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THESIS

SYNTHESIS OF ZINC OXIDE PARTICLES USING MICROWAVE PLASMA TECHNIQUES

by

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June 2021

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**SYNTHESIS OF ZINC OXIDE PARTICLES USING MICROWAVE PLASMA
TECHNIQUES**

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ABSTRACT

Zinc oxide (ZnO) nanoparticles are important engineering materials with a multitude of applications. For example, ZnO can be readily sulfurized to ZnS, which can be used in forward-looking infrared optics and transparent ceramic windows that have myriad applications. There is a need to synthesize nanometric and spherical ZnO particles to ease processability and consolidation into bulk form. Atmospheric microwave plasma techniques have proven successful in the generation of spherical, nano-sized metal and ceramic particulates. Specifically, the aerosol-through-plasma (ATP) method has been successfully utilized to synthesize spherical boron nitride, a material with a hexagonal structure. Hence, ATP is a promising method to synthesize spherical ZnO, which also has a hexagonal structure (wurtzite). This thesis explores the use of atmospheric microwave plasma techniques using diverse operating parameters (between 700 and 900 watts), different Zn containing precursors, and various flow rates of carrier and plasma gases to produce ZnO particulates. The products generated using the atmospheric microwave plasma approach were characterized employing scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. The optimized conditions to produce nanometric spherical ZnO were identified, providing a proof of concept for the utilization of plasma techniques to tailor the compositional and microstructural features of materials of interest.

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LIST OF ACRONYMS AND ABBREVIATIONS

ARL	Army Research Laboratory
A-T-P	aerosol-through-plasma
CLS	CaLa_2S_4
GPS	Global Positioning System
LWIR	long-wave infrared radiation
OM	optical microscopy
QMS	quadrupole mass spectrometer
SEM	scanning electron microscope
slpm	standard liters per minute
STA	simultaneous thermal analysis
UHP	ultra high purity
XRD	X-ray diffraction
Zn	zinc
ZnO	zinc oxide
ZnS	zinc sulfide

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I. INTRODUCTION AND OBJECTIVES

This chapter provides the motivation, applications, and background inspiring this work—to produce zinc oxide (ZnO). Additionally, a hypothesis and overview of the thesis work is presented.

A. BACKGROUND

The following section introduces long-wave infrared radiation (LWIR) and the need for transparent ceramic windows. It presents the state-of-art material for the windows, zinc sulfide (ZnS). This leads to an introduction for the need of ZnO that could subsequently be sulfurized into ZnS. Then, ZnO production methods and the need for nanometric, spherical ZnO are discussed. Finally, the aerosol-through-plasma (A-T-P) method is introduced.

1. Naval / Defense Applications

Long-wave infrared radiation (LWIR) has many applications. Specifically for the armed forces, LWIR can be used for offensive and defensive countermeasures such as “heat-seeking” missiles that use infrared radiation emitted from the exhaust of targets [1]. The continued use of LWIR creates a demand for improved transparent windows and domes for munitions and weapons that have better mechanical and transmission properties.



Figure 1. LWIR is used in primary fire control systems for Abrams tanks (left) and in battlefield imaging (right)

Source: [2].

The use of LWIR is beneficial in environments where Global Positioning System (GPS) guidance is denied, such as rain, fog, and other adverse weather conditions. However, the current industry standard of materials for LWIR windows and domes suffers from erosion and other damage in these environments. In addition, these windows are exposed to wind and debris such as dust that damage the windows.

2. State of the Art

Germanium was the industry standard for transmissible windows and domes until research in the 1960s sought materials that exhibited improved light transmission and mechanical properties [3]. Germanium transmits light from 2 microns to 11 microns, covering short-wave infrared to long-wave infrared wavelengths [1]. It fails to transmit visible light from 0.4 microns to 0.7 microns, and fails to transmit well at elevated temperatures [3].

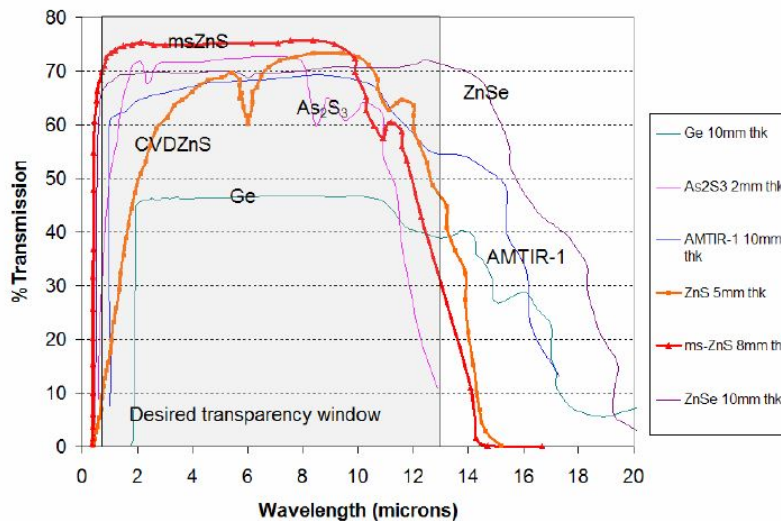


Figure 2. Transmission of various materials. Source: [3].

To move on to better materials that remedy the pitfalls of germanium, research was conducted in the mid-1960s. Replacements for germanium such as chalcogenide glasses began to emerge. These glasses exhibited shortcomings as well, in regard to thermal shock

due to low thermal conductivity [3]. ZnS then became the industry standard, as it exhibits good transmission properties including a range from 8–10 microns [1] as well as structural durability and mechanical strength [3]. ZnS continues to be the leading candidate for LWIR windows and domes; however, industry continues to look at higher performance systems. Thus, research continues to find improved materials such as transparent ceramics that would exhibit greater transmission, structural, and mechanical properties [4].

3. ZnO Uses and Production Methods

ZnO is a semiconductor material with a myriad of applications. ZnO has been used in society since the times of ancient Egypt and Rome for various ointments, skin treatments, etc. [5]. It finds uses in electronic, chemical, and biological applications [5]. ZnO also is used to coat fabrics and sunglasses and its antibacterial, deodorizing, and ultraviolet-absorbing characteristics make it practical for sunscreens [6]. In 2019, over 18,000 academic papers were reported on ZnO [5]. The need for continued research in ZnO production methods and uses is felt across many industries.

Many different production methods are used to synthesis ZnO powders or crystals. Some of them include hydrothermal techniques [7], solid-state pyrolytic reactions [8], and microwave and ultrasonic techniques [9]. With each production method, unique sizes, shapes, and properties of ZnO particles are achieved. For example, thin ZnO films with thicknesses of a few nanometers, are produced by pulsed laser deposition and useful in photocatalysis applications [5].

For transparent domes, with advantageous transmission properties as aforementioned, ZnO can be sulfurized into ZnS and then sintered and consolidated into windows and domes. This specific application would require geometries with isotropic properties that are easily sintered. In the sintering process, spherical particles pack more efficiently and smaller particles will sinter more easily [1]. Spherical particles will also yield more isotropic properties. Thus, the need for a production method of nanometric and spherical ZnO particles exists. Additionally, at higher temperatures, differences in structures can be overcome such as evidenced by cubic and hexagonal structures being able to be sintered together seamlessly at temperatures upwards of 2000°C [1]. This thesis exists

to investigate a high temperature ZnO production method that would produce ideal geometries, and sizes.

