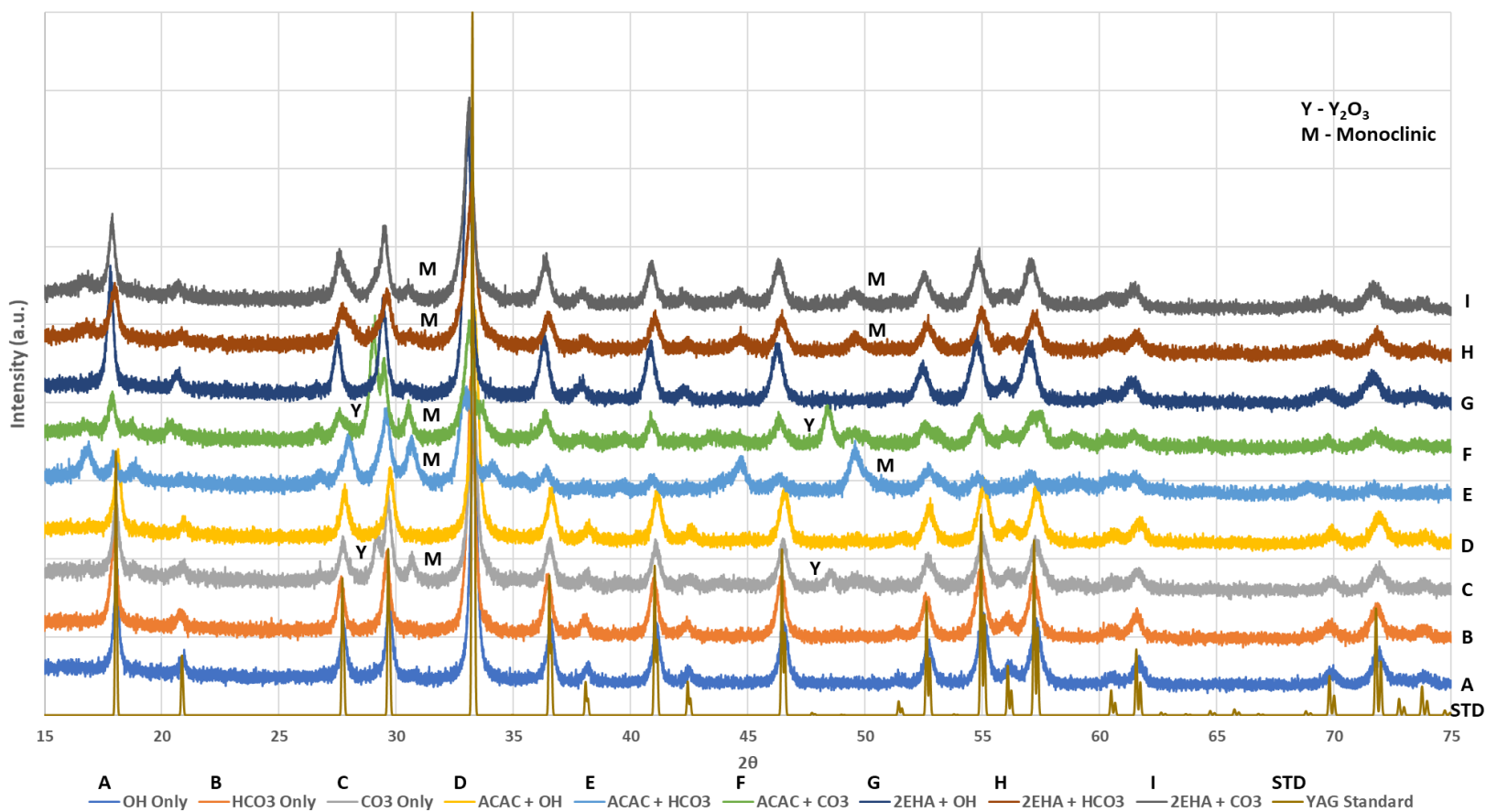


Figure 56 Combined plot of all PXRDs of the powders sintered at 1000°C. Labelled A) OH only, B) HCO₃- only, C) CO₃-2 only, D) OH+ACAC, E) HCO₃+ACAC, F) CO₃-2+ACAC, G) OH+2EHA, E) HCO₃+2EHA, F) CO₃-2+2EHA

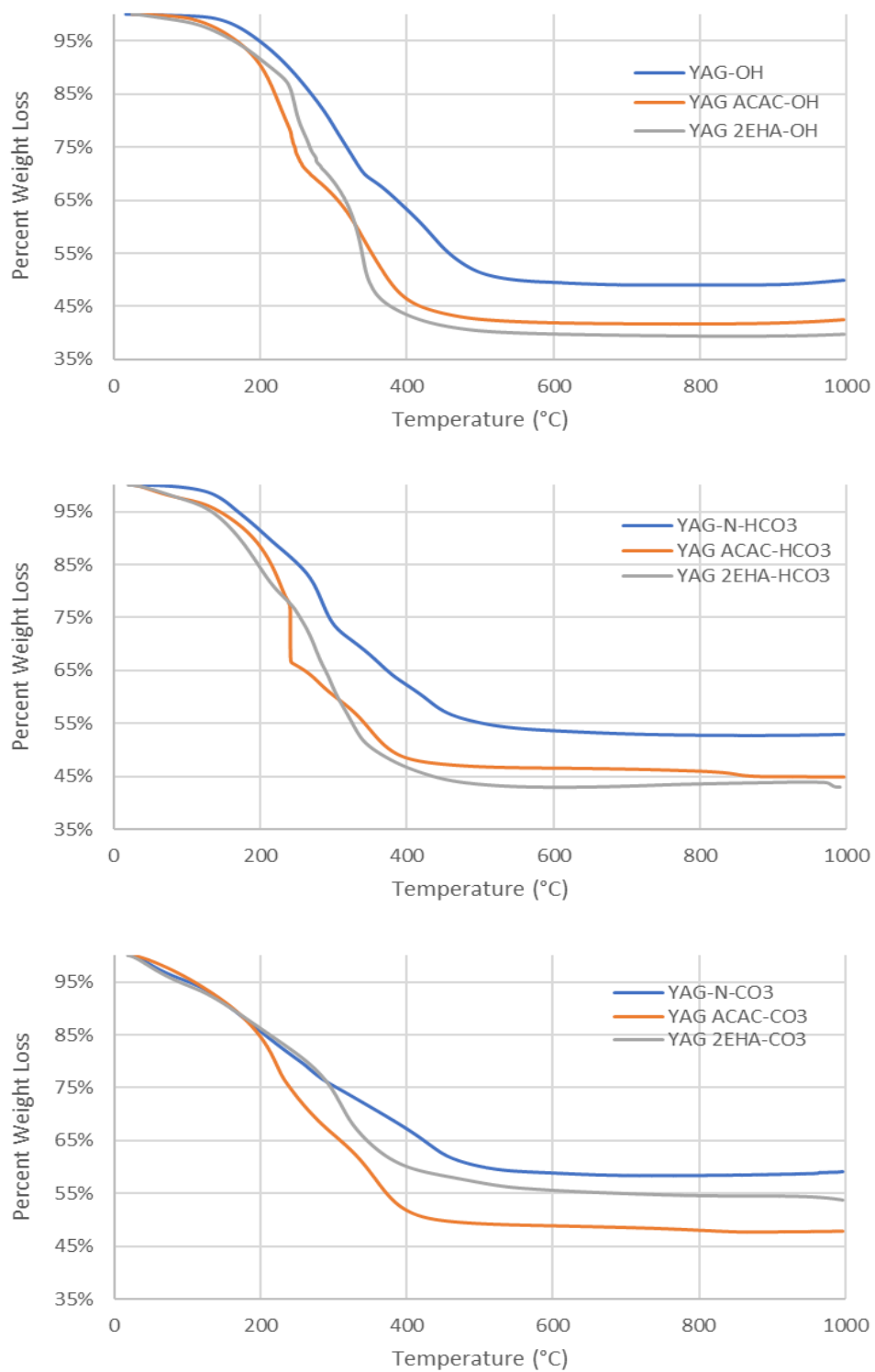


Figure 57 Combined TGAs of the precipitated material.

solvent is noticed until roughly 250°C, which is consistent with literature.^{[105][114]} Decomposition of the organic additives^{[157][159]} and conversion of the material to oxide from >250°C causes the two samples (orange and grey) to see more steep weight loss as compared to the sample (blue) made without any additive.

Figure 57(Middle) is similar to Figure 57(Top) with the initial weight loss due to solvent loss and decomposition of the organic to result in an oxide. The plateau portion from 600-1000°C shows a slow, downward trend, which is often attributed to residual carbonate that slowly degrades with increasing temperature.^{[153][160]} Of note, the experiment for YAG with ACAC (orange) added to the precipitation was repeated and also saw a similar sharp drop in weight at 240°C. This is potentially due to volatilization of material, which the rare earth acetylacetonates are known for.^[161] The plots in Figure 57(Bottom) show less weight loss than in Figure 57(Top), likely due to the powdery metal carbonates formed, which do not absorb much liquid as do the gelatinous metal hydroxides seen in Figure 57(Top).^{[159][160]}

For characterization of the amorphous and calcined powders, infrared analysis was used. This fingerprinting technique shows the effects of each precipitation on the resulting powder by how much precipitant follows over, organic modifier accompanies the product, and any residue that remains after calcination.

Calcination at 650°C was chosen from the TGAs because of the plateau where the majority of conversion to an oxide is done and the material is still amorphous. Some attributable stretches of the precipitants and additives can be seen in Table 5 so labelled

Table 5 Showing the bends and stretches of the precipitants and modifiers

NH ₄ HCO ₃ ^{[117][118]}		(NH ₄) ₂ CO ₃ ^[117]		2EHA ^[166]		ACAC ^[165]	
2343 cm ⁻¹	CO ₂ (aq)	1558 cm ⁻¹	COO- asymm stretch	3400- 2400 cm ⁻¹	O-H Stretch	3000 cm ⁻¹	CH3 in plane
1650 cm ⁻¹	C-O asymm stretch	1540 cm ⁻¹	N-H bend	2951 cm ⁻¹	Asymmetric CH2 stretch	2900 cm ⁻¹	CH3 out of plane
1640 cm ⁻¹	H2O	1446 cm ⁻¹	NH3 sym bend	2868 cm ⁻¹	Symmetric CH2 Stretch	1700 cm ⁻¹	C=C-C=O vibration
1545 cm ⁻¹	N-H bend	1397 cm ⁻¹	-CO asym stretch	1697 cm ⁻¹	Carboxylic acid C=O Stretch	1600 cm ⁻¹	C=O
1458 cm ⁻¹	NH- bend	1296 cm ⁻¹	C-OH sym stretch	1458 cm ⁻¹	In plane O-H Stretch	1410 cm ⁻¹	CH3 in plane
1413 cm ⁻¹	-CN symm stretch	1023 cm ⁻¹	C-N stretch	1276 cm ⁻¹	C-O Stretch	1350 cm ⁻¹	CH3 Stretch
1395 cm ⁻¹	-CO asymm stretch	952 cm ⁻¹	NH3+ coupled	938 cm ⁻¹	Out of plane O- H stretch	1245 cm ⁻¹	C-C=C stretch
1365 cm ⁻¹	C-O symm stretch	833 cm ⁻¹	NCOO- out of plane bend	776 cm ⁻¹	CH2 Rocking	1160 cm ⁻¹	C-H
1300 cm ⁻¹	C-OH sym stretch	704 cm ⁻¹	NCO- bend			995 cm ⁻¹	OH
1120 cm ⁻¹	-CN symm stretch	686 cm ⁻¹	COO- in plane bend			910 cm ⁻¹	C-CH3
1111 cm ⁻¹	NH3 bend					780 cm ⁻¹	OH
1005 cm ⁻¹	C-OH asymm stretch					630 cm ⁻¹	Ring bending

peaks can be found more easily. Standards of the organic additives are also added to applicable graphs of Figure 58 (grey lines) for reference.

In Figure 58 (Column A) the precipitations with no organic additive, the presence of the alcohol stretch at 1040 cm^{-1} can be seen remaining in the precursor (blue lines) after drying. The alcohol surviving the drying is likely due to a proposed interaction between hydroxides and alcohol resulting in adsorption.^[162] The carbonate samples (Figure 58, graphs A2 and A3) both match for their respective peaks from the resulting metals carbonate produced by the reactions. The absorption peaks in these spectra match the spectra from other literature.^{[114][163][164]} In the calcined sample (orange lines) some carbonate stretches were noted, showing the persistence of carbonate beyond 650°C . The hydroxide sample (Figure 58, graph A1) does not have a carbonate peak because no carbonate was present in its synthesis.

Figure 58 combines the display of acetylacetone modified material in column B with an ACAC standard reference spectrum (grey line) in each subfigure for referencing. This shows the enol form of the diketone at the $3500\text{-}2200\text{cm}^{-1}$.^{[156][165]} Metal-ACAC complexes are apparent with numerous fingerprint peaks in the $<1700\text{cm}^{-1}$ region in the precursor (blue lines). The calcined samples (orange lines) all have peaks from carbonate that have survived through the 650°C calcination.

The 2-ethylhexanoic acid samples seen in Figure 58 (Column C) have the reference spectrum (grey line) with a distinct peak at 1700cm^{-1} . This is missing in all of the precursor spectra (blue lines) because that peak corresponds to the $\text{C}=\text{O}$ of the carboxylic acid. The lack of a peak shows that oxygen is contributing to the coordination with a metal.^[166] The

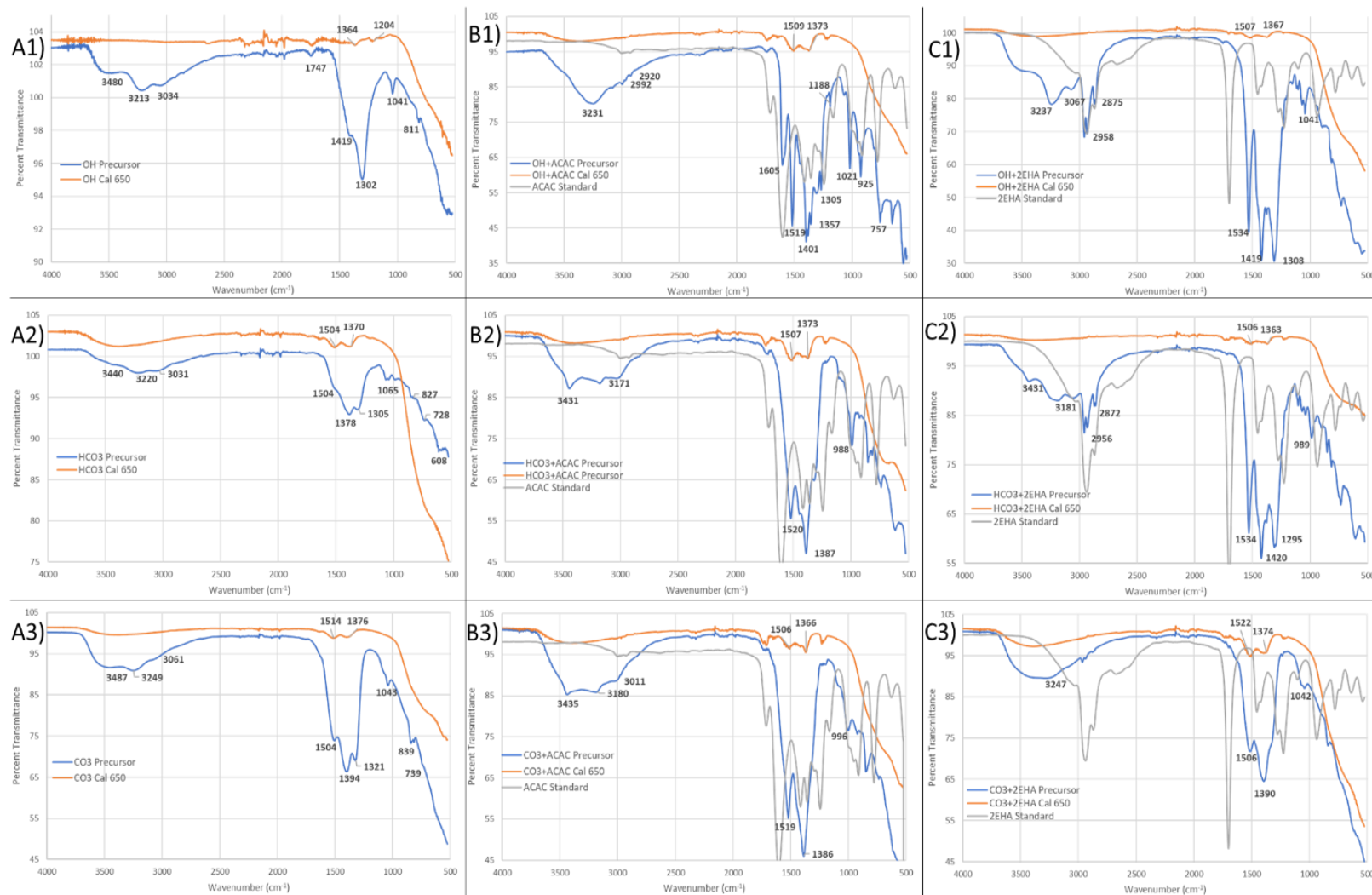


Figure 58 Combined figure of the nine systems FTIR's where column A) No organic, B) ACAC, and C) 2EHA. Row 1) OH⁻, 2) HCO₃⁻, 3) CO₃²⁻ precipitants.

carbonate precipitations (Figure 58, graphs C2 and C3) both have fingerprints of metal carbonates present in their spectra as the product is a mixture of metal carbonates and ethylhexanoates. The calcined samples (orange lines) have a pronounced presence of carbonate.