4. Atmospheric Plasma Techniques

Plasma processing is used in many different applications. Some of these applications include thin film deposition for items such as integrated circuits [10]. Additional applications include the improvement of surface coatings on polymers films that increase material properties such as adhesion strength, and sterility [10]. However, for this thesis work, a plasma technique was employed for the production of particulates with desirable shape, composition and material properties. The aerosol-through-plasma (A-T-P) technique, specifically, is one of many plasma techniques used in the production of materials. A particular interest exists for a production method of nano-sized particles. A-T-P methods have demonstrated success in the production of nanoparticles; from metal, ceramics, and carbonaceous materials to their combinations [10-14]. This technique quickly exposes precursors to a hot zone created through the guiding of low-power microwaves toward a stream of argon plasma gas and a combination of an argon carrier gas combined with the precursors. The combination of the precursor and the argon carrier gas forms the aerosol gas stream. This technique is fully described in the work of Phillips et al. [10], [13], Lambert [11], Osswald [12], and Weigle et al. [14].

The plasma hot zone is shown in Figure 3.

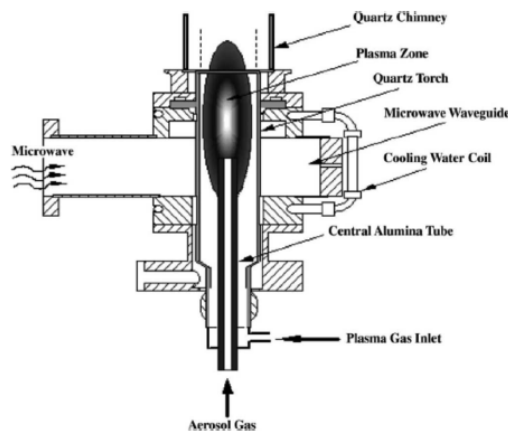


Figure 3. Schematic of the torch area. Source: [10].

In the system, a carrier gas flows into a beaker containing the solid or liquid precursor. Due to agitation from a vibration source located directly below the beaker and the flow of the carrier gas, the precursor is picked up and combined with the carrier gas to form an aerosol gas coming in below the quartz torch through an alumina tube. The plasma gas and aerosol gas combination is heated up by the microwave radiation incident upon the stream in the torch. The temperatures in the torch are upwards of 3200°C, and the particle stream is exposed to these conditions for fractions of a second [10]. The high temperature and short duration of time create a unique processing technique that has proved advantageous in particle production [11,13].

B. HYPOTHESIS

The use of an aerosol through plasma method, adequate precursors, and appropriate parameters will allow for the synthesis of nanometric and spherical ZnO particulates.

C. OVERVIEW OF THESIS

Chapter II covers the experimental procedures of this thesis. It starts with an overview of all the materials employed for this thesis, their chemistries, the base line characterization of their compositions, crystalline components, microstructures and measured material properties. Next, is an in-depth description of the ATP method detailing the apparatus, procedure, and overall process that happens in each plasma run. Following that, is a section on the characterization of the materials produced in the plasma runs. These products were analyzed by X-ray diffraction (XRD), and scanning electron microscopy using a scanning electron microscope (SEM) this characterization is compared to that of the same materials before the plasma run, referred to as precursors.

Chapter III contains the results and discussion regarding the parametric study of the plasma runs, the geometries and microstructures observed, the composition, and the crystal structure of the plasma products. Included in this chapter is a discussion of the successes and shortcomings of the methodology employed as well as the benefits and disadvantages of the plasma method used in comparison to existing literature on ZnO synthesis. Additionally, the chapter discusses how future work can continue and expand upon the work completed in this thesis. This work is completed in part as a collaborative effort with

the Army Research Laboratory (ARL) with the hopes of becoming a multi-year effort to first synthesize ZnS, then to investigate the effect that different precursors and conditions have on the morphology and particulate composition targeting the production of CaLa_2S_4 (CLS), and finally to refine the process for homogeneity in morphology and size distribution of particulates as well as repeatability and scaling of production. Chapter IV summarizes the conclusions discussed in Chapter III.

II. EXPERIMENTAL PROCEDURES

This chapter will present the materials, methods, and characterization techniques employed to fabricate ZnO. The raw precursors employed included zinc and a zinc nitrate. The method to convert the precursors into ZnO was a plasma torch operating at atmospheric conditions. The characterization methods were X-ray diffraction analysis and scanning electron microscopy. The sections that follow provide the details of each of the steps taken.

A. MATERIALS

Zinc and zinc nitrate were the two precursors run through the plasma for this thesis work. The zinc powder used was obtained from Acros Organics with a purity of 99.999%, mesh 40 (sieved through 0.4191 mm). Due to the large particle size of the zinc powder, five grams of the precursor were run through a cryogenic mechanical mill in order to decrease the particle size and increase the ability of the powder to be picked up by the carrier gas to form the aerosol gas.

Two different samples of zinc nitrate hydrate were used in this thesis. The first sample, $\text{Zn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, was obtained from Fisher Scientific Z45-500, as ACS Certified. The second was received from the sponsor of this work, acquired commercially from Sigma Aldrich as $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ having a 99.999% trace metal basis. Zinc nitrate is fairly hygroscopic and tends to form large agglomerates if exposed to any moisture in the atmosphere. The first sample suffered greatly from this and would not be carried by the gas through the plasma system. The second zinc nitrate sample consisted of large dry, elongated crystals. Before passing the second sample through the plasma, it had to be crushed with a mortar and pestle to form a powder; but overall, it was less hygroscopic and easier to work with and store when compared to the one former.

B. CRYOGENIC MECHANICAL MILLING

Cryogenic mechanical milling (cryo-milling) was done on the zinc powder in order to reduce the size of the precursor powder particles. A SPEX 6870 Freezer/Mill cryogenic impact grinder was used and is pictured in Figure 4.



Figure 4. The SPEX 6870 Freezer/Mill cryogenic impact grinder, vial and grinding media employed

Five grams of zinc powder were run at 10 impacts per second with a 1-minute cool down between cycles for a 5-minute cycle, two 10-minute cycles, and finally, for six 10-minute cycles. The zinc powder was placed in a polycarbonate vial with stainless steel ends (plugs) and a stainless steel impactor as the grinding media, then closed and placed into the cryo-mill. The vial is then submerged in liquid nitrogen and vibrated back and forth repeatedly with the grinding media moving from one end to the other of the vial 10 times per second, thereby pulverizing the zinc powder in the process. The vial and grinding media are shown in Figure 4.

Due to the submergence in liquid nitrogen, the sample is embrittled and in an environment around -196°C , well below the melting temperature of zinc at 419°C , allowing for the pulverization of the sample without melting [15].

C. OPTICAL MICROSCOPY

Optical microscopy (OM) was performed on the zinc powder to gather initial characterization data such as particle size and shape. A Nikon Epiphot 200 optical microscope (shown in Figure 5) was used to capture images via Nikon software.



Figure 5. Nikon Epiphot 200 optical microscope

D. SIMULTANEOUS THERMAL ANALYSIS

In order to have a baseline comparison of what happens during the thermal decomposition of zinc nitrate, thermogravimetry was performed via a simultaneous thermal analyzer (STA) with the zinc nitrate precursor. The STA used was a NETZSCH 449 F1 Jupiter, shown in Figure 6.