SEM has been employed to depict the sizes and the morphologies of the products from the nine experiments. Prior to the SEM imaging, all samples were calcined at 650°C in air for six hours. The SEM images are shown in Figures 59. The image bar in Figure 59 is 100 nm.

When no organic additive has been used, tightly packed particles are evident in the NH_4OH system, but for the HCO_3^- and CO_3^{2-} systems, the particles are finely dispersed and measure roughly 30 nm in size. The samples from the CO_3^{2-} system show some platelets, likely yttrium carbonate.^[167] This observation agrees with the loss of stoichiometry seen in the corresponding PXRD pattern.

The three samples produced with 2-ethylhexanoic acid additive show different morphologies. The NH_4OH system has spherical particles loosely packed and about 100 nm in size. The HCO_3^- system shows large particles which are irregular in their morphologies. The CO_3^{2-} system reveals finely dispersed particles about 50 nm in size. Again, PXRD indicate different stoichiometries based on the different phases.

The three samples made with acetylacetone as the additive show an array of sizes and morphologies. The NH_4OH particles look like flowers with many ridges and spikes on a relatively large ball. The HCO_3^- system yielded small particles mixed with platelets

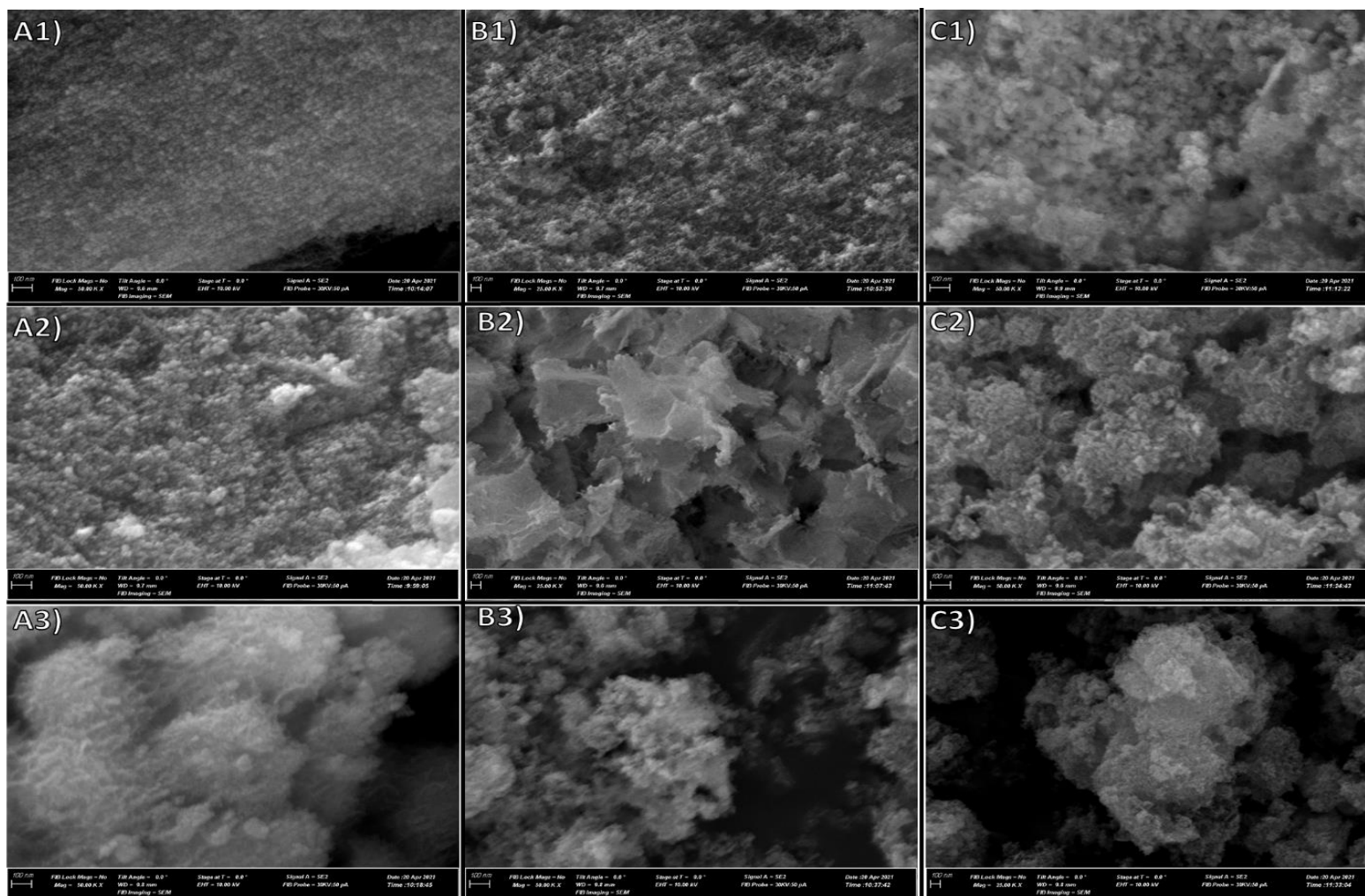


Figure 59 A near-field view of the powder calcined at 650°C where column A) No organic, B) ACAC, and C) 2EHA. Row 1) OH⁻, 2) HCO₃⁻, 3) CO₃²⁻ precipitants. The scale bars are 100 nm in size.

similar to the CO_3^{2-} with no organic additive system. The CO_3^{2-} system produced tightly packed particles with much necking and bridging between the spheroids.

The previous paragraphs led to the selection of the HCO_3^- system with no organic additive because it was the best and simplest system. To demonstrate the value of the frit delivery of the concentrated metal ion solution (0.8 M), the HCO_3^- system with no additive was compared with a widely employed dropwise coprecipitation system. Note that in both cases 0.8 M metal ion solution was introduced into a HCO_3^- solution. The SEM results for these two cases are displayed in Figure 60. Frit delivery gives finely sized and distributed nanoparticles, whereas dropwise delivery yields varying large clumps of tightly packed particles. It is well known that to obtain smaller particles in the latter case, the metal ion concentration must be reduced.^[78]

Concurrent with these nine studies, an investigation into the effects of a fine frit with smaller pores on the resulting precipitant was conducted. Ultrafine glass frits, P5 European or Very Fine and Ultrafine American glass frit porosity ratings were avoided because of advice from a glassblower that these would not be easy to place in the glass tubing setup without compromising the frit's integrity. This left chromatography grade frits, which can come in even finer porosity than glass frits. A titanium frit with a plastic polyether ether ketone enclosure from Analytical Scientific Instruments US with a rated average pore size of 0.2 μm , was chosen because of titanium's oxide coat which is resistant to dilute acids and bases. A holder was designed to retain the frit with a plate as shown in Figure 43 where the light grey body is formed from a titanium rod and the dark grey plate is from a rigid and thin sheet of titanium. This would be held in place by

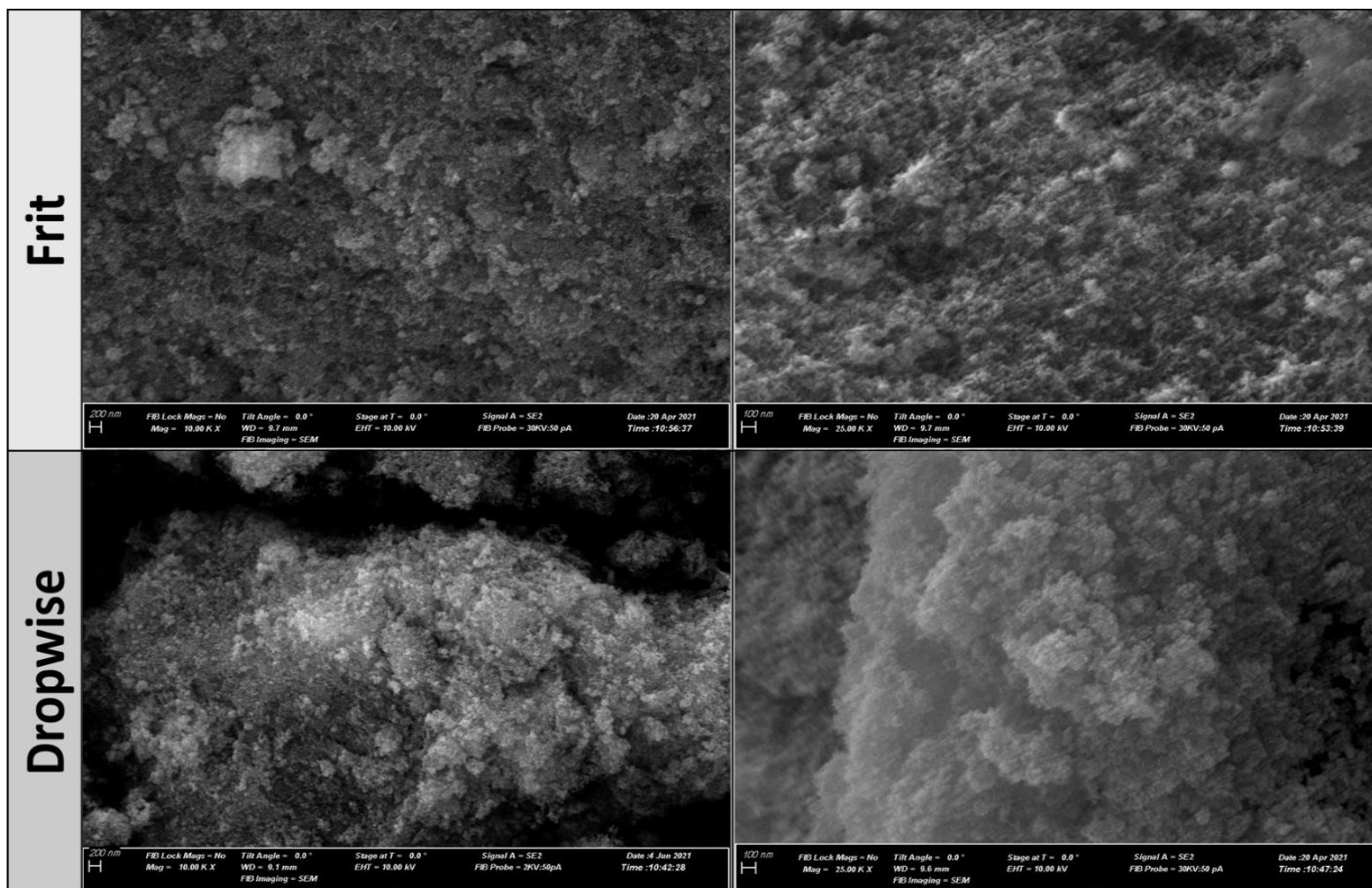


Figure 60 A combined image setup showing the frit (top) and dropwise (bottom) additions in a far and close-up view. Left is a 200nm scale bar, right is a 100nm scale bar.

titanium screws and the front hole would be plugged with a titanium screw plug. The rear hole was fit with some titanium tubing making this holder rigid and resilient, capable of chemically resisting the acidic conditions of the precursor solution inside and alkaline conditions of the precipitating solution outside as well as physically resist the rapid stirring.

The experiment worked well, but a screw was not able to be tightened enough due to a shallow hole resulting in a leak from the plate. Due to time and the modification needed, this experiment was not able to be conducted again. SEM images of this experiment can be seen in Figures 61. These figures show some large particles, likely resulting from the leak, and a distribution of smaller particles, which might be attributed to precipitated material from the frit. If the smaller particles are from the titanium frit, then their size is an order of magnitude smaller than those from the fine glass frit. Further, the agglomeration of these smaller particles onto the larger material may corroborate to the hypothesis about thinner skin, less developed particles may stick together if they meet early enough in the particle growth. The proximity of the leak and the frit were immediately next to each other in the flow of the solution.

Revisiting the previous attempted synthesis using a titanium chromatography frit, which had failed due to a leak from an improperly seated O-ring, another attempt with extra care given to the setup of the frit holder was performed. This setup used ammonium bicarbonate as the precipitant and an 0.8 M metal-ion precursor solution fed through the frit and into the precipitant. Stirring was kept at a constant 1000 RPM and the feed rate of solution through the small frit was limited to 3 mL per minute. Early glass frit

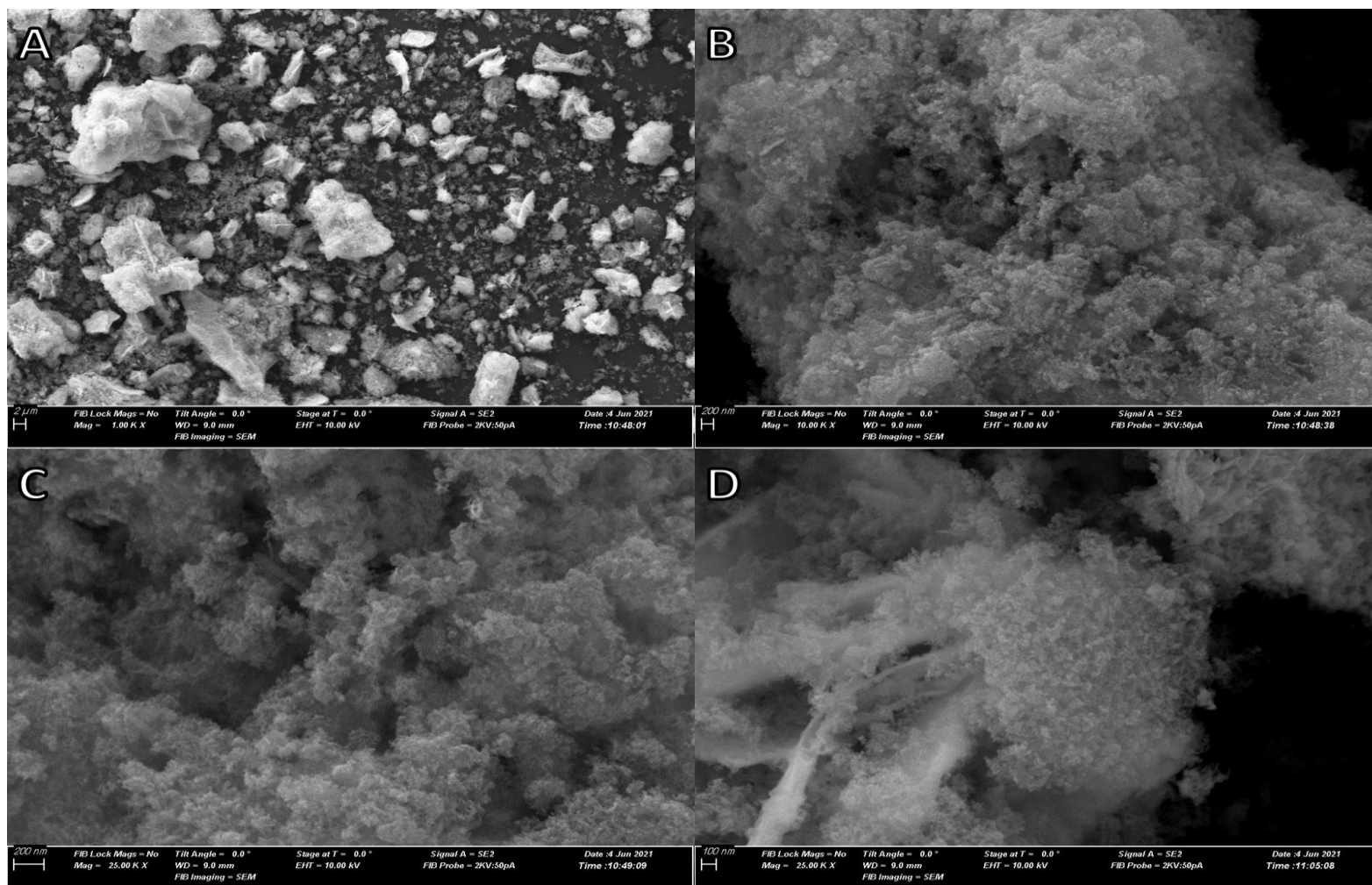


Figure 61 YAG powder precipitated by passing the 0.85 molar solution through an ultrafine titanium frit into an ammonium bicarbonate solution.

precipitations like those in Figure 45 were also done at 3 mL per minute, for the reader's reference. The results from the second attempt with the titanium frit can be seen in Figures 62 and 63 give two wide views of the bulk material and then close-ups of a specific region. Particles measured were found to be less than 30 nm consistently. Finally, a comparison between the ultrafine titanium frit to more YAG precipitate from a fine glass frit at a precursor flow rate of 3 mL per minute is shown in Figure 64 where the effects of the titanium frit are apparent. Attributing this to the finer pore size and limited flow rate, the particles made with a titanium frit are about one tenth the size of those seen in the glass frit pictures. This is some preliminary research into how pore size can affect the particles produced and could potentially be used to tailor the size of nanoparticles as a function of pore sizes, not only concentration. More research needs to be done to elucidate the details between pore size and particles, as well as other variables which influence this system: namely precursor flow rate, stir rate, turbulence, frit proximity to the stir blades, viscosity, and surface tension. The relationship between the variables will help define the system and potentially allow the predicting of nanoparticle sizes.

Finally, an issue arising from the use of ammonium bicarbonate as the primary precipitant is residual carbonate which persists until 850-900°C, as seen in the TGA from Figure 57, where some samples continue to decompose past 800°C, and the FTIR spectra in Figure 58, where the 1400 and 1300cm⁻¹ stretches indicate the presence of carbonate.^{[117][118]} The goal of an amorphous powder for manipulation in post-processing will not permit going to those temperatures due to the onset of the crystalline phase and sintering of the powder. Researchers have found that carbonate

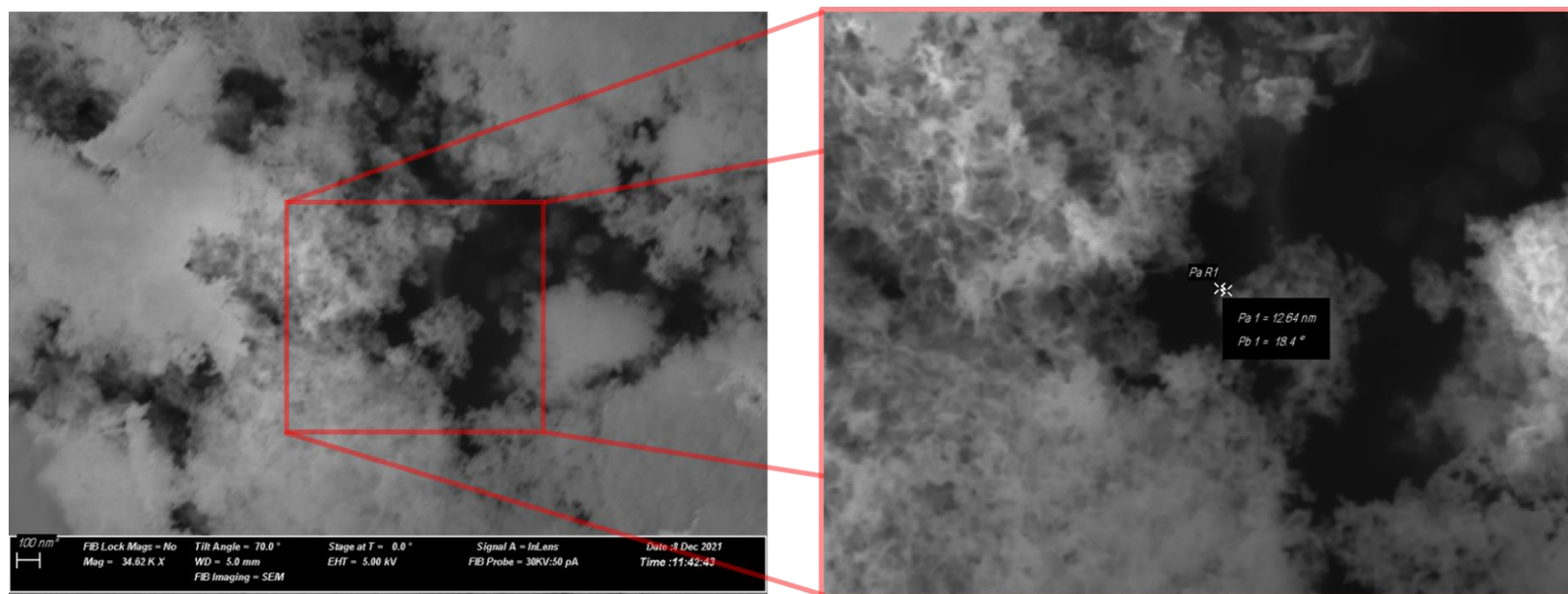


Figure 62 Left is a wide field view (100 nm scale bar) of the Ti frit produced powder spread across an SEM platform, an enlarged section (right) can be seen with a measurement of a particle of 12 nm.

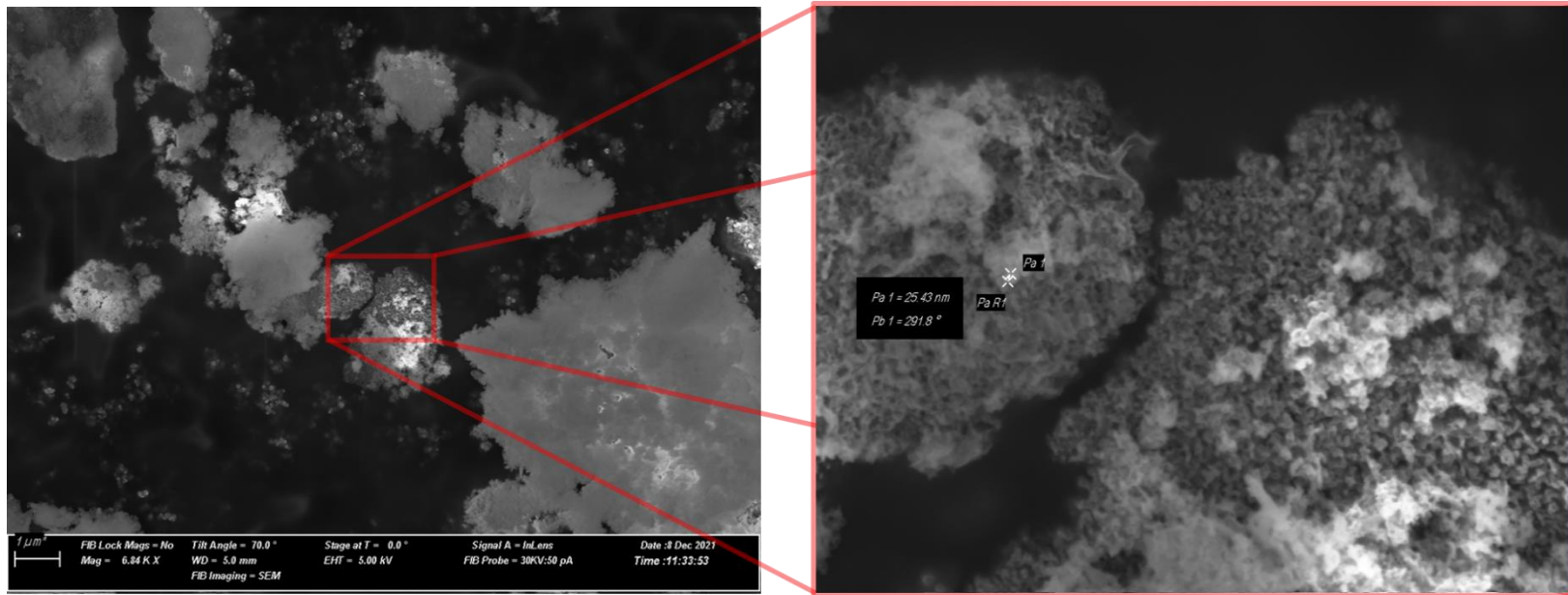


Figure 63 Left is a wide field view (1 µm scale bar) of the Ti frit produced powder spread across an SEM platform, an enlarged section (right) can be seen with a measurement of a particle of 25 nm.

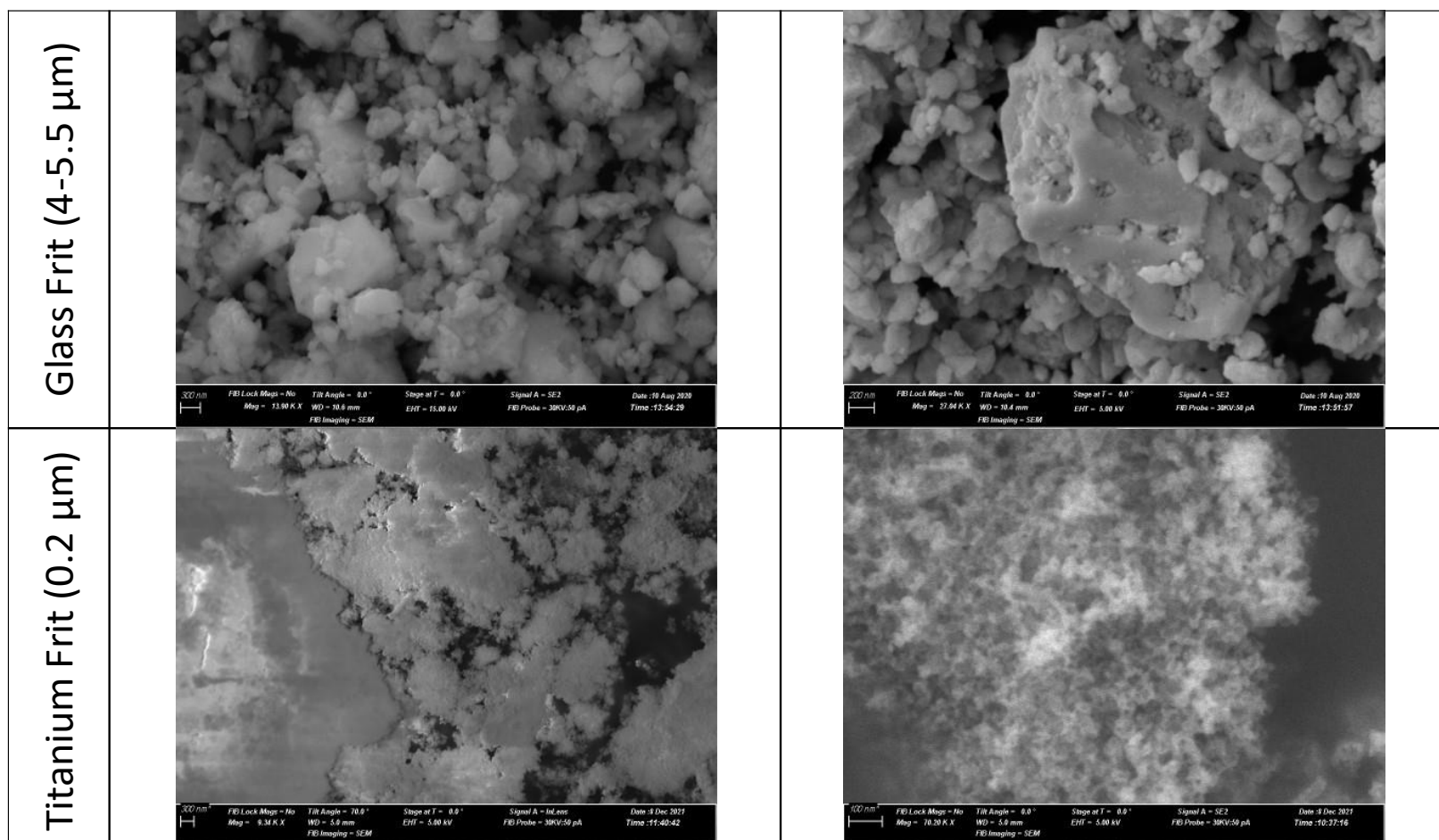


Figure 64 YAG precipitation comparison between the fine glass frit and the ultrafine titanium frit at 3 mL per minute. Scale bars for the top row are 300 and 200 nm (left and right), for the bottom they are 300 and 100 nm (left and right).

cannot be eliminated by microwave calcination at 750°C ^{[168][169]}, which is one hundred degrees higher than the current temperature used here. Alternatively, other researchers have shown that calcium carbonate can be decomposed simply by steaming the powder and processing in the furnace at significantly lower temperatures.^{[170][171]}

The microwave calcinations were replicated using a Microwave Research & Applications BP-110 microwave furnace with high temperature liner using a hybrid heating method. This heating method employs a susceptor, in this case silicon carbide, to heat up in the presence of microwave irradiation and passively warm up the sample until the sample itself becomes susceptible to the microwaves. The temperature for YAG susception is around 700°C .^[172] Samples in Figures 65 and 67-70 were microwave calcined and then examined via FTIR spectroscopy. Figures 66 & 71 show the thermogravimetric analysis of some samples and demonstrate clearly the presence of something which decomposes at 825°C . When compared with the FTIR analyses this is likely carbonate.

Following the experiments of Lin, et al. (2015) and Chen, et al. (2020), microwaving was expected to be sufficient for the removal of carbonate because of induced suceptance of the carbonate around 600°C . Figure 65 shows the FTIR spectrum first attempt of a precipitation involving only ammonium bicarbonate. After a treatment the carbonate species persists, but its response to the analysis is reduced likely indicating less carbonate is present. Figure 66 has a TGA of the sample and shows the decomposition of carbonate at $\sim 825^{\circ}\text{C}$. Figure 67 shows the FTIR spectrum of a second experiment involving 2-ethyhexanoic acid and ammonium hydroxide. Unexpectedly, the signature stretches of the

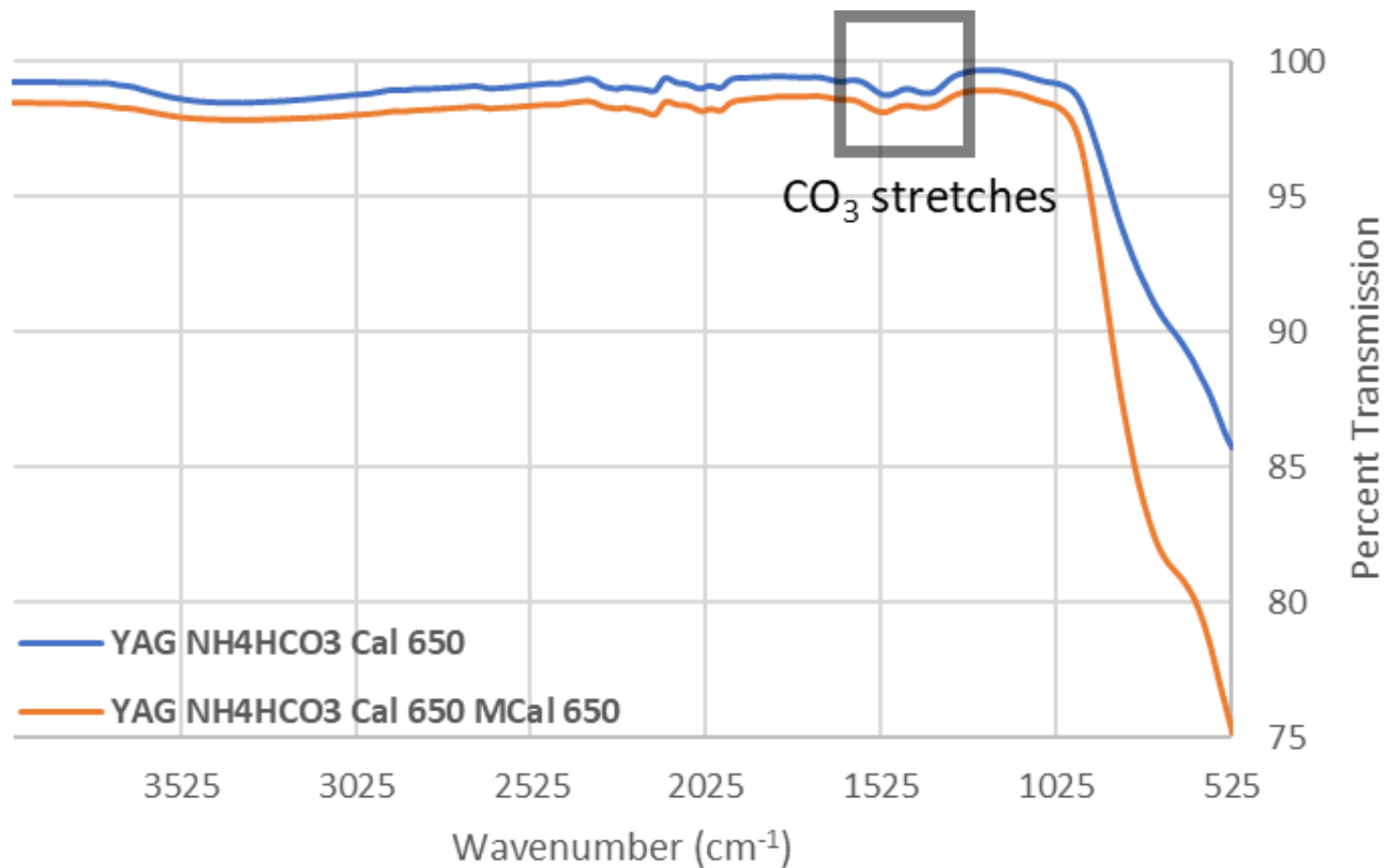


Figure 65 FTIR spectrum of a precipitation performed with ammonium bicarbonate and calcined at 650°C for 6 hours under oxygen (blue) and then microwave calcined at 650°C for 6 hours under air (orange). The carbonate stretches are marked by the box.