Figure 6. STA and QMS used for thermal analysis of zinc nitrate decomposition. Source: [16].

The settings for the thermal analysis were 20 minutes of purging with a mixture of ultra-high purity (UHP) oxygen gas mixed with inert gas to simulate the mixing ratio encountered in air atmospheres with a gas flow rate of 244.3 mL/minute. An independent flow of UHP argon at 244.3 mL/min was employed to keep the microbalance under inert conditions. The sample was heated from room temperature to 500°C at a rate of 2°C/min. Mass change as a function of temperature increase was measured.

E. AEROSOL THROUGH PLASMA METHOD

An A-T-P synthesis method was employed in this thesis work. Included in this section is a description of the various parts of the apparatus as well as the procedure followed for each plasma experiment.

1. Apparatus

The A-T-P apparatus is shown in Figure 7. Subsequently described are the sub systems involved in the apparatus including the microwave power generation, microwave guide, gas, vibration, coolant, and collection systems.

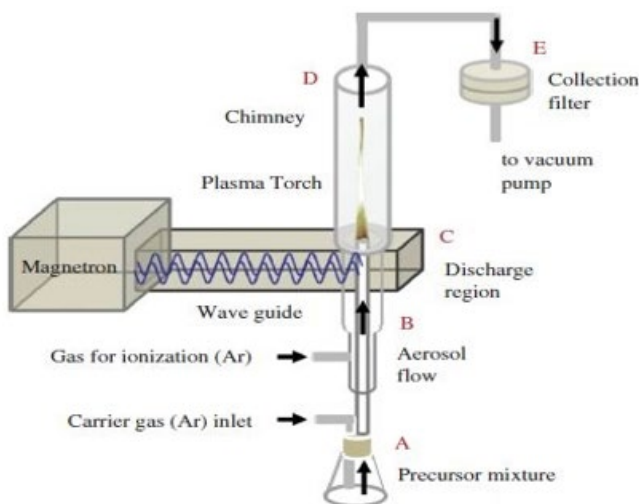


Figure 7. Plasma system apparatus. Adapted from [12].

a. Microwave Power Generator

Forward watts are provided via an ASTEX S-1500i microwave power generator operating at 2.45 GHz and pictured in Figure 8. This machinery operates similar to that of a household microwave oven where microwaves are produced inside by current passing through an electron tube [17]. The microwaves are then directed downstream toward the discharge region (Figure 7.C). The power levels used in this thesis work ranged from 700-900 W and were altered by adjusting the analog power set dial on the lower right-hand corner of the microwave power generator.



Figure 8. ASTEX S-1500i Microwave Power Generator used for the plasma

To turn on the microwave power generator, the white switch in the upper left-hand corner was flipped on. The displays should read 000 and 000. If the coolant system is in place, on, and the plasma gas is open, the HV on button can be pressed to ignite the torch. If the torch does not immediately light then the plasma should be struck with a metal tip. If the plasma is not immediately started, the reflected wattage will be too much for the waveguide to handle and will severely damage the system. Forward watts should read 600 or greater and reflected watts should remain around 8% of the forward watts reading.

b. Microwave Guide

The guidance system for the microwaves is an ASTEX Smartmatch interface, which uses a valve consisting of a disk rotating on an axis across the diameter of a pipe to regulate the gas flow, as in the throttles of many engines, in conjunction with an MKS 600

Series Pressure Controller to stabilize the system at 10 torr below atmospheric pressure. There are three stubs on the Smartmatch interface with which the reflected power level can be reduced to acceptable and stable values. Once stability is achieved and the system is hermetically closed (chimney placed and connection between chimney and filter assembly closed) then the Smartmatch interface can be switched to automatic.

c. Gas System

Two gases flow through the plasma apparatus; the plasma gas and the carrier gas. These gases are stored in air tanks and are controlled by regulators. UHP argon was used in this thesis as both the carrier and the plasma gas. From the regulator, the gas is directed through a Matheson Trigas analog flow meter for direct control of the plasma flow rate. The flowmeter calibration charts are attached in Appendix B. For all of the experiments conducted, the plasma gas flow rate was between 30 and 35 in flowmeter size 604 with a stainless-steel ball, which corresponds to a range of 4.41 to 5.17 in slpm. The carrier gas was also argon from the same air tank and regulator but run through a flowmeter size 603 with a stainless-steel ball at flow rates between 45 and 100. These flow rates correspond to 2.3941 and 4.7951 standard liters per minute (slpm), respectively.

From the flowmeters, the gases flow through individual tubes. The plasma gas is run to the base of the torch just before the discharge region. The carrier gas is directed into a beaker holding the precursor powder (Figure 7.A). This flow and the agitation of the precursor allow the powder to be picked up, combined, and carried away as an aerosol gas. Also in the beaker, is another tube that will take away the newly formed aerosol gas and direct it through an alumina tube of diameter 6.35mm (0.25 inches) to the base of the discharge region. Figure 9 shows the beaker with precursor in the bottom and the tube for the carrier gas (of smaller diameter tube at a length that reaches the bottom of the beaker) and a tube (of larger diameter near the mouth of the beaker) to carry the aerosol gas downstream to the torch (Figure 7.B).



Figure 9. A beaker holding precursors with tubes for aerosol and carrier gases inside

The plasma and aerosol gases will combine in the quartz torch and ionize due to the microwaves; this causes a plasma discharge. A schematic of the plasma torch area can be seen in Figure 10.

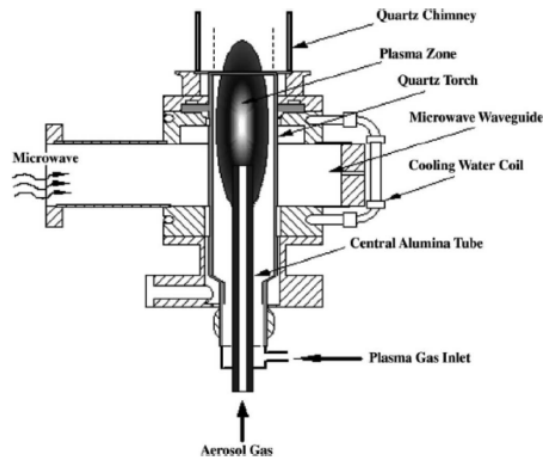


Figure 10. Schematic of the torch area. Source: [10].

d. Vibration System

The precursor powders need to be continuously agitated in order to be picked up by the carrier argon gas. The agitation of the precursors is very important for the success of

the plasma synthesis method. Some of the powders are too heavy to be picked up and carried by the carrier gas alone. Some of the powders are also extremely hygroscopic and therefore will absorb moisture and form agglomerates too big to be carried away as well. Vibration and agitation overcome some of these challenges. In order to have effective agitation, many techniques were tried including various vibration sources such as a sonic bath. The best technique discovered was to use a circular oscillating block (source of vibration) and hold the beaker in contact with the agitator while the carrier gas was flowing. The vibrations as well as the flow of the carrier gas caused the powder particles to be carried away as an aerosol gas. The oscillating block setup first used in this thesis can be seen in Figure 11.