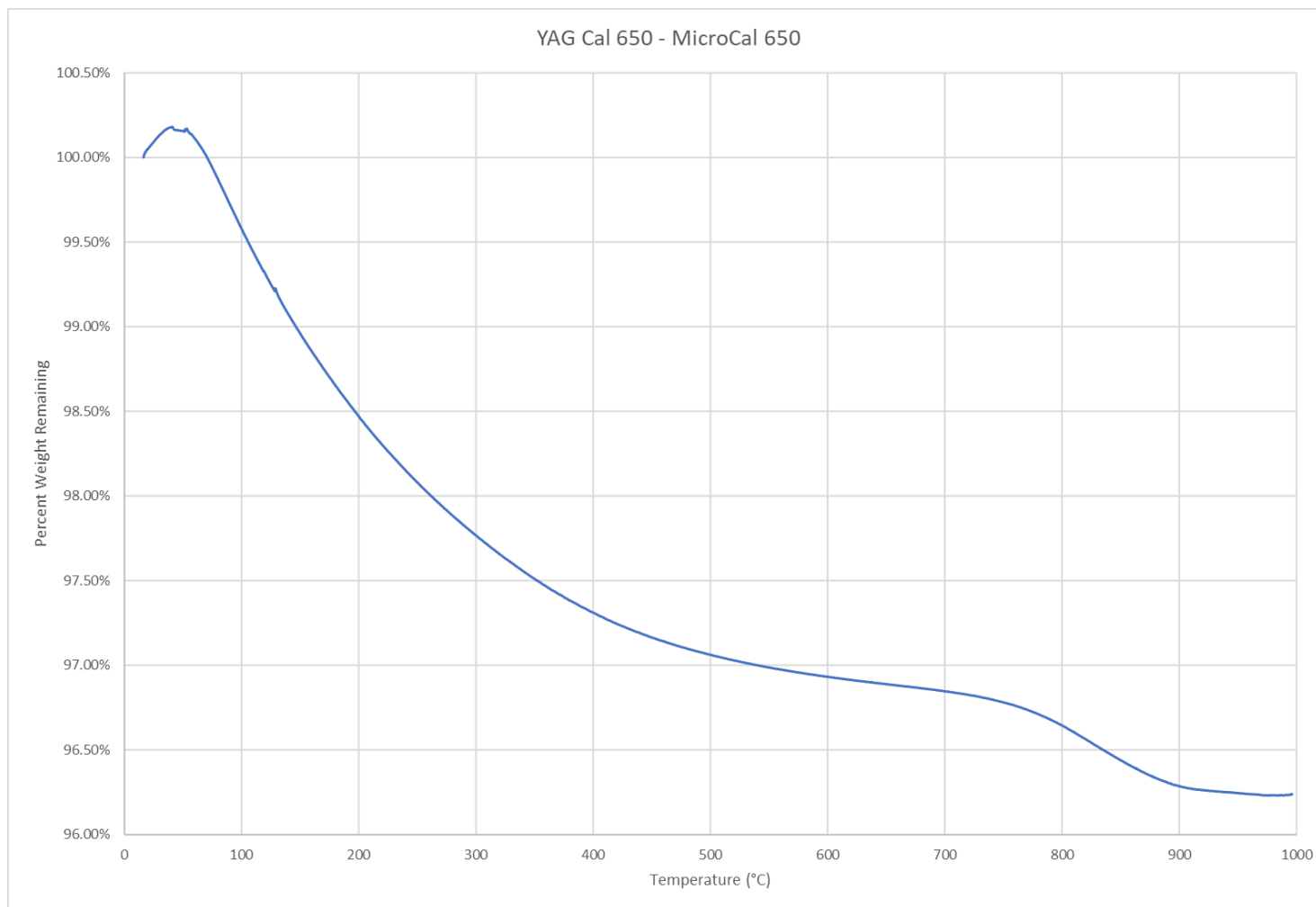


Figure 66 Thermogravimetric analysis of the YAG sample calcined at 650°C for 6 hours under oxygen and then microwave calcined at 650°C for 6 hours under air.

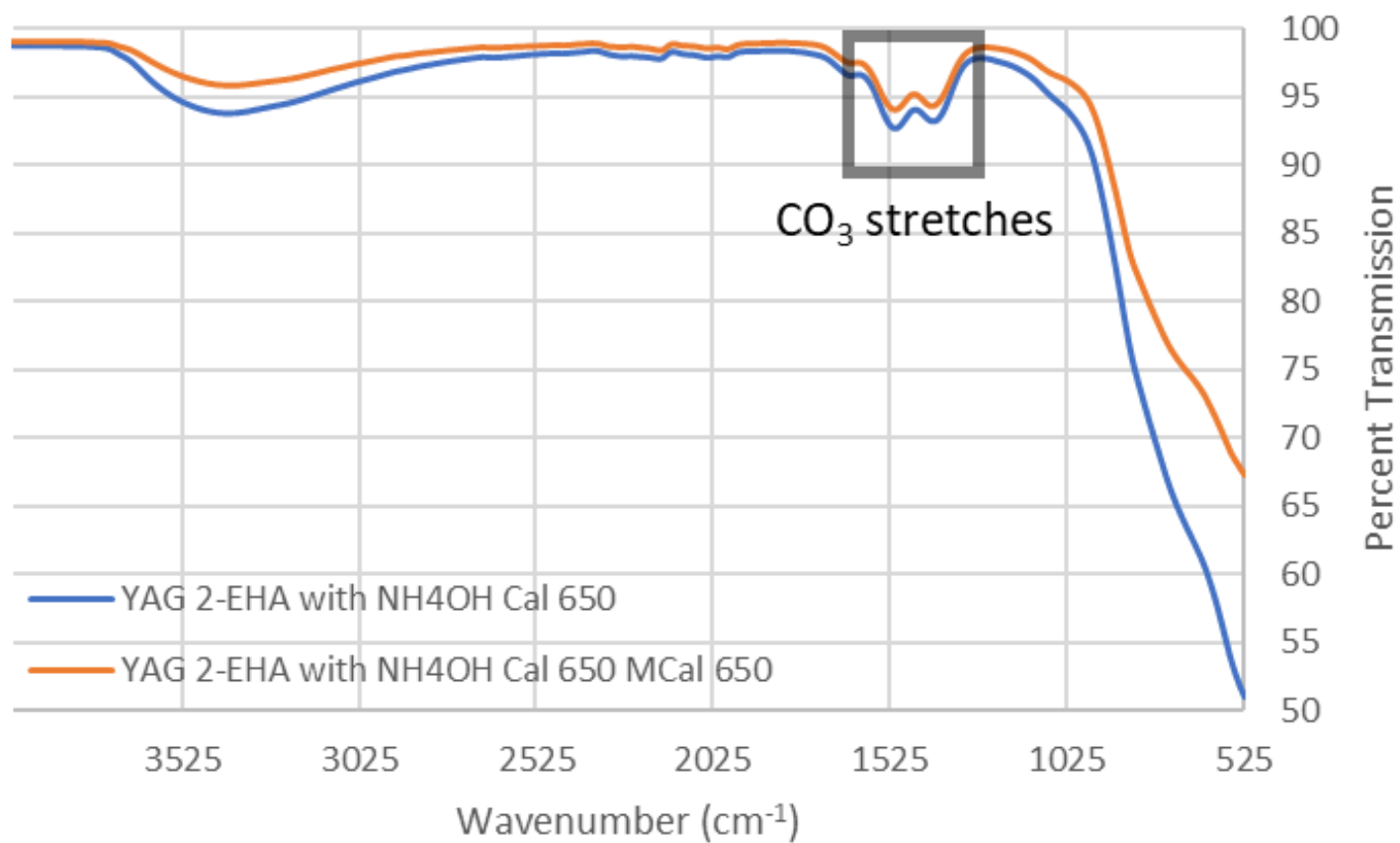


Figure 67 FTIR spectrum of a precipitation performed with ammonium hydroxide and 2-ethylhexanoic acid and calcined at 650°C for 6 hours under oxygen (Blue) and then microwave calcined at 650°C for 6 hours under air (Orange). The carbonate stretches are marked by the box.

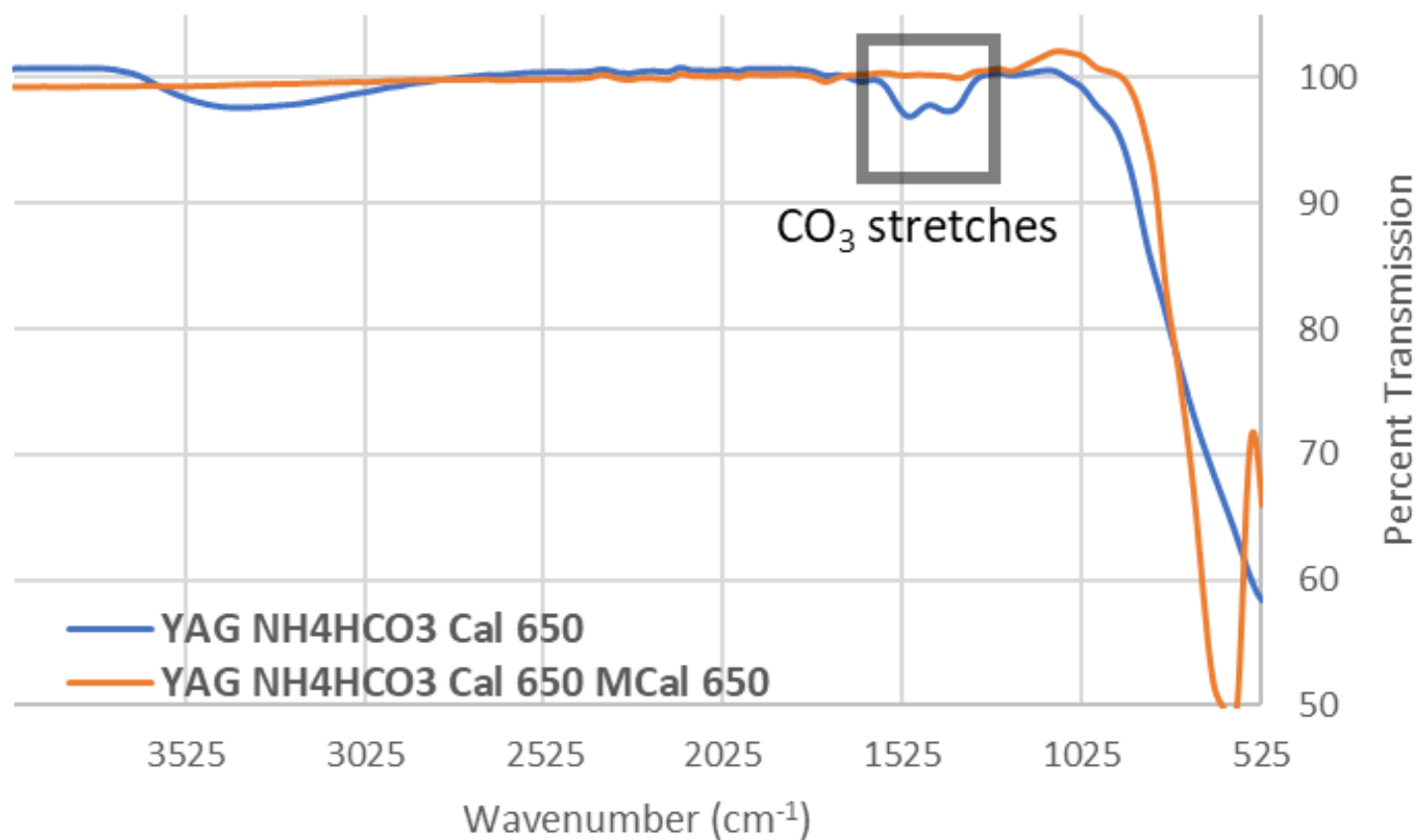


Figure 68 FTIR spectrum of another precipitation performed with ammonium bicarbonate and calcined at 650°C for 6 hours under oxygen (Blue) and then microwave calcined at 650°C for 6 hours under air (Orange). The carbonate stretches are marked by the box.

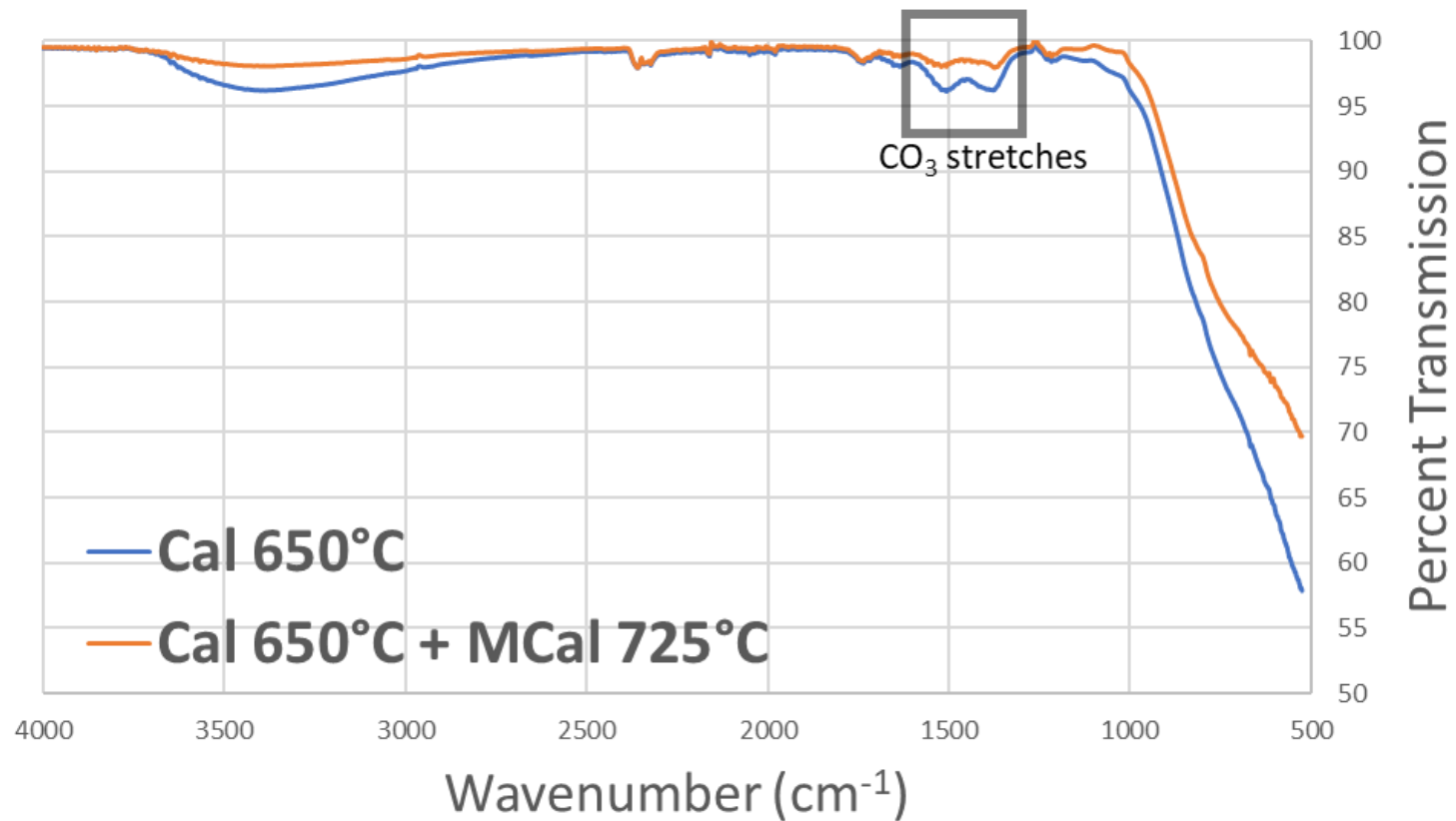


Figure 69 FTIR spectrum of a precipitation performed with ammonium hydroxide and 2-ethylhexanoic acid and calcined at 650°C for 6 hours under oxygen (Blue) and then microwave calcined at 725°C for 6 hours under air (Orange). The carbonate stretches are marked by the box.

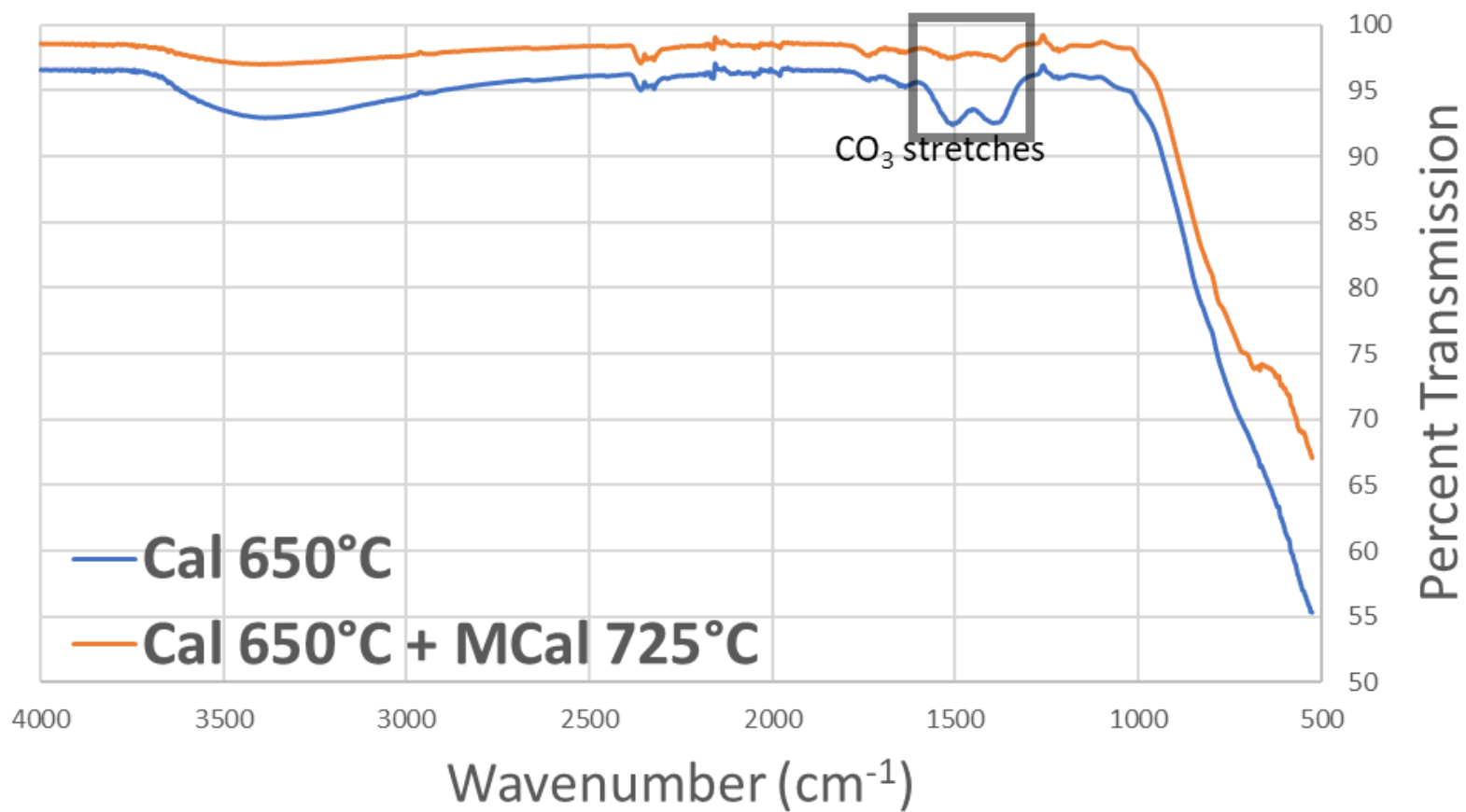


Figure 70 FTIR spectrum of another precipitation performed with ammonium bicarbonate and calcined at 650°C for 6 hours under oxygen (Blue) and then microwave calcined at 725°C for 6 hours under air (Orange). The carbonate stretches are marked by the box.

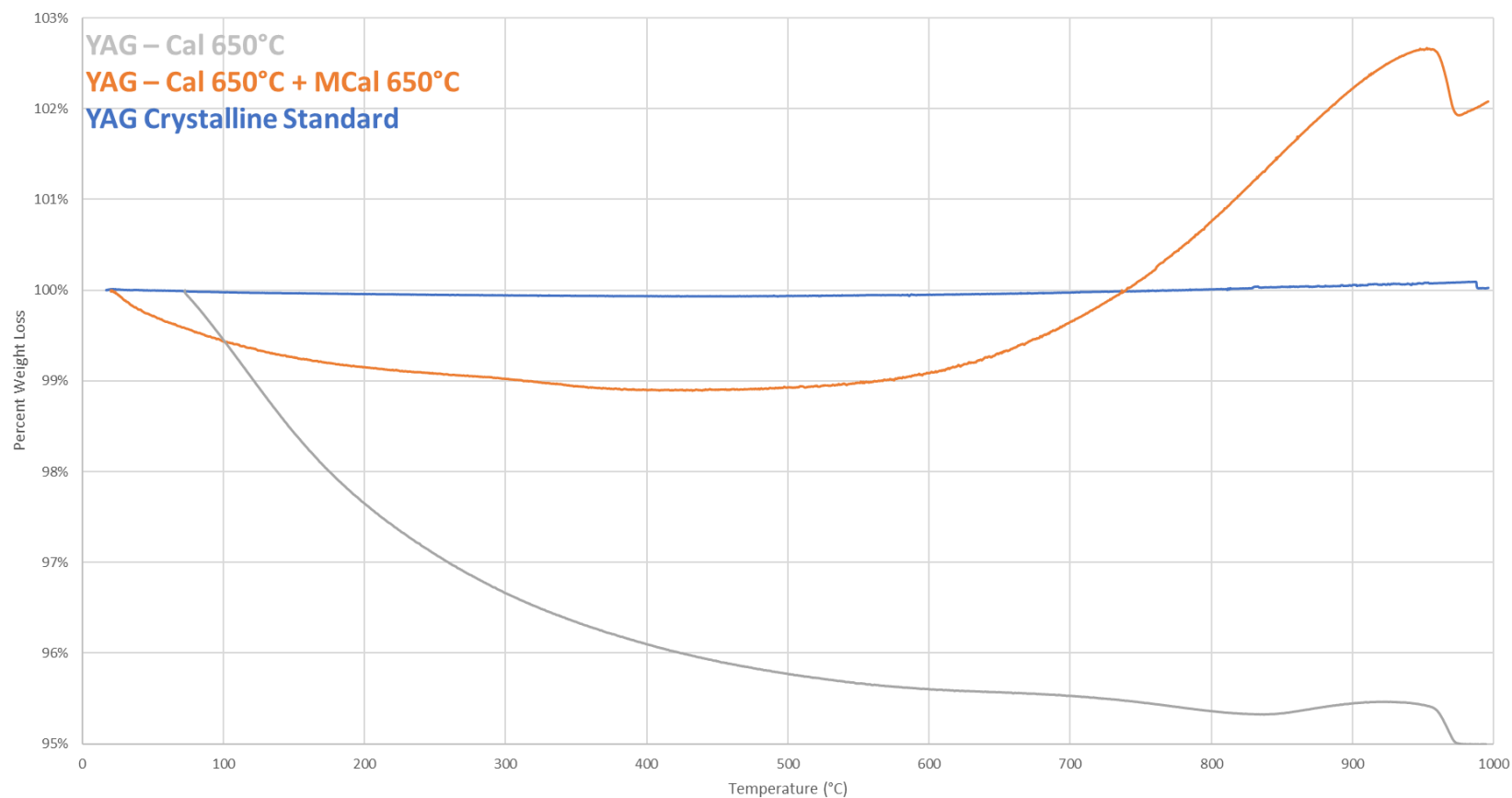


Figure 71 YAG calcination at 650°C for 6 hours under oxygen followed by microwave calcination at 725°C for 6 hours under air. A standard is included as a reference for the high temperature response where the crystalline phase sets in

carbonate increased slightly than in the originally calcined sample. The reason for this increase is not clear. Figure 68 is another spectrum of the ammonium bicarbonate sample which had not been microwave calcined, being treated in a manner similar to the sample from Figure 65. Unexpectedly for this sample, the carbonate response has decreased to near background levels indicating some other variable may be influencing the system. Figures 69 and 70 are samples of 2-EHA + OH and ammonium bicarbonate only, respectively, which were treated at a 725°C instead of 650°C. Both of these show significantly reduced response in their FTIR spectra, but an unwanted side effect was sintering of the powder from inconsistent heating of the sample. This non-uniform heating may have contributed to the reduced signal seen in Figure 68's sample. A combined TGA of the ammonium bicarbonate sample's progression in Figure 71 shows the persistence of carbonate from traditional calcination, but the sample calcined at 725°C has lost enough that the weight reported increases with temperature as the sample powder begins to densify, concluding with weight loss as the crystalline phases set in at 950°C. A similar response can be seen in the standard from Alfa Aesar. Temperatures of 750°C were attempted, but poor insulation in the microwave furnace led to steady heat loss leaving 725°C as the highest temperature attainable as the microwave continuously tried to reach higher temperatures.

Microwave roasting at different temperatures to remove the carbonate was inconsistent with its results. The data show some samples responded to the microwave treatment, while others show little to no change. To avoid the undesired sintering and coarsening of the powders at higher temperatures from microwave irradiation, an alternate approach was needed. Papers by Giammaria, et al. (2019) and Silakhori, et al. (2021) have

shown with calcium carbonate that decomposition can occur in the presence of high temperature steam. The proposed mechanism is a step-wise decomposition to a bicarbonate species which at the elevated temperatures is decomposed to a hydroxide and carbon dioxide. To test the effect of water a sample was left in a desiccator filled with 500 mL deionized water and a sample in an alumina crucible was loosely covered with aluminum foil to protect the sample from condensation and allow gas exchange. This whole setup was covered by the desiccator lid and placed in an 80°C oven over the weekend. A diagram of this setup can be seen in Figure 72. The sample was then subjected to microwave calcination and the results can be seen in Figure 73 showing the progression of the material as it was made, furnace calcined for 6 hours under air, steamed for 72 hours, and microwave calcined for 6 hours under air. To prevent unwanted sintering of powder, the sample was placed inside one crucible which was then placed inside another snug fitting crucible to give a small air gap to equilibrate temperature. No unwanted sintering was seen from this setup.

From the initial calcined sample (blue line, 650°C for 6 hours under oxygen) to the microwave calcined step (orange line, 700°C for 6 hours under air), a reduced absorbance from the carbonate is seen. However, an equivalent response returns when the sample is steamed for three days at 80°C (grey line) but accompanied by an Al-OH stretch at roughly 1100cm⁻¹ giving confidence that water has thoroughly saturated the sample from the steam chamber.^[173] In a final microwave treatment for 700°C for 6 hours under air the FTIR spectrum in yellow in Figure 73 shows a background response in the region where carbonate would be expected.

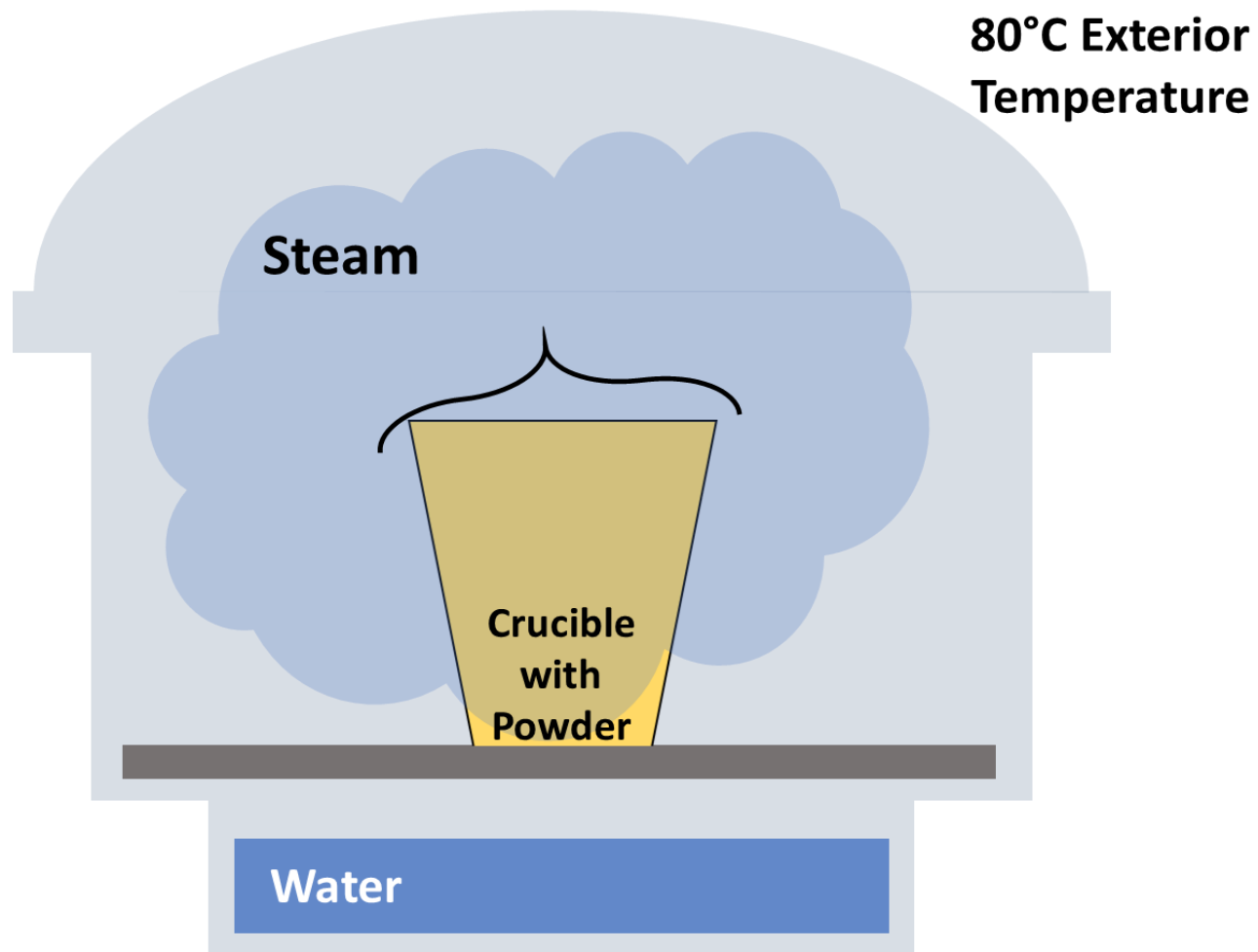


Figure 72 Diagram of the setup for steaming the powder in a loosely covered crucible contained within a desiccator.

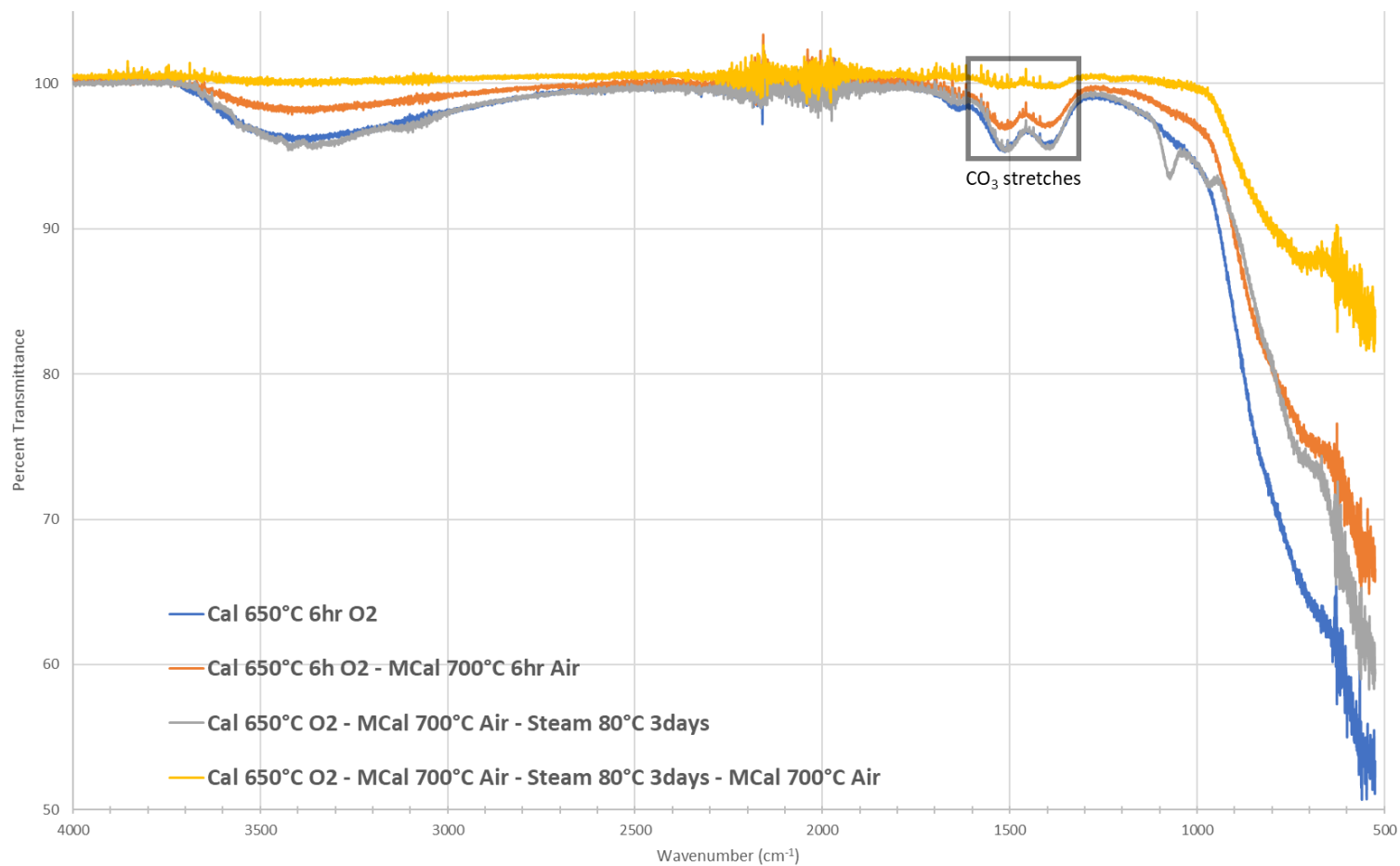


Figure 73 Calcination of carbonate residue contaminated powder. It has been recorded as it was originally calcined, calcined again in a furnace, then in a microwave, then steamed, and a final microwave treatment. All calcinations were done a 650°C for 6 hours

The results from this experiment represents the first time this type of decomposition has been reported for rare earth-based materials and that flowing steam is not necessary, a static treatment can suffice. The success seen in elimination of the carbonate after a microwave treatment can be a large time savings for other processes which leave residual carbonate contamination behind.

Conclusion

Several experiments were conducted exploring the idea of direct injection through an immersed frit to divide the metal ion precursor solution into finer liquid streams. Demonstrated through the numerous experiments and a comprehensive study of ideal precipitant for precipitation and influence of organic modifiers it was found that ammonium bicarbonate was the ideal candidate for nanoparticles. This is one of the first times results like this have been reported and through more investigations this method could have a solid foundation to broaden the potential applications. Its simplicity and significant increase in the operating regime of precipitation make it highly appealing and approachable for more research to be conducted.