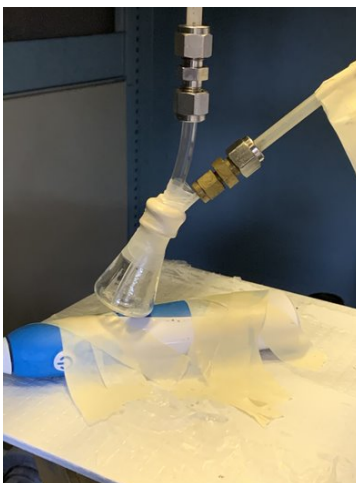


Figure 11. Initial agitator setup with the agitator secured on a platform and the precursor beaker resting on top

This initial setup worked sufficiently enough to produce a material; however, the precursor beaker was rarely in contact with the agitator as it was free to move around and would enter and exit from contact. In order to increase consistency in the vibration system and ideally increase yield the agitator setup was adjusted a few times throughout the experiments. Figure 12 shows the second iteration of the vibration system.



Figure 12. Second iteration of the vibration system. A rotary power tool with oscillating block positioned on the corner of the beaker containing precursor.

This iteration produced a much more consistent yield. Changing the agitator also allowed for independence from battery power or automatic shutoffs, which were both downfalls of the first agitator chosen. Issues still arose with this setup, however. One issue that arose was that the beaker would still lose the perfect contact needed for the optimal agitation of the precursor.

In order to hold the precursor beaker in precisely the correct orientation a custom part was designed using Solidworks 3D modeling software, sliced using Ultimaker Cura slicing software and then printed using a WASP 2040 Pro with WASP SPITFIRE RED Extruder (0.4 mm nozzle). The part needed to have some structural integrity due to its use in the testing apparatus so an infill density of 20% was selected for the 3D print. This part would slide over the agitator (which was secured in place by a ring stand and clamp) and then slide over the precursor beaker keeping them at the correct distance so that the beaker corner was in contact with the agitator tip. This setup can be seen in Figure 13.



Figure 13. Final iteration for agitator setup utilizing a custom 3D-printed part

e. Coolant System

Reaching temperatures upwards of 3200°C requires the plasma system to be cooled. A chiller is run at all times before, during and for at least 15 minutes after a plasma run. The chiller runs coolant through lines and copper coils that cool the entire system down. Particularly near the hot zone of the torch the copper coils play a large role in cooling the system. The coolant (chilled water) remained at 10°C .

f. Collection System

The system, as aforementioned, is run slightly below atmospheric pressure (10 torr below) this difference in pressure is provided by a vacuum pump. Upstream of the vacuum pump is a collection plate with filter paper (Figure 7.E) that collects the particulates produced as they flow out of the chimney (Figure 7.D), into the exhaust system. The membrane filters employed, supor-100 from Pali Corporation, had a 0.1 micron rating (100 nm). Collection of particulates was also possible from the chimney itself. A fume hood was used during operation to prevent the leaking of gases into the workspace. A fume hood would also be necessary in any future work using sulfur gas or sulfide particulates. Figure 14 shows the exhaust system open with the collection plate filter paper full of plasma-generated particulates from one of the plasma runs.



Figure 14. Collection plate after a plasma run

From this filter paper the sample is scraped off and collected for characterization in the XRD and SEM. After quite a few experiments, it became necessary to organize the test samples. Again, 3D printing was able to assist in this thesis work and a custom sample holder was designed and printed. This part was not meant for structural support, and thus, a 0% infill density was chosen. The sample holder can be seen in Figure 15.

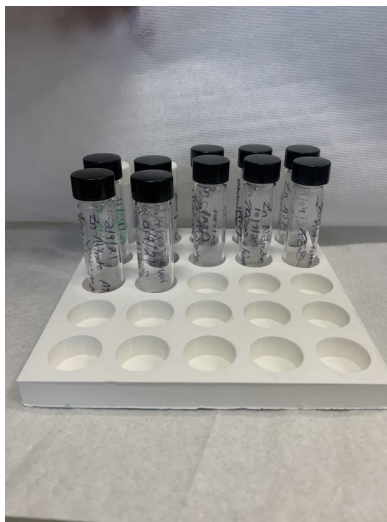


Figure 15. Custom sample holder printed via a WASP 2040 Pro 3D printer.

2. Procedure

The standard operating procedure followed for each plasma run is attached in Appendix A. Before running the plasma, the chiller, pressure controller, Smartmatch interface, and vacuum pump all have to be turned on. The chiller should be set to 10°C. Next, the argon flow has to be started and the fume hood should be turned on. It is critical for argon gas to be flowing through the system before the plasma is turned on. The microwave power generator can then be turned on as explained in the previous section. The next step is to work with the Smartmatch interface and the MKS pressure controller simultaneously as the chimney is placed and slowly closed. Once the system is stable the vibration system and aerosol gas can be turned on. The plasma should run for no more than 45 minutes. To turn the plasma system off, the vibration system should be turned off, followed by the aerosol gas. Next, the chimney should be open using the welding gloves. The MKS pressure controller can now be switched to close and the microwave power generator can be turned off. The system needs to cool for at least 15 minutes and then the white switch on the power generator can be switched off by pressing the HV power off button. Following these steps, the plasma gas can be turned off as well as the fume hood and other devices. In the case of emergencies or severe instability in the plasma system the HV off button could be pressed followed by the shutting off of the gases, vacuum pump and other devices.

The variables that were controlled for each plasma run included the power level of the microwave power generator, the flow rates of the plasma and aerosol gases and the precursor powder that was used. Table 1 shows the plasma runs that were performed and the parameters for each run. Varying the precursors as well as the other parameters run through the plasma system were altered in the effort to achieve ideal size, shape and composition of the plasma products. After each run was completed, the powder collected downstream of the plasma system on the filter paper was collected for characterization in the SEM and the XRD.

Table 1. Parameters for the plasma runs

Power level (Watts)	Precursor	Ar plasma flow rate (slpm)	Ar aerosol flow rate 603 (slpm)	SEM completed?	XRD completed?
900	Zn	4.41	4.7951	No	No
900	Zn Nitrate (Fisher)	5.17	4.7951	No	No
900	Zn Cryo-milled (20 min)	5.17	2.3941	Yes	Yes
800	Zn Cryo-milled (60 min)	5.17	2.3941	Yes	Yes
700	Zn Cryo-milled (60 min)	5.17	2.3941	Yes	Yes
700	Zn Nitrate (Sigma)	4.41	4.7951	Yes	No
800	Zn Nitrate (Sigma)	4.41	4.4269	Yes	No
900	Zn Nitrate (Sigma)	4.41	4.0271	Yes	No
900	Zn Nitrate (Sigma)	4.41	2.6463	Yes	Yes
900	Zn Nitrate (Sigma)	4.41	3.5956	No	No

Zinc powder that had been cryo-milled was used as a precursor and was run through the plasma at three different power levels (700, 800, and 900 watts) while holding the plasma and aerosol gas flow rates constant. All of the runs were conducted at 10 torr below atmospheric pressure for that day. The plasma gas flow rate for all of the runs was 5.17 slpm (35 on 604 flowmeter) UHP argon gas. For the aerosol gas, the flow rate was 2.3941 slpm (45 on 603 flowmeter) UHP argon. Zinc nitrate was passed through the plasma at three different power levels (700, 800, and 900 watts) at varying aerosol gas flow rates from 2.6463 slpm (50 on 603 flowmeter) to 4.7951 slpm (100 on 603 flowmeter).