The hypothesis this was based on was regarding frit pores having the ability to make nanoparticles from concentrated metal ion precursor solution.

Compared to the previous methods in Table 6 this setup was simple and inherently divided the liquid through the pores of the frit, requiring no other mechanical, pneumatic, or electric influence to divide the solution. It was capable of making product which met the

desired morphology and characteristics as well as stoichiometry and composition. The simplicity of the system limits the number of steps to process the precursor for precipitation and makes the setup conducive to alteration for continuous production, in-line monitoring of the product, and waste recycling. The only marks against this method are regarding the contamination and yield efficiency since YAG is not what is being made by the process, rather a secondary material that can be heated and made into YAG. Further in the case of carbonate, samples may have some residual contamination to contend with. Though this contamination was shown to be manageable through processing with a humid atmosphere. There remains more work to be done to understand this method and test its limitations. The work shown here demonstrated its ability to perform at high concentration and synthesis powders with the desired characteristics and composition.

Table 6 Comparison of the precipitation techniques with a delineation to highlight the frit assisted technique.

<i>(In regard to oxide syntheses)</i>	Dropwise Precipitation	Ultrasonic- Influenced Precipitation	Aerosol Spray Precipitation	Ultrasonic Nebulization Precipitation	Frit Assisted Precipitation
Product meets desired composition	A	A	A	A	A
Product meets desired characteristics	B	B	A	C	A
Process is Energy Efficient	A	A	A	A	A
Process is Cost Efficient	A	A	A	A	A
Process is Yield Efficient	C	C	B	B	B
Process is Flexible	A	C	B	B	A
Process has a Minimum of Steps	B	C	C	C	A
Product is Reproducible	A	A	A	A	A
Residual Contamination Elimination	B	B	B	B	B
Capable of Continuous Operation	A	C	A	A	A
Process can be Monitored In- Line	A	A	A	A	A
Process has Minimal Hazards	B	B	B	B	A
Waste and Disposal are Manageable	B	B	B	B	A
Excellent	Good	Poor	Unsatisfactory		
A	B	C	D		

CHAPTER 6

OVERALL SUMMARY AND PROSPECTS

This project's goal was to make yttrium aluminum garnet nanoparticles of consistent size for industrial production and at low cost. Numerous synthetic methods were tested in experimental detail to ascertain which methods might be fruitful for further development. These methods included ball milling, solution combustion synthesis, microwave assisted combustion synthesis, flame spray pyrolysis, hydrothermal treatment, and coprecipitation. These methods were judged based on criteria from Darr, et al. (2017) and expanded in this dissertation to allow for more detail. These modified criteria were that the:

- Product meets desired composition
- Product meets desired characteristics
- Process is energy efficient
- Process is cost efficient
- Process is yield efficient
- Process is flexible
- Process has a minimum of steps
- Product is reproducible
- Residual contamination is eliminated
- Process is capable of continuous operation
- Process can be monitored in-line
- Process has minimal hazards

- Waste and disposal are manageable

These points were summarized in tables at the ends of the chapters. Initially a simple system of ✓'s, —'s, and ✕'s was used to rate these processes in each category, but this evolved into an A-D system to give more options for rating and reflect more subtly of the processes. Gauging the performance of the methods after experimental testing led to the conclusion that precipitation had the most promising synthesis approach due to its simplicity and low-cost.

Reflecting on the initial investigations into the synthesis methods mentioned in the first paragraph highlights their disadvantages as compared to precipitation. Ball milling was originally enticing because it offered a totally solid-state approach, bypassing the need for solvents, and leading directly to the complex oxide. Unfortunately, the hardness of the aluminum and yttrium oxides led to degradation of the milling media and containers. The degraded material was found in the product and there were no simple means of removing the contamination. The small batch nature of this approach also limited its usefulness.

The shortcomings of ball milling emphasized the need for a non-contaminating synthesis capable of directly producing YAG powder. This consideration led to solution combustion synthesis. The redox reaction of aluminum and yttrium nitrates with a fuel, such as urea, occurred upon heating and resulted in a rapid exotherm. The reaction was quite vigorous and produced a foamed powder and corrosive gases. The powder produced had particles which varied widely in shape and size. Further, the corrosive gases degraded several furnaces. An alternate approach using ashless filter paper as a template was tried, but this was not favorable because of residual contamination from the filter paper.

An alternate approach to heating used microwave irradiation to contain the corrosive gases in the microwave cavity, away from the heating source and control the microwave more easily. Once again, the gases eventually destroyed the microwave and emphasized the adverse character of the batchwise combustion approaches. Similar to the previous combustion syntheses, the particles making up the foam were irregular in size and shape, and the batchwise nature of this was not ideal.

Attention turned to flame spray pyrolysis because it can make oxide particles from metal nitrates dissolved in a flammable organic solution sprayed through a flame. Using both an industrial and bench-top setup, the collection of the product became problematic with considerable loss. The use of a flammable solution and troublesome preparation were also considered unsafe.

Precipitation was tried next because it was safer and required less preparation than flame spray pyrolysis. The soft technique, where the product is a steppingstone to the final desired product, is something that had not been attempted yet because these need post processing. This intermediate stopping point also allows for greater control over the product by the use of capping agents or other organic modifiers. Results from this were promising because of the simple setup and the batch-wise setup could be adapted to a continuous flow if desired, but it did require dilute metal ion solutions to make nanoparticles.

A final method tested was a simple hydrothermal synthesis. The apparatus employed was a Teflon liner encapsulated in a stainless-steel container. The PTFE liner limited the temperature to 240°C. Precipitant from the previous precipitation was added to

the hydrothermal reactor and treated for 24 hours. FTIR results showed conversion YAG was incomplete with a large presence of original material. It is possible that a more capable apparatus might have better results. This limitation and the batch-wise reaction setup made this technique less desirable.

Since precipitation was selected from these preliminary tests, more testing was needed to explore it and improve its concentration limitation. The influence of ultrasonic irradiation and acoustic micro-mixing of the precipitant was explored next. A focused apparatus was built, and the intensity was tested with luminol. Dropwise addition of the metal-ion solution into a bottle of the sonicating precipitant, which could not be stirred or it would invalidate the ultrasonic waves, resulted in a floating ‘raft’ of precipitated material. This led to a mass of material which, after calcination, was coarse and not a viable powder.

Several sources have used spray precipitations to produce nanoparticles, which benefited from finely divided droplets to promote the formation of nanoparticles. Two setups were tested and a third was proposed using aerosolized liquid, ultrasonically nebulized liquid, and proposed was electrospray. Aerosol spray was simple in its approach to disperse droplets, but the carrier gas caused droplet ejection which coalesced droplets and caused large particles to form, though the SEM images showed consistent nano-sized particles among the large pieces. Ultrasonic nebulization was attempted to bypass the need for a carrier gas and limit droplet ejection, but this was futile as the turbulence from stirring led to droplet ejection and coalescence and SEM images showed powder of very poor morphology and size. Attempts to modify these using capping agents had minimal effect and clogged the capillary. For both previous experiments, more concentrated solutions

were attempted, but it was found that this led to large droplets or a failure to spray in the case of the ultrasonic nebulization. Electrospray was proposed and setup to use electromotive forces to drive droplets to the oppositely charged solution, but the flows were difficult to control, and corona discharges were apparent. Each method was discontinued because of these factors not meeting ideal criteria in yield efficiency, cost efficiency, and safety.

Underpinning all these precipitation approaches was the requirement for dilute solutions, ultimately affecting the yield efficiency. If this barrier could be overcome, then it would improve this approach considerably. The concept of division from a spray seemed promising, but the accompanying problems left significant room for improvement. If division could happen within the precipitant liquid by direct injection, then there would be limited time for unwanted side effects to occur. The result of this was direct injection of liquid through a frit into a vigorously stirred precipitant. This innovation was surprisingly successful with a concentrated metal-ion solution. Thus, the yield problem was solved and preliminary investigations with a fine pore size frit indicated that small particles resulted. This novel immersed frit-assisted precipitation process holds great promise in that it quite likely will function for production of many other kind of nanoparticles (chalcogens, other oxides, and metals or alloys, for examples). In addition, the adaptation of the apparatus for continuous production appears to be straight forward. Also, the employment of other porous media to substitute for the frit is worth exploring. The frits present random exits, but more orderly membranes are available in which the exit channels are in a consistent array. Experiments with these might elucidate the drop-production process and lead to

further improvements. Other means of turbulence production could also give rise to smaller extruded droplets.

REFERENCES

1. Fuchs, B.; Berlien, H.-P.; Philipp, C.; Mueller, G., Fundamentals of Nd: YAG laser applications. In *Applied laser medicine*, Springer: 2003; pp 199-203.
2. Berends, A. C.; van de Haar, M. A.; Krames, M. R., YAG: Ce³⁺ Phosphor: From Micron-Sized Workhorse for General Lighting to a Bright Future on the Nanoscale. *Chemical Reviews* **2020**, *120* (24), 13461-13479.
3. Cherepy, N.; Seeley, Z.; Payne, S.; Beck, P.; Swanberg, E.; Hunter, S.; Ahle, L.; Fisher, S.; Melcher, C.; Wei, H. In *High energy resolution with transparent ceramic garnet scintillators*, Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XVI, International Society for Optics and Photonics: 2014; p 921302.
4. Speghini, A.; Piccinelli, F.; Bettinelli, M., Synthesis, characterization and luminescence spectroscopy of oxide nanopowders activated with trivalent lanthanide ions: the garnet family. *Optical Materials* **2011**, *33* (3), 247-257.
5. Xia, Z.; Meijerink, A., Ce ³⁺-Doped garnet phosphors: composition modification, luminescence properties and applications. *Chemical Society Reviews* **2017**, *46* (1), 275-299.
6. Cantarano, A.; Ibanez, A.; Dantelle, G., Garnet-type nanophosphors for white LED lighting. *Frontiers in Materials* **2020**, *7*, 210.
7. Liu, G.; Wang, B.; Li, J.; Cao, B.; Lu, Y.; Liu, Z., Research progress of gadolinium aluminum garnet based optical materials. *Physica B: Condensed Matter* **2021**, *603*, 412775.

8. Li, J.; Pan, Y.; Zeng, Y.; Liu, W.; Jiang, B.; Guo, J., The history, development, and future prospects for laser ceramics: a review. *International Journal of Refractory Metals and Hard Materials* **2013**, *39*, 44-52.
9. Johnson, R.; Biswas, P.; Ramavath, P.; Kumar, R.; Padmanabham, G., Transparent polycrystalline ceramics: an overview. *Transactions of the Indian Ceramic Society* **2012**, *71* (2), 73-85.
10. Chaim, R.; Levin, M.; Shlayer, A.; Estournès, C., Sintering and densification of nanocrystalline ceramic oxide powders: a review. *Advances in Applied Ceramics* **2008**, *107* (3), 159-169.
11. Fang, Z.; Wang, H., Densification and grain growth during sintering of nanosized particles. *International Materials Reviews* **2008**, *53* (6), 326-352.
12. Taylor, N. J.; Stangeland-Molo, S.; Laine, R. M., Bottom-up vs reactive sintering of Al₂O₃-YAG-YSZ composites via one or three-phase nanoparticles (NPs). Bottom-up processing wins this time. *Journal of the American Ceramic Society* **2017**, *100* (6), 2429-2438.
13. Serrano, A.; Caballero-Calero, O.; García, M. Á.; Lazić, S.; Carmona, N.; Castro, G. R.; Martín-González, M.; Fernández, J. F., Cold sintering process of ZnO ceramics: effect of the nanoparticle/microparticle ratio. *Journal of the european ceramic society* **2020**, *40* (15), 5535-5542.
14. Somton, K.; Dateraksa, K.; McCuiston, R. C. In *A Study of Alumina Spray Dried Granules on Packing Density and Sintering Shrinkage of Simple and Complex Shape*, Key Engineering Materials, Trans Tech Publ: 2014; pp 175-180.

15. Barbaran, J. H.; Aragi, M. G.; Javaheri, I.; Baharvand, B.; Tabasi, M.; Ahan, R. L.; Jangjo, E., The growth of Ho: YAG single crystals by Czochralski method and investigating the formed cores. *Crystallography Reports* **2015**, *60* (7), 1151-1154.
16. Yoshimura, M.; Sakata, S.-i.; Yamada, S.; Taishi, T.; Hoshikawa, K., The growth of Al₂O₃/YAG: Ce melt growth composite by the vertical Bridgman technique using an a-axis Al₂O₃ seed. *Journal of Crystal Growth* **2015**, *427*, 16-20.
17. Belyakov, A.; Kulikov, N., Methods for synthesizing yttrium-aluminum garnet nanopowders from solutions. *Refractories and Industrial Ceramics* **2011**, *52* (2), 155.
18. Darr, J. A.; Zhang, J.; Makwana, N. M.; Weng, X., Continuous hydrothermal synthesis of inorganic nanoparticles: applications and future directions. *Chemical reviews* **2017**, *117* (17), 11125-11238.
19. Gupta, K.; Muley, A.; Yadav, P.; Joshi, C.; Moharil, S., Combustion synthesis of YAG: Ce and related phosphors. *Applied Physics B* **2011**, *105* (2), 479-484.
20. Marchal, J.; John, T.; Baranwal, R.; Hinklin, T.; Laine, R. M., Yttrium aluminum garnet nanopowders produced by liquid-feed flame spray pyrolysis (LF-FSP) of metalloorganic precursors. *Chemistry of materials* **2004**, *16* (5), 822-831.
21. Abd, H. R.; Hassan, Z.; Ahmed, N. M.; Alsultany, F. H.; Omar, A. F., Ce-doped YAG phosphor powder synthesized via microwave combustion and its application for white LED. *Optical Engineering* **2019**, *58* (2), 027110.

22. Yang, H. K.; Jeong, J. H., Synthesis, crystal growth, and photoluminescence properties of YAG: Eu³⁺ phosphors by high-energy ball milling and solid-state reaction. *The Journal of Physical Chemistry C* **2010**, *114* (1), 226-230.
23. Su, J.; Zhang, Q.; Gu, C.; Sun, D.; Wang, Z.; Qiu, H.; Wang, A.; Yin, S., Preparation and characterization of Y₃Al₅O₁₂ (YAG) nano-powder by co-precipitation method. *Materials Research Bulletin* **2005**, *40* (8), 1279-1285.
24. Takacs, L., Quicksilver from cinnabar: The first documented mechanochemical reaction? *JOM* **2000**, *52* (1), 12-13.
25. Do, J.-L.; Friščić, T., Mechanochemistry: a force of synthesis. *ACS central science* **2017**, *3* (1), 13-19.
26. Fischer, E. K., Dispersion of pigments by ball and pebble mills. *Industrial & Engineering Chemistry* **1941**, *33* (12), 1465-1471.
27. Moll, I., Aspects of Pigment Dispersion related to Usage. *Journal of the Society of Dyers and Colourists* **1960**, *76* (3), 141-150.
28. Mucsi, G., A review on mechanical activation and mechanical alloying in stirred media mill. *Chemical Engineering Research and Design* **2019**, *148*, 460-474.
29. Suryanarayana, C., Mechanical alloying: a novel technique to synthesize advanced materials. *Research* **2019**, *2019*.
30. Zhu, J.; Li, H.; Zhong, L.; Xiao, P.; Xu, X.; Yang, X.; Zhao, Z.; Li, J., Perovskite oxides: preparation, characterizations, and applications in heterogeneous catalysis. *Acs Catalysis* **2014**, *4* (9), 2917-2940.

- 31.Rojac, T.; Kosec, M.; Malič, B.; Holc, J., The application of a milling map in the mechanochemical synthesis of ceramic oxides. *Journal of the European Ceramic Society* **2006**, 26 (16), 3711-3716.
- 32.Burgio, N.; Iasonna, A.; Magini, M.; Martelli, S.; Padella, F., Mechanical alloying of the Fe– Zr system. Correlation between input energy and end products. *Il nuovo cemento D* **1991**, 13 (4), 459-476.
- 33.McDonald, K. A.; McDonald, M. R.; Bailey, M. N.; Schweitzer, G. K., Parametric study on the production of the GAGG: Ce and LSO: Ce multicomponent oxide scintillator materials through use of a planetary ball mill. *Dalton Transactions* **2018**, 47 (37), 13190-13203.
- 34.Guo, X.; Sakurai, K., Formation of yttrium aluminum perovskite and yttrium aluminum garnet by mechanical solid-state reaction. *Japanese Journal of Applied Physics* **2000**, 39 (3R), 1230.
- 35.Zhang, Q.; Saito, F., Mechanochemical solid reaction of yttrium oxide with alumina leading to the synthesis of yttrium aluminum garnet. *Powder technology* **2003**, 129 (1-3), 86-91.
- 36.Li, J.; Liu, W.; Jiang, B.; Zhou, J.; Zhang, W.; Wang, L.; Shen, Y.; Pan, Y.; Guo, J., Synthesis of nanocrystalline yttria powder and fabrication of Cr, Nd: YAG transparent ceramics. *Journal of alloys and compounds* **2012**, 515, 49-56.
- 37.Varma, A.; Mukasyan, A. S.; Rogachev, A. S.; Manukyan, K. V., Solution combustion synthesis of nanoscale materials. *Chemical reviews* **2016**, 116 (23), 14493-14586.

38. Aruna, S. T., Solution Combustion Synthesis - An Overview. In *Combustion Synthesis: Novel Routes to Novel Materials*, Lackner, M., Ed. Bentham Science: 2010; Vol. 1, pp 206-221.
39. Muenchausen, R. E.; McKigney, E. A.; Jacobsohn, L. G.; Blair, M. W.; Bennett, B. L.; Cooke, D. W., Science and application of oxyorthosilicate nanophosphors. *IEEE Transactions on Nuclear Science* **2008**, 55 (3), 1532-1535.
40. Finholt, J. E., The ammonium dichromate volcano as an introductory laboratory project. *Journal of Chemical Education* **1970**, 47 (7), 533.
41. Wen, W.; Wu, J.-M., Nanomaterials via solution combustion synthesis: a step nearer to controllability. *Rsc Advances* **2014**, 4 (101), 58090-58100.
42. Kakade, M.; Ramanathan, S.; Ravindran, P., Yttrium aluminum garnet powders by nitrate decomposition and nitrate–urea solution combustion reactions—a comparative study. *Journal of alloys and compounds* **2003**, 350 (1-2), 123-129.
43. Kingsley, J.; Suresh, K.; Patil, K., Combustion synthesis of fine particle rare earth orthoaluminates and yttrium aluminum garnet. *Journal of Solid State Chemistry* **1990**, 88 (2), 435-442.
44. Ramanathan, S.; Kakade, M.; Roy, S.; Kutty, K., Processing and characterization of combustion synthesized YAG powders. *Ceramics International* **2003**, 29 (5), 477-484.
45. Laishram, K.; Mann, R.; Malhan, N., Single step synthesis of yttrium aluminum garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$) nanopowders by mixed fuel solution combustion approach. *Ceramics International* **2011**, 37 (8), 3743-3746.

46. Wu, H.; Yang, C.; Zhang, Z.; Tang, Y., Photoluminescence and thermoluminescence of Ce³⁺ incorporated Y₃Al₅O₁₂ synthesized by rapid combustion. *Optik* **2016**, *127* (3), 1368-1371.
47. Rosa, R.; Veronesi, P.; Leonelli, C., A review on combustion synthesis intensification by means of microwave energy. *Chemical Engineering and Processing: Process Intensification* **2013**, *71*, 2-18.
48. Kingston, H. M.; Haswell, S. J., *Microwave-enhanced Chemistry: Fundamentals, Sample Preparation, and Applications*. American Chemical Society: 1997.
49. Fu, Y.-P., Preparation of Y₃Al₅O₁₂: Eu powders by microwave-induced combustion process and their luminescent properties. *Journal of alloys and compounds* **2005**, *402* (1-2), 233-236.
50. Dimesso, L., Pechini processes: an alternate approach of the sol–gel method, preparation, properties, and applications. *Handbook of Sol-Gel Science and Technology* **2016**, *2*, 1-22.
51. Vaidhyanathan, B.; Binner, J., Microwave assisted synthesis of nanocrystalline YAG. *Journal of materials science* **2006**, *41* (18), 5954-5957.
52. Potdevin, A.; Pradal, N.; François, M.; Chadeyron, G.; Boyer, D.; Mahiou, R., Microwave-induced combustion synthesis of luminescent aluminate powders. *Sintering: Methods and Products* **2012**, *9*, 189-212.
53. Wegner, K.; Schimmoeller, B.; Thiebaut, B.; Fernandez, C.; Rao, T. N., Pilot plants for industrial nanoparticle production by flame spray pyrolysis. *KONA Powder and Particle Journal* **2011**, *29*, 251-265.

54. Strobel, R.; Pratsinis, S. E., Effect of solvent composition on oxide morphology during flame spray pyrolysis of metal nitrates. *Physical Chemistry Chemical Physics* **2011**, *13* (20), 9246-9252.
55. Meierhofer, F.; Fritsching, U., Synthesis of Metal Oxide Nanoparticles in Flame Sprays: Review on Process Technology, Modeling, and Diagnostics. *Energy & Fuels* **2021**, *35* (7), 5495-5537.
56. Rosebrock, C. D.; Wriedt, T.; Mädler, L.; Wegner, K., The role of microexplosions in flame spray synthesis for homogeneous nanopowders from low-cost metal precursors. *AIChE Journal* **2016**, *62* (2), 381-391.
57. Pratsinis, S. E., Aerosol-based technologies in nanoscale manufacturing: from functional materials to devices through core chemical engineering. *AIChE journal* **2010**, *56* (12), 3028-3035.
58. Rane, A. V.; Kanny, K.; Abitha, V.; Thomas, S., Methods for synthesis of nanoparticles and fabrication of nanocomposites. In *Synthesis of inorganic nanomaterials*, Elsevier: 2018; pp 121-139.
59. Lee, J. S.; Gupta, S.; Kumar, P.; Ranade, M. B.; Singh, R. K., Synthesis and Characterization of YAG: Ce³⁺ Nanophosphor prepared by Flame Spray Pyrolysis. *ECS Transactions* **2009**, *16* (30), 1.
60. Purwanto, A. In *Fabrication of functional nanomaterials using flame assisted spray pyrolysis*, AIP Conference Proceedings, American Institute of Physics: 2014; pp 48-51.

61. Clever, H. L.; Johnston, F. J., The solubility of some sparingly soluble lead salts: an evaluation of the solubility in water and aqueous electrolyte solution. *Journal of Physical and Chemical Reference Data* **1980**, 9 (3), 751-784.
62. Rice, G. W., Potentiometric and photometric methods for determining the solubility of lead iodide. *Journal of Chemical Education* **1990**, 67 (5), 430.
63. Redlich, O.; Maranville, L., The silver chloride electrode. *Journal of Chemical Education* **1943**, 20 (1), 10.
64. Ramette, R., Solubility and equilibria of silver chloride. *Journal of Chemical Education* **1960**, 37 (7), 348.
65. Levanov, A.; Isaikina, O. Y.; Lunin, V., Determining the Potential of a Silver/Silver Chloride Electrode at Different Temperatures. *Russian Journal of Physical Chemistry A* **2019**, 93 (4), 770-773.
66. Watt, G. W., Relative solubilities of salts of calcium, strontium, and barium. *Journal of Chemical Education* **1947**, 24 (4), 174.
67. Thorat, A. A.; Dalvi, S. V., Liquid antisolvent precipitation and stabilization of nanoparticles of poorly water soluble drugs in aqueous suspensions: Recent developments and future perspective. *Chemical Engineering Journal* **2012**, 181, 1-34.
68. Joye, I. J.; McClements, D. J., Production of nanoparticles by anti-solvent precipitation for use in food systems. *Trends in Food Science & Technology* **2013**, 34 (2), 109-123.

69. Wang, Q.; Li, Z.; Pang, S.; Li, X.; Dong, C.; Liaw, P. K., Coherent precipitation and strengthening in compositionally complex alloys: a review. *Entropy* **2018**, *20* (11), 878.
70. Kolomiets, T. Y.; Tel'nova, G.; Ashmarin, A.; Chelpanov, V.; Solntsev, K., Synthesis and sintering of submicron Nd: YAG particles prepared from carbonate precursors. *Inorganic Materials* **2017**, *53* (8), 874-882.
71. Liu, Q.; Chen, C.; Dai, J.; Hu, Z.; Chen, H.; Li, J., Effect of ammonium carbonate to metal ions molar ratio on synthesis and sintering of Nd: YAG nanopowders. *Optical Materials* **2018**, *80*, 127-137.
72. Rahmani, M.; Mirzaee, O.; Tajally, M.; Loghman-Estarki, M. R., A comparative study of synthesis and spark plasma sintering of YAG nano powders by different co-precipitation methods. *Ceramics International* **2018**, *44* (9), 10035-10046.
73. Li, J. S.; Sun, X. D.; Liu, S. H.; Huo, D.; Li, X. D.; Li, J. G.; Zhu, Q.; Zhang, M. In *Synthesis of Dispersed Y₂O₃ Nanopowder from Yttrium Stearate*, Key Engineering Materials, Trans Tech Publ: 2013; pp 3-7.
74. Li, J.; Sun, X.; Liu, S.; Li, X.; Li, J.-G.; Huo, D., A homogeneous co-precipitation method to synthesize highly sinterability YAG powders for transparent ceramics. *Ceramics International* **2015**, *41* (2), 3283-3287.
75. Uekawa, N.; Hokama, Y.; Wen, C. M.; Kojima, T.; Kakegawa, K., Synthesis of Ce³⁺-doped Y₃Al₅O₁₂ phosphor particles by precipitation method with diamine molecules as precipitating agent. *Journal of the Ceramic Society of Japan* **2014**, *122* (1421), 54-57.

- 76.Chikulina, I.; Kravtsov, A.; Nikova, M.; Malyavin, F.; Lapin, V.; Kuleshov, D. In *Synthesis of highly dispersed precursor nanopowders for YAG: Yb ceramics by the use of hexamethylenetetramine*, IOP Conference Series: Materials Science and Engineering, IOP Publishing: 2019; p 012013.
- 77.Tong, S.; Lu, T.; Guo, W., Synthesis of YAG powder by alcohol–water co-precipitation method. *Materials Letters* **2007**, *61* (21), 4287-4289.
- 78.Dehsari, H. S.; Ribeiro, A. H.; Ersöz, B.; Tremel, W.; Jakob, G.; Asadi, K., Effect of precursor concentration on size evolution of iron oxide nanoparticles. *CrystEngComm* **2017**, *19* (44), 6694-6702.
- 79.Shandilya, M.; Rai, R.; Singh, J., Hydrothermal technology for smart materials. *Advances in Applied Ceramics* **2016**, *115* (6), 354-376.
- 80.Cundy, C. S.; Cox, P. A., The hydrothermal synthesis of zeolites: history and development from the earliest days to the present time. *Chemical reviews* **2003**, *103* (3), 663-702.
- 81.Crane, J. L.; Anderson, K. E.; Conway, S. G., Hydrothermal synthesis and characterization of a metal–organic framework by Thermogravimetric analysis, powder X-ray diffraction, and infrared spectroscopy: an integrative inorganic chemistry experiment. *Journal of Chemical Education* **2015**, *92* (2), 373-377.
- 82.Takamori, T.; David, L. D., Controlled nucleation for hydrothermal growth of yttrium-aluminum garnet powders. *American Ceramic Society Bulletin* **1986**, *65* (9), 1282-1286.

- 83.Li, X.; Liu, H.; Wang, J.; Cui, H.; Han, F., YAG: Ce nano-sized phosphor particles prepared by a solvothermal method. *Materials Research Bulletin* **2004**, 39 (12), 1923-1930.
- 84.Linxiang, W.; Min, Y.; Changxin, G.; ZHANG, W., Synthesis and luminescent properties of Ce³⁺ doped LuAG nano-sized powders by mixed solvo-thermal method. *Journal of Rare Earths* **2010**, 28 (1), 16-21.
- 85.Šepelák, V.; Düvel, A.; Wilkening, M.; Becker, K.-D.; Heitjans, P., Mechanochemical reactions and syntheses of oxides. *Chemical Society Reviews* **2013**, 42 (18), 7507-7520.
- 86.Zyryanov, V., Mechanochemical synthesis of complex oxides. *Russian chemical reviews* **2008**, 77 (2), 105.
- 87.Massola, C. P.; Chaves, A. P.; Albertin, E., A discussion on the measurement of grinding media wear. *Journal of Materials Research and Technology* **2016**, 5 (3), 282-288.
- 88.Lennon, E.; Tanzy, M.; Volpert, V.; Mukasyan, A.; Bayliss, A., Combustion of reactive solutions impregnated into a cellulose carrier: Modeling of two combustion fronts. *Chemical engineering journal* **2011**, 174 (1), 333-340.
- 89.Mukasyan, A. S. In *Solution combustion as a promising method for the synthesis of nanomaterials*, Advances in Science and Technology, Trans Tech Publ: 2010; pp 187-196.

90. Anwar, J.; Shafique, U.; Rehman, R.; Salman, M.; Dar, A.; Anzano, J. M.; Ashraf, U.; Ashraf, S., Microwave chemistry: Effect of ions on dielectric heating in microwave ovens. *Arabian Journal of Chemistry* **2015**, 8 (1), 100-104.
91. Teoh, W. Y.; Amal, R.; Mädler, L., Flame spray pyrolysis: An enabling technology for nanoparticles design and fabrication. *Nanoscale* **2010**, 2 (8), 1324-1347.
92. McDonald, K. A., Planetary Ball Mill and Solution Combustion Approaches for the Production and Size Control of Nanophosphors. **2018**.
93. Bailey, M. N., Mechanochemical and Combustion Syntheses of Cerium-Doped Lutetium Oxyorthosilicate Powders and Preliminary Studies into the Syntheses of Optically-Active Beta-Germanium (IV) Oxide and Alpha-Quartz Nanoparticles. **2019**.
94. Gao, W.; Chen, F.; Wang, X.; Meng, Q., Recent advances in processing food powders by using superfine grinding techniques: A review. *Comprehensive Reviews in Food Science and Food Safety* **2020**, 19 (4), 2222-2255.
95. Tukhtaev, R.; Boldyrev, V.; Gavrilov, A.; Larionov, S.; Myachina, L.; Savel'Eva, Z., Metal sulfide synthesis by self-propagating combustion of sulfur-containing complexes. *Inorganic materials* **2002**, 38 (10), 985-991.
96. Kumar, A.; Wolf, E.; Mukasyan, A., Solution combustion synthesis of metal nanopowders: Nickel—Reaction pathways. *AIChE journal* **2011**, 57 (8), 2207-2214.

97. Patil, K.; Hegde, M.; Rattan, T.; Aruna, S. T., *Chemistry of nanocrystalline oxide materials: combustion synthesis, properties and applications*. World Scientific: 2008.
98. Rogachev, A. S.; Mukasyan, A. S., *Combustion for material synthesis*. CRC press: 2014.
99. Taylor, N. J. Liquid-Feed Flame Spray Pyrolysis Synthesis of Oxide Nanopowders for the Processing of Ceramic Composites. 2015.
100. Karthikeyan, J.; Berndt, C.; Tikkanen, J.; Wang, J.; King, A.; Herman, H., Preparation of nanophase materials by thermal spray processing of liquid precursors. *Nanostructured Materials* **1997**, 9 (1-8), 137-140.
101. Sutorik, A. C.; Baliai, M. S. In *Solid solution Behavior of $Ce_xZr_{1-x}O_2$ nanopowders prepared by flame spray pyrolysis of solvent-borne precursors*, Journal of Metastable and Nanocrystalline Materials, Trans Tech Publ: 2002; pp 371-376.
102. Liu, J., Preparation and Properties of Liquid Nitrate Ester. In *Liquid Explosives*, Springer: 2015; pp 181-268.
103. Young, L. B.; Trahanovsky, W. S., Oxidation of organic compounds with cerium (IV). VII. Formation constants for 1: 1 cerium (IV)-alcohol complexes. *Journal of the American Chemical Society* **1969**, 91 (18), 5060-5068.
104. Chen, T.-M.; Chen, S.; Yu, C.-J., Preparation and characterization of garnet phosphor nanoparticles derived from oxalate coprecipitation. *Journal of solid state chemistry* **1999**, 144 (2), 437-441.

105. Rahmani, M.; Mirzaee, O.; Tajally, M.; Loghman-Estarki, M. R., Comparison of synthesis and spark plasma sintering of YAG nano particles by variation of pH and precipitator agent. *Ceramics International* **2018**, *44* (18), 23215-23225.
106. Apte, P.; Burke, H.; Pickup, H., Synthesis of yttrium aluminum garnet by reverse strike precipitation. *Journal of materials research* **1992**, *7* (3), 706-711.
107. Li, J.; Sun, X.; Liu, S.; Li, X.; Huo, D.; Li, J.-G.; Zhu, Q.; Zhang, M.; Sang, Y.; Liu, H., A novel stearate melting method for synthesizing highly reactive YAG nanopowders. *Journal of alloys and compounds* **2014**, *585*, 48-53.
108. Ji, X.; Deng, J.; Kang, B.; Huang, H.; Wang, X.; Jing, W.; Xu, T., Thermal decomposition of Y₃Al₅O₁₂ precursor synthesized by urea homogeneous co-precipitation. *Journal of analytical and applied pyrolysis* **2013**, *104*, 361-365.
109. Wang, L.; Zhao, F.; Zhang, M.; Hou, T.; Li, Z.; Pan, C.; Huang, H., Preparation and photoluminescence properties of YAG: Ce³⁺ phosphors by a series of amines assisted co-precipitation method. *Journal of Alloys and Compounds* **2016**, *661*, 148-154.
110. Liu, W.; Zhang, W.; Li, J.; Kou, H.; Shen, Y.; Wang, L.; Shi, Y.; Zhang, D.; Pan, Y., Influence of pH values on (Nd³⁺ Y³⁺): Al molar ratio of Nd: YAG nanopowders and preparation of transparent ceramics. *Journal of Alloys and Compounds* **2010**, *503* (2), 525-528.
111. Ikegami, T. In *Nanosized Oxide Powders Fabricated by Mimic Alkoxide Methods and their Sintering*, Key Engineering Materials, Trans Tech Publ: 2003; pp 51-56.