F. CHARACTERIZATION OF PRECURSORS AND A-T-P MATERIALS

Characterization of A-T-P materials was completed by XRD analysis, scanning electron microscopy, and particle size analysis.

1. X-ray Diffraction Analysis of Crystalline Components

XRD analysis employs Bragg's law $n\lambda = 2d \sin \theta$, which relates the diffraction angle and lattice spacing of a crystalline sample to the wavelength of radiation incident on a sample [18]. XRD was a characterization technique used in this thesis work to determine

the crystalline phases in the samples under study. Both the precursor powders as well as the particulates generated in the plasma system were characterized by XRD analysis. XRD results appear as charts with intensity of diffracted x-rays counted as a function 2 theta angle. XRD was used to determine crystalline structure of components before and after each plasma run.

A Rigaku Miniflex 600 X-ray diffractometer was used and is shown in Figure 16.



Figure 16. Rigaku Miniflex 600 X-ray Diffractometer

This instrument allows for the determination of crystalline structure, percent crystallinity, and lattice parameters. The main use of XRD analysis was to compare the makeup of the powders before and after the A-T-P process. The XRD parameters used in analysis were standard 40 kV/15 mA, 2θ scanning range of 10 degrees to 120 degrees at a speed of $5^\circ/\text{min}$. PDF-4+ 2020 RDB, a product of the international Centre for Diffraction Data was used as a database reference to obtain industry accepted PDF cards for suspected substances in order to make comparisons and draw conclusions to the experimentally obtained results.

2. Scanning Electron Microscopy

Since 1948, SEMs have been used to generate three dimensional images of objects [19]. The improvements in scanning electron microscopy have advanced so much so that

they allow for the viewing of features on the nanometric scale. A SEM directs a beam of electrons incident on an object and generates a high resolution of the image of backscattered electrons, or secondary electrons [19]. The electron beam is directed by an electron gun with a fine gun tip that concentrates the electrons into a beam directed at the object of interest. SEM is completed most times, including during this thesis work, in a vacuum chamber to minimize the obstruction of the electrons [19]. SEM was completed as part of this thesis work in order to characterize the shape, size, and microstructural features of the particulates generated.

Microscopy was performed using Zeiss Neon 40 dual beam FIB-SEM. The SEM is shown in Figure 17. The in-lens secondary electron detector was used to image the particulates produced in the plasma system. Images were captured at instrument magnifications ranging from 200x to 100,000x.



Figure 17. Zeiss Neon 40 Scanning Electron Microscope

In order to minimize charging, samples had to be sputter coated using a Cressington 208HR Sputter Coater and a Cressington mtm-20 thickness controller shown in Figure 18. The samples that were sputtered were coated with a 2 nm layer of palladium.



Figure 18. Cressington 208HR Sputter Coater Cressington mtm20 thickness controller

Parameters used in the SEM were a standard 30 μm aperture and an electron accelerating voltage ranging from 2 kV to 5 kV. The accelerating voltage was adjusted to address charging in the sample. SEM imaging sessions for this thesis work were conducted with a system vacuum level of approximately 4×10^{-6} mbar and an electron gun vacuum pressure of 1.5×10^{-10} mbar. During each session of imaging, the SEM was re-aligned. The astigmatism, aperture, and working distance were adjusted to improve image quality.

3. Particle Size Analysis

Particle size distribution analysis and average particle size calculations were completed using ImageJ software. The image being evaluated was divided into five equal sections by four horizontal lines. The scale was adjusted and set to measure pixels/nanometer based on the known scale in the image. Any particle that touched the horizontal lines was measured. Roughly 80–150 measurements were taken per image and the distributions for those measurements were plotted. The mean, median and mode for particle size was also calculated. An example of an image divided up in ImageJ is shown in Figure 19.

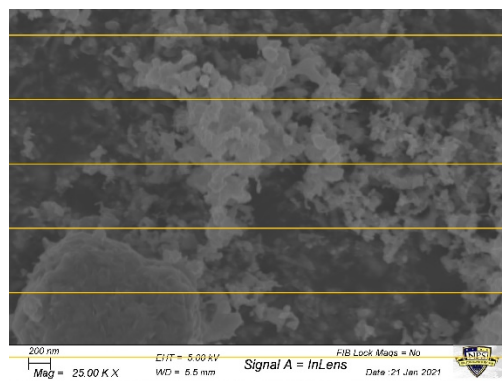


Figure 19. ImageJ grid applied to complete particle size analysis

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III. RESULTS AND DISCUSSIONS

This chapter presents the data generated for most of the experiments performed, the characterization results either by XRD or SEM, the analysis of particle sizes, shapes, crystal phases identified and a discussion. The latter summarizes findings and compares and contrasts the outcome of using a plasma system against other methods to produce ZnO found in the literature.

A. ZINC AS A PRECURSOR

Presented below are results regarding plasma runs and characterization of zinc as a precursor in the A-T-P method. SEM results and particle size distributions are presented for particles collected in the chimney and the filter for varying power levels.

1. Raw Material

Zinc powder, before cryo-milling, has individual particles easily distinguished by the naked eye, with sizes in the range of 400 - 650 μm with irregular shapes. Some particulates exhibit a flake-like appearance while others are elongated, almost needle-like, as can be seen in Figure 20.

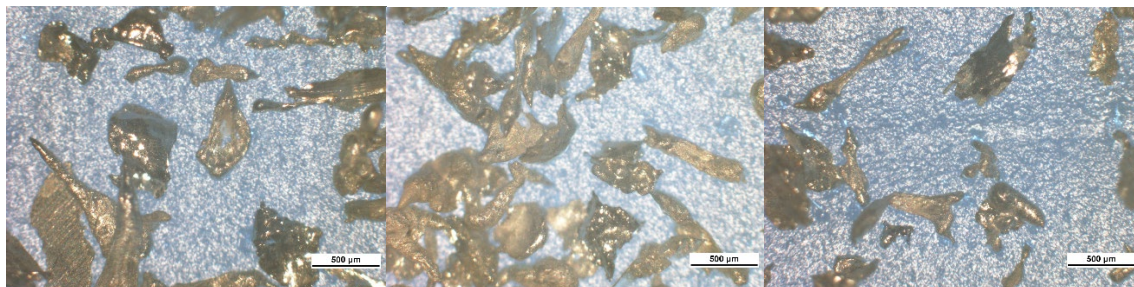


Figure 20. Optical microscopy images of zinc precursor. Scale bar: 500 microns.

The density of zinc metal is 7.133 g/cm^3 , with melting point of 420°C and a boiling point of 907°C [15]. Considering the density and particle size just reported, the difficulties of converting the particulates into an aerosol when combined with the argon gas employed

as carrier, become evident. It has been reported that 0.001 to 100 microns are the typical particulate sizes that can effectively generate an aerosol with particulates larger than 100 microns usually settling too quickly [20]. Thus, the zinc powder particulates were too large and too heavy to be carried by the carrier gas creating an aerosol and had to be reduced in size by cryo-milling.

The zinc powder was initially cryo-milled for five minutes and 20 minutes and then later for 60 minutes upon conclusion that cryo-milling would not introduce foreign species. Even with the naked eye, the zinc sample appeared to be much finer after 60 minutes of cryo-milling compared to 20 minutes and five minutes of cryo-milling. An image of the three samples is shown in Figure 21.

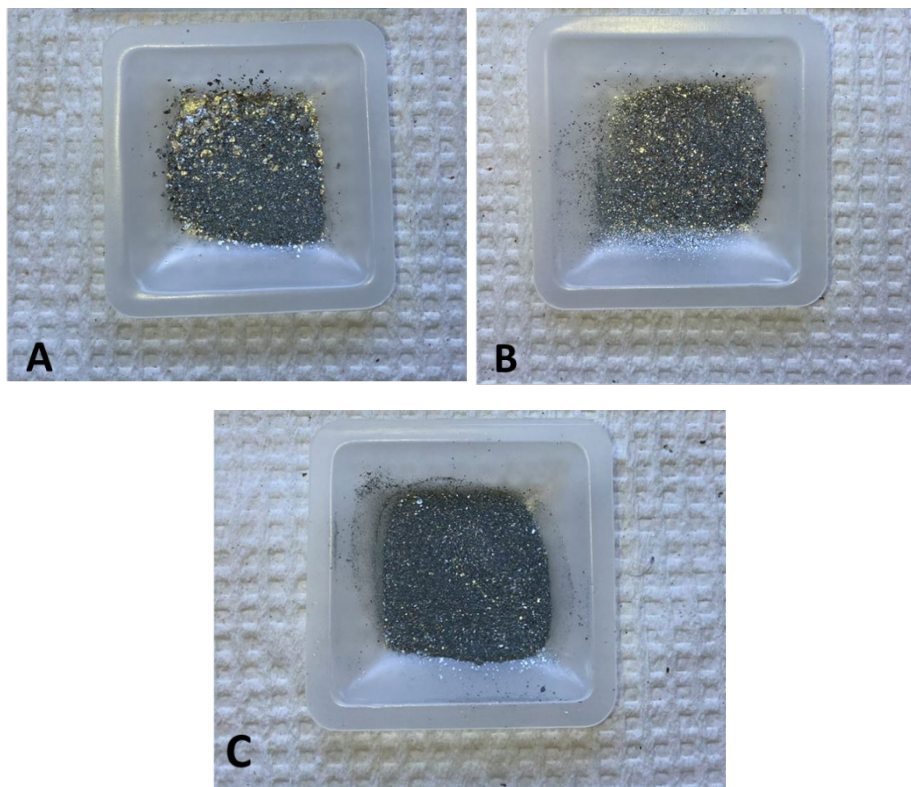


Figure 21. Zinc after cryo-milling 5 minutes (A), 20 minutes (B), and 60 minutes (C)

The zinc sample cryo-milled for a longer period of time seemed to have more uniformity in particle size, and be finer upon visual inspection. To confirm this observation, and to verify that no additional species were introduced in the milling process, the 20 minute and five minute samples were imaged with the SEM and characterized with the XRD. The SEM comparison between the samples is shown in Figure 22.

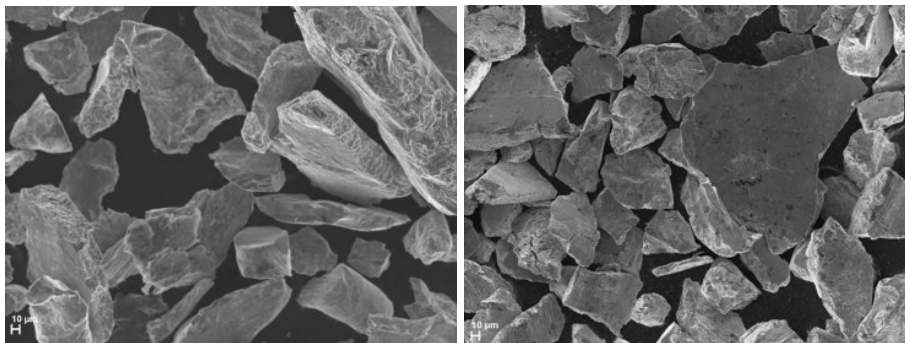


Figure 22. Cryo-milled zinc after 5 minutes (left) and 20 minutes (right).
Scale bar: 10 µm

The above images demonstrate the reduction of large particles with longer milling times. The particles appear to approach a more uniform size as they break up in the mill, supported by visual observations as well.

XRD analysis showed the crystalline phases as result of the cryo-milling process. Figure 23 shows the XRD pattern for the zinc powder before cryo-milling, confirmed to correspond to zinc metal (PDF card 00-004-0831), and Figure 24 shows the zinc powder after cryo-milling for five minutes.

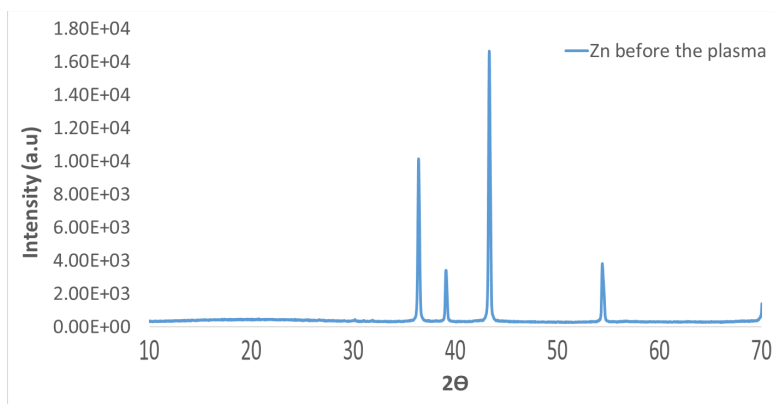


Figure 23. XRD for zinc before cryo-milling all peaks were confirmed to correspond to zinc metal

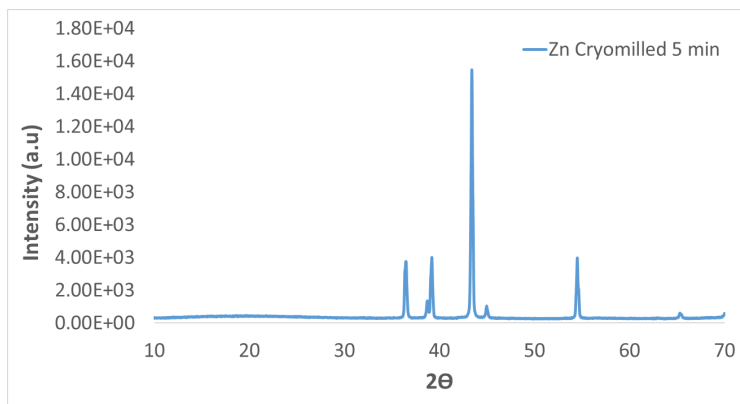


Figure 24. XRD for zinc after 5 minutes of cryo-milling

The XRD results shown in Figure 24 display additional peaks at 39.0, 45.1, and 65.7 degrees (2 theta) that correspond to aluminum (PDF card 01-089-4037). These additional peaks are most likely due to residue in the grinding vial or XRD powder sample holder. Those additional peaks do not occur in Figure 25, which shows the XRD results for zinc after 20 minutes of cryo-milling.

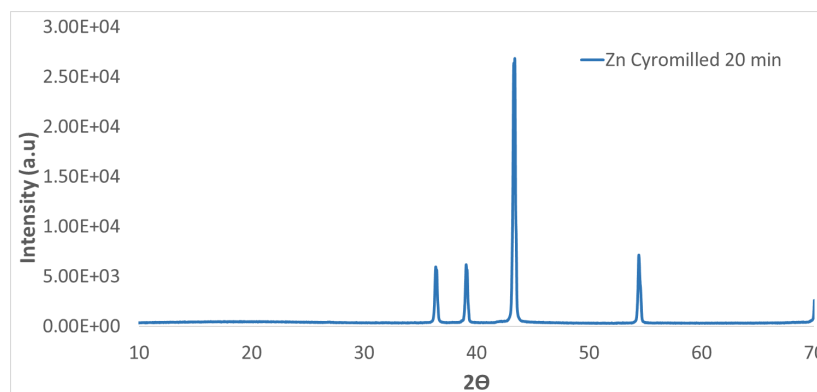


Figure 25. XRD for zinc after 20 minutes of cryo-milling all peaks were confirmed to correspond to zinc metal

With proper cleaning of the grinding vial and XRD sample holder, there was no other contamination of the zinc sample. Additionally, the sample milled for a longer period of time produced finer, smaller, and more uniform particles. The smaller particles from the 20 minute milling were able to be carried by the carrier gas into the aerosol stream for a plasma run that had a collectable yield of 1.3 mg/min compared to previous attempts which had little to no yield. Thus, five grams of zinc powder was milled with an undamaged grinding media for 60 minutes for additional plasma runs.

2. Plasma Products

a. XRD Results

XRD results indicate that the zinc precursor when run through the plasma turns into ZnO with some slight residual zinc depending on the plasma run. Figure 26 shows the XRD results for zinc as a precursor run through the plasma at 700 and 900 watts. It is worth noting that the system was not hermetically close, and when the experiments were carried out at 10 torr below atmospheric conditions, air leaks in the reaction zone of the chimney introducing oxygen into the system.

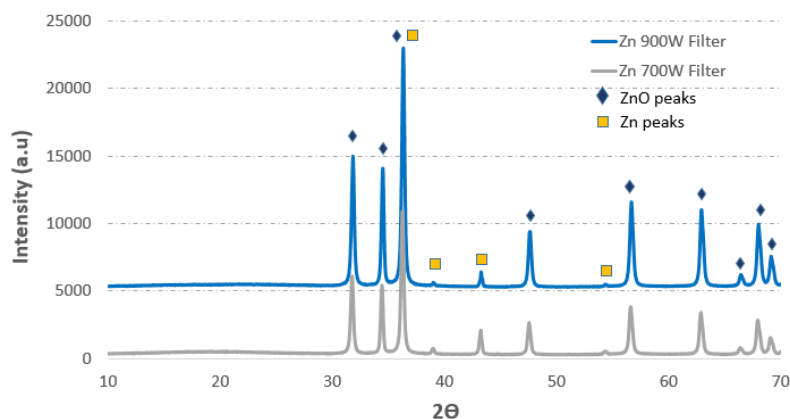


Figure 26. XRD results for zinc as a precursor run through the plasma at 700 and 900 W

The XRD response indicates that the only species after the A-T-P method are ZnO and zinc. The peaks for both of these species are indicated on Figure 26. The precursor is almost completely converted to hexagonal wurtzite ZnO (PDF card 00-036-1451) with only slight remnants of un-oxidized zinc (PDF card 00-004-0831). The difference in power level for the plasma system had little to no effect on the XRD results.

b. Chimney Particles

Figures 27-29 show the particulates collected from the chimney residue for plasma runs of three different power levels (700, 800, and 900 watts) for the microwave plasma generator. These images were captured in the SEM at 200x, 10,000x, and 25,000x magnification.

It is worth noting that despite the particle sizes not being identifiable at the 200x magnification, the images show that all particulates are forming soft agglomerates and no micron size individual particles are observed, in contrast with the zinc nitrate precursor, which will be presented in section 3.B.

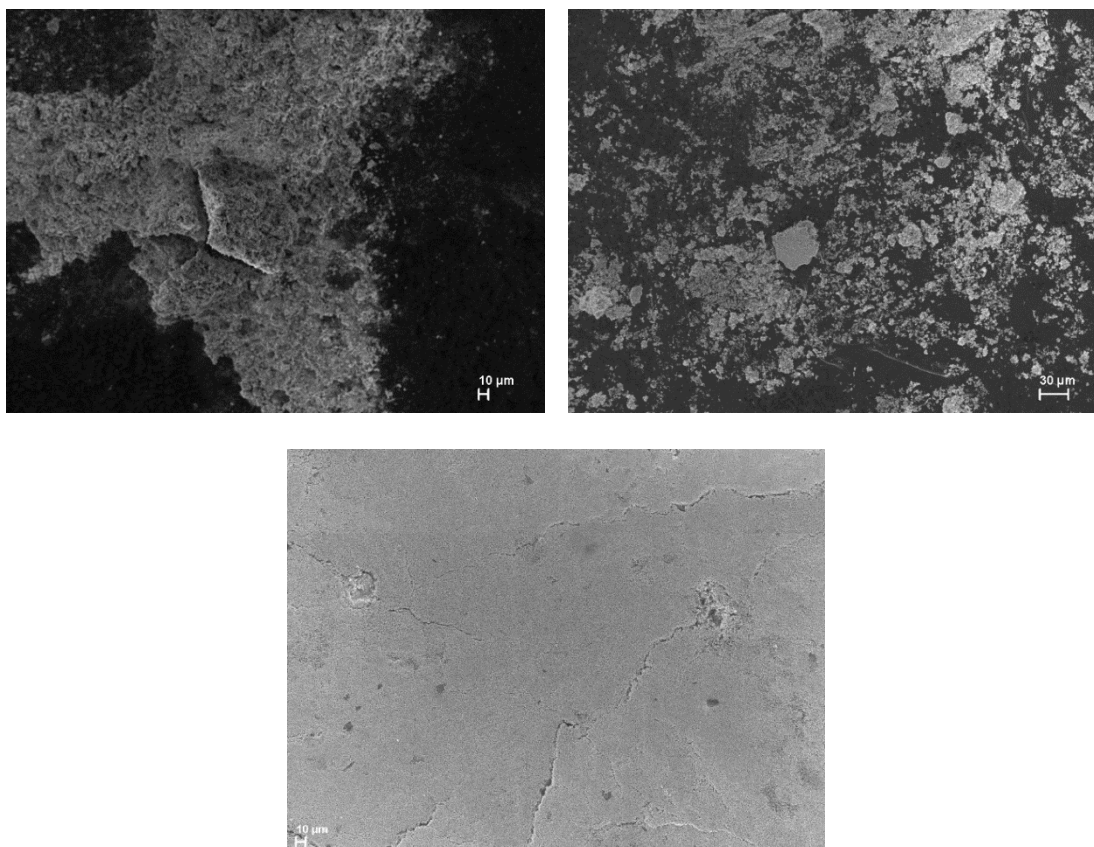


Figure 27. Zinc as a precursor run through the plasma at 700 W (top left), 800 W (top right), and 900 W (bottom) at 200x magnification collected in the chimney

At 200x instrument magnification (Figure 27), the powder collected appears very fine and homogenous. A great reduction in particle size and shape can be seen compared to the zinc precursor before the A-T-P method (Figure 22). Taking a closer look with 10,000x magnification image (Figure 28), the particles have submicron sizes. At the sub-micron level, however, three distinct particle shapes can be seen. One, circled in red on Figure 29, appears to be spherical in nature with sizes ranging from 50-250 nm. Another, circled in green, shows thin needle-like rods that appear of different widths (typically 20-120 nm) and lengths (typically 100-350 nm). Finally, circled in blue are a combination of a spherical center with needle like rods growing outward.

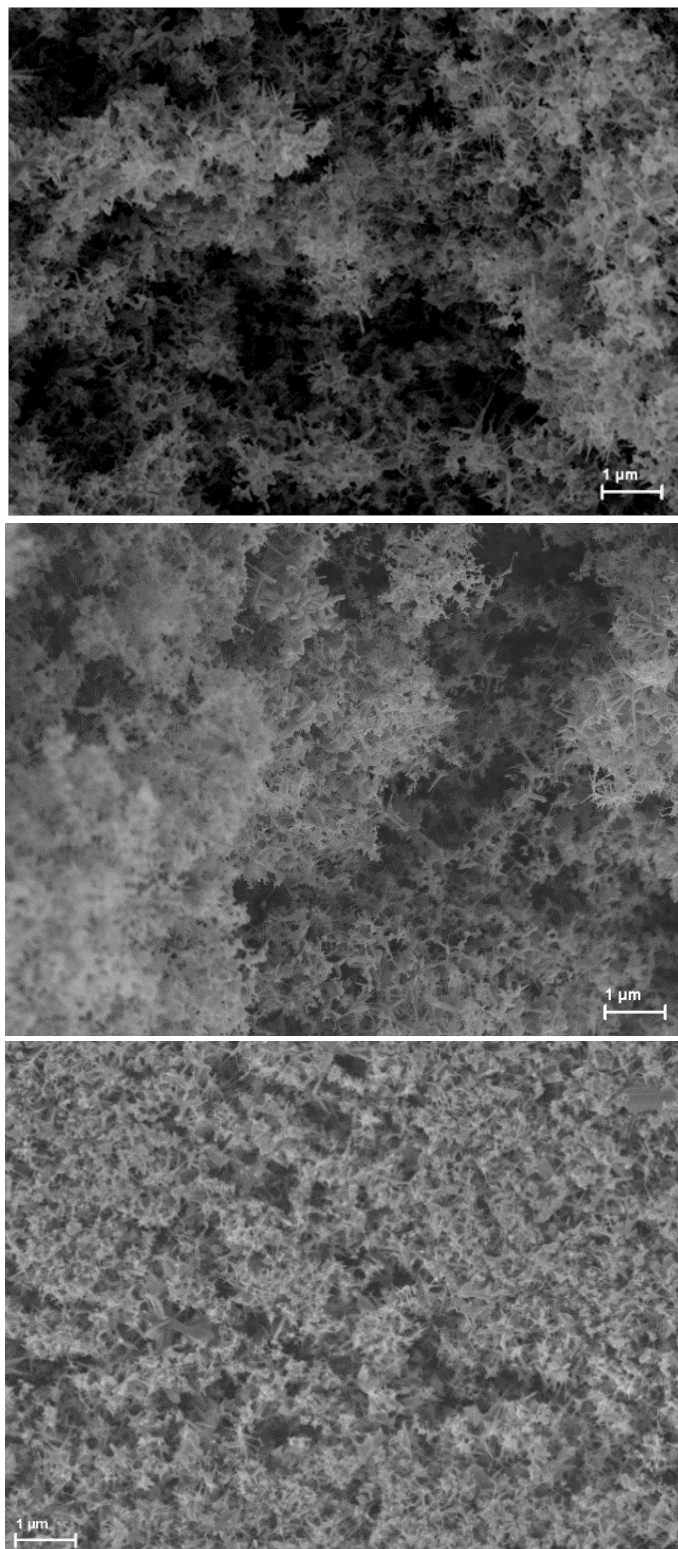


Figure 28. Zinc as a precursor run through the plasma at 700 W (top), 800 W (middle), and 900 W (bottom) at 10,000x magnification collected in the chimney

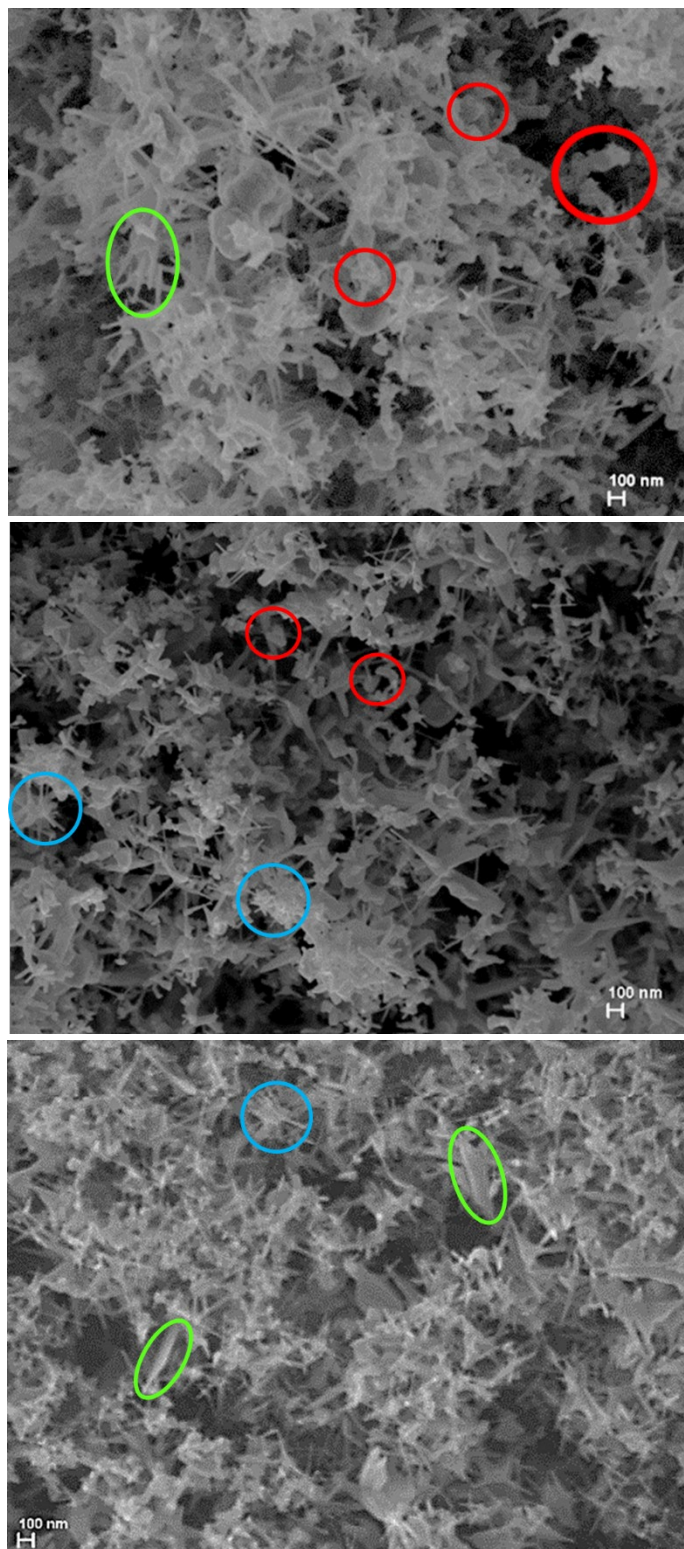