112. Sheu, H.-H.; Jian, S.-Y.; Lin, T.-T.; Lee, Y.-W., Effect of rotational speed of an electromagnetic stirrer on neodymium-doped yttrium aluminum garnet nanoparticle size during co-precipitation. *Microelectronic Engineering* **2017**, *176*, 33-39.
113. Kaliszewski, M. S.; Heuer, A. H., Alcohol interaction with zirconia powders. *Journal of the American Ceramic Society* **1990**, *73* (6), 1504-1509.
114. Montanaro, L.; Belgacem, K.; Llewellyn, P.; Rouquerol, F.; Merlo, F.; Palmero, P., Ageing of wet-synthesized oxide powders: role of surface carbonation, effect on sintering, restoration. *Journal of thermal analysis and calorimetry* **2007**, *88* (3), 789-793.
115. Matveev, V.; Yakovlev, K.; Kuznetsov, V. Y.; Zalkind, O., Synthesis and properties of yttrium ammonium carbonate. *Inorganic Materials* **2020**, *56* (12), 1258-1264.
116. Danchevskaya, M.; Ivakin, Y. D.; Maryashkin, A.; Muravieva, G., Stepwise synthesis of fine crystalline Ce-doped yttrium aluminum garnet in water medium in subcritical and supercritical conditions. *Russian Journal of Physical Chemistry B* **2011**, *5* (7), 1056-1068.
117. Khanna, R.; Moore, M., Carbamic acid: molecular structure and IR spectra. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **1999**, *55* (5), 961-967.

- 118.Milella, F.; Mazzotti, M., Estimating speciation of aqueous ammonia solutions of ammonium bicarbonate: application of least squares methods to infrared spectra. *Reaction Chemistry & Engineering* **2019**, 4 (7), 1284-1302.
- 119.Chaturvedi, S.; Dave, P. N., Review on thermal decomposition of ammonium nitrate. *Journal of Energetic Materials* **2013**, 31 (1), 1-26.
- 120.Sobolev, A.; Kossenko, A.; Zinigrad, M.; Borodianskiy, K., An investigation of oxide coating synthesized on an aluminum alloy by plasma electrolytic oxidation in molten salt. *Applied Sciences* **2017**, 7 (9), 889.
- 121.Aboulaich, A.; Deschamps, J.; Deloncle, R.; Potdevin, A.; Devouard, B.; Chadeyron, G.; Mahiou, R., Rapid synthesis of Ce 3+-doped YAG nanoparticles by a solvothermal method using metal carbonates as precursors. *New Journal of Chemistry* **2012**, 36 (12), 2493-2500.
- 122.Djuričić, B.; Pickering, S., Nanostructured cerium oxide: preparation and properties of weakly-agglomerated powders. *Journal of the European Ceramic Society* **1999**, 19 (11), 1925-1934.
- 123.Li, X.; Wang, W., Preparation of uniformly dispersed YAG ultrafine powders by co-precipitation method with SDS treatment. *Powder technology* **2009**, 196 (1), 26-29.
- 124.Deineka, T.; Doroshenko, A.; Mateychenko, P.; Tolmachev, A.; Vovk, E.; Vovk, O.; Yavetskiy, R.; Baumer, V.; Sofronov, D., Influence of sulfate ions on properties of co-precipitated Y₃Al₅O₁₂: Nd³⁺ nanopowders. *Journal of Alloys and Compounds* **2010**, 508 (1), 200-205.

- 125.Jiang, Z.; Zhang, L.; Zhen, F.; Yao, Q.; Bu, W.; Zhou, T.; Ma, Y.; Sun, R.; Chen, H.; Wang, Y., Ammonium sulfate and PEG composite surfactant to promote dispersibility of precursors and Y₂O₃ powders for transparent ceramics. *Ceramics International* **2018**, *44* (14), 16859-16867.
- 126.Nichols, G.; Byard, S.; Bloxham, M. J.; Botterill, J.; Dawson, N. J.; Dennis, A.; Diart, V.; North, N. C.; Sherwood, J. D., A review of the terms agglomerate and aggregate with a recommendation for nomenclature used in powder and particle characterization. *Journal of pharmaceutical sciences* **2002**, *91* (10), 2103-2109.
- 127.Que, M.; Que, W.; Zhou, T.; Shao, J.; Kong, L., Enhanced photoluminescence property of sulfate ions modified YAG: Ce³⁺ phosphor by co-precipitation method. *Journal of Rare Earths* **2017**, *35* (3), 217-222.
- 128.Sander, J. R.; Zeiger, B. W.; Suslick, K. S., Sonocrystallization and sonofragmentation. *Ultrasonics sonochemistry* **2014**, *21* (6), 1908-1915.
- 129.Gopi, K.; Nagarajan, R., Advances in nanoalumina ceramic particle fabrication using sonofragmentation. *IEEE Transactions on Nanotechnology* **2008**, *7* (5), 532-537.
- 130.Hwangbo, S.; Kim, J.; Chu, M.; Kim, M. In *Nanoparticle dispersion by focused ultrasound from cylindrical transducer*, Ultrasonics Symposium (IUS), 2013 IEEE International, IEEE: 2013; pp 2126-2129.
- 131.Li, Q.; Zhang, L.; Wei, S.; Zhang, Y.; Sun, R.; Zhou, T.; Bu, W.; Yao, Q.; Jiang, Z.; Chen, H., Weakly agglomerated α -Al₂O₃ nanopowders prepared by a novel spray precipitation method. *Ceramics International* **2018**, *44* (10), 11374-11380.

- 132.Li, Z.; Zhang, L.; Zhou, T.; Wang, L.; Wong, C. P.; Yang, H.; Zhang, Q., A novel spray co-precipitation method to prepare nanocrystalline Y_2O_3 powders for transparent ceramics. *Journal of Materials Science: Materials in Electronics* **2017**, 28 (6), 4684-4689.
- 133.Yin, D.; Wang, J.; Liu, P.; Luo, D.; Kong, L. B.; Dong, Z.; Tang, D., Yttria nanopowders with low degree of aggregation by a spray precipitation method. *Ceramics International* **2018**, 44 (16), 20472-20477.
- 134.Dong, L.; Ma, M.; Jing, W.; Xu, T.; Bin, K.; Guo, R., Synthesis of highly sinterable Yb: Lu_2O_3 nanopowders via spray co-precipitation for transparent ceramics. *Ceramics International* **2019**, 45 (15), 19554-19561.
- 135.Jing, W.; Li, F.; Yu, S.; Ji, X.; Xu, T.; Zhang, J.; Pan, Z.; Yuan, Z.; Kang, B.; Deng, J., High efficiency synthesis of Nd: YAG powder by a spray co-precipitation method for transparent ceramics. *Journal of the European Ceramic Society* **2018**, 38 (5), 2454-2461.
- 136.Kashani, A.; Mostaghimi, J., Aerosol Characterization of Concentric Pneumatic Nebulizer Used in Inductively Coupled Plasma—Mass Spectrometry (ICP-MS). *Atomization and Sprays* **2010**, 20 (5).
- 137.Tsai, S.; Song, Y.; Tsai, C.; Yang, C.; Chiu, W.; Lin, H., Ultrasonic spray pyrolysis for nanoparticles synthesis. *Journal of materials science* **2004**, 39 (11), 3647-3657.

138. Hu, Y.; Xia, H.-P.; Zhang, L., Emission Properties of Eu-doped Nano-Lu₃Al₅O₁₂ Powders by Ultrasonic Atomization and Co-precipitation Method [J]. *Acta Photonica Sinica* **2011**, *40* (11), 1646-1651.
139. You, Y.; Qi, L.; Li, X.; Pan, W., Preparation of YAG nano-powders via an ultrasonic spray co-precipitation method. *Ceramics International* **2013**, *39* (4), 3987-3992.
140. Konermann, L.; Ahadi, E.; Rodriguez, A. D.; Vahidi, S., Unraveling the mechanism of electrospray ionization. ACS Publications: 2013.
141. Luo, C.; Okubo, T.; Nangrejo, M.; Edirisinghe, M., Preparation of polymeric nanoparticles by novel electrospray nanoprecipitation. *Polymer International* **2015**, *64* (2), 183-187.
142. Low, L. E.; Wong, S. K.; Tang, S. Y.; Chew, C. L.; De Silva, H. A.; Lee, J. M. V.; Hoo, C. H.; Kenrick, K., Production of highly uniform Pickering emulsions by novel high-intensity ultrasonic tubular reactor (HUTR). *Ultrasonics sonochemistry* **2019**, *54*, 121-128.
143. Gao, J. X.; Huang, H. Q.; Li, X. X.; Du, F. H.; Li, L. B.; Li, J. S., Breakage and Particle Size Redistribution in an Ultrasound-Intensified Leaching Process. *Chemical Engineering & Technology* **2015**, *38* (9), 1665-1670.
144. Fedorov, P.; Il'in, N., Yttrium carbonate thermolysis. *Russian Journal of Inorganic Chemistry* **2012**, *57* (2), 237-241.

145. Gancy, A. B.; Wamser, C. A., Solubility of aluminum sulfate in aqueous ethanol at 30 and 80. degree. C. *Journal of Chemical and Engineering Data* **1979**, 24 (3), 192-194.
146. Cheng, X. Z.; Cheng, K.; Liu, J.; Sun, X. F. In *Synthesis and characterizations of nanoparticle sulfur using eggshell membrane as template*, Materials Science Forum, Trans Tech Publ: 2011; pp 279-282.
147. Pourmortazavi, S. M.; Taghdiri, M.; Samimi, N.; Rahimi-Nasrabadi, M., Eggshell bioactive membrane assisted synthesis of barium tungstate nanoparticles. *Materials Letters* **2014**, 121, 5-7.
148. Xiang, L.; Xiang, Y.; Wen, Y.; Wei, F., Formation of CaCO₃ nanoparticles in the presence of terpeneol. *Materials Letters* **2004**, 58 (6), 959-965.
149. Feng, B.; Yong, A. K.; An, H., Effect of various factors on the particle size of calcium carbonate formed in a precipitation process. *Materials Science and Engineering: A* **2007**, 445, 170-179.
150. Fuchise-Fukuoka, M.; Oishi, M.; Goto, S.; Isogai, A., Preparation of CaCO₃ nanoparticle/pulp fiber composites using ultrafine bubbles. *Nordic Pulp & Paper Research Journal* **2020**, 35 (2), 279-287.
151. Wan, Y.; Yi, H.; Wang, Y.; Luo, G., Preparation of uniform γ -alumina microspheres with large pore volumes in a coaxial microchannel. *Industrial & Engineering Chemistry Research* **2018**, 57 (34), 11636-11644.

152. Yu, H.; Wang, M.; Zhou, J.; Yuan, B.; Luo, J.; Wu, W.; Chen, Z.; Yu, R., Microreactor-assisted synthesis of α -alumina nanoparticles. *Ceramics International* **2020**, 46 (9), 13272-13281.
153. Li, J.-G.; Ikegami, T.; Lee, J.-H.; Mori, T.; Yajima, Y., Co-precipitation synthesis and sintering of yttrium aluminum garnet (YAG) powders: the effect of precipitant. *Journal of the European Ceramic Society* **2000**, 20 (14-15), 2395-2405.
154. Sun, Y.; Qi, L.; Lee, M.; Lee, B. I.; Samuels, W. D.; Exarhos, G. J., Photoluminescent properties of Y₂O₃: Eu³⁺ phosphors prepared via urea precipitation in non-aqueous solution. *Journal of luminescence* **2004**, 109 (2), 85-91.
155. Schweitzer, G. K.; Pesterfield, L. L., *The aqueous chemistry of the elements*. OUP USA: 2010.
156. Alarcon-Flores, G.; Aguilar-Frutis, M.; García-Hipolito, M.; Guzman-Mendoza, J.; Canseco, M.; Falcony, C., Optical and structural characteristics of Y₂O₃ thin films synthesized from yttrium acetylacetonate. *Journal of materials science* **2008**, 43 (10), 3582-3588.
157. Chudoba, T.; Lester, E.; Łojkowski, W.; Poliakoff, M.; Li, J.; Grzanka, E.; Presz, A., Synthesis of nano-sized yttrium-aluminum garnet in a continuous-flow reactor in supercritical fluids. *Zeitschrift für Naturforschung B* **2008**, 63 (6), 756-764.
158. Xu, X.; Sun, X.; Liu, H.; Li, J. G.; Li, X.; Huo, D.; Liu, S., Synthesis of monodispersed spherical yttrium aluminum garnet (YAG) powders by a

- homogeneous precipitation method. *Journal of the American Ceramic Society* **2012**, 95 (12), 3821-3826.
- 159.Hosseinzadeh, S.; Elahi, P.; Behboudnia, M.; Sheikhi, M.; Mohseni, S., Structural and magnetic study of metallo-organic YIG powder using 2-ethylhexanoate carboxylate-based precursors. *Modern Physics Letters B* **2019**, 33 (09), 1950100.
- 160.Zeng, M.; Ma, Y.; Wang, Y.; Pei, C., The effect of precipitant on co-precipitation synthesis of yttrium aluminum garnet powders. *Ceramics International* **2012**, 38 (8), 6951-6956.
- 161.Maruyama, T.; Arai, S., Aluminum oxide thin films prepared by chemical vapor deposition from aluminum acetylacetonate. *Applied physics letters* **1992**, 60 (3), 322-323.
- 162.Chen, Z.-H.; Yang, Y.; Hu, Z.-G.; Li, J.-T.; He, S.-L., Synthesis of highly sinterable YAG nanopowders by a modified co-precipitation method. *Journal of alloys and compounds* **2007**, 433 (1-2), 328-331.
- 163.Ru, Y.; Jie, Q.; Min, L.; Guoqiang, L., Synthesis of yttrium aluminum garnet (YAG) powder by homogeneous precipitation combined with supercritical carbon dioxide or ethanol fluid drying. *Journal of the European Ceramic Society* **2008**, 28 (15), 2903-2914.
- 164.Shevchenko, G.; Tret'yak, E.; Rakhmanov, S.; Malashkevich, G., Effect of polyvinylpyrrolidone on the morphology and spectral luminescence of $Y_3Al_5O_{12}: Ce^{+3}$. *Russian Journal of Physical Chemistry A* **2013**, 87 (8), 1397-1403.

165. Tayyari, S. F.; Milani-Nejad, F., Vibrational assignment of acetylacetone. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2000**, 56 (14), 2679-2691.
166. Lu, C.-H.; Bhattacharjee, B.; Chen, S.-Y., Microwave synthesis of manganese-ion-doped zinc sulfide nano-phosphors using a novel monomer. *Journal of Alloys and Compounds* **2009**, 475 (1-2), 116-121.
167. Bassous, N. J.; Garcia, C. B.; Webster, T. J., A Study of the Chemistries, Growth Mechanisms, and Antibacterial Properties of Cerium-and Yttrium-Containing Nanoparticles. *ACS Biomaterials Science & Engineering* **2020**, 7, 1787-1807.
168. Lin, G.; Zhang, L.; Yin, S.; Peng, J.; Li, S.; Xie, F., Study on the calcination experiments of rare earth carbonates using microwave heating. *Green Processing and Synthesis* **2015**, 4 (4), 329-336.
169. Chen, K.; Guo, S.; Zeng, Y.; Huang, W.; Peng, J.; Zhang, L.; Yin, S., Facile preparation and characterization of lanthanum oxide powders by the calcination of lanthanum carbonate hydrate in microwave field. *Ceramics International* **2020**, 46 (1), 165-170.
170. Giammaria, G.; Lefferts, L., Catalytic effect of water on calcium carbonate decomposition. *Journal of CO2 Utilization* **2019**, 33, 341-356.
171. Silakhori, M.; Jafarian, M.; Chinnici, A.; Saw, W.; Venkataraman, M.; Lipiński, W.; Nathan, G. J., Effects of steam on the kinetics of calcium carbonate calcination. *Chemical Engineering Science* **2021**, 246, 116987.

172. Esposito, L.; Piancastelli, A.; Bykov, Y.; Egorov, S.; Ereemeev, A., Microwave sintering of Yb: YAG transparent laser ceramics. *Optical Materials* **2013**, 35 (4), 761-765.
173. Frederickson, L. D., Characterization of hydrated aluminas by infrared spectroscopy. *Analytical Chemistry* **1954**, 26 (12), 1883-1885.

VITA

Matthew McDonald grew up around Atlanta, GA. He attended Georgia Southern University where he originally majored in psychology but continued to take more chemistry courses and changed majors because it interested him more. He transferred to the University of Georgia, where he conducted research under Dr. Richard Dluhy investigating nanolithography for surface enhanced Raman spectroscopy applications. In this setting Matt learned many techniques for monolayer deposition of polystyrene nanospheres, chemical vapor deposition, spin coating, plasma cleaning, laser spectroscopy, and various analytical techniques.

Upon completion of his undergraduate studies, he went on to work as a research assistant in the laboratory of Dr. George Schweitzer. After two years of research into the reduction and separation of samarium, europium, and ytterbium ions, Matt had the opportunity to attend graduate school for a Ph.D. in inorganic chemistry at the University of Tennessee, Knoxville under the supervision of Dr. Schweitzer. His research interests shifted to the applied synthesis of yttrium aluminum garnet and the techniques for its synthesis. Along the way he employed a variety of techniques to achieve this goal, like ball milling, solution combustion synthesis, microwave-assisted combustion synthesis, flame spray pyrolysis, precipitation, hydrothermal synthesis, and other modified precipitation techniques. He also explored the other fields of microwave chemistry, electrochemistry, materials recycling, supercritical fluids, and ultrasonication to broaden his grasp on basic concepts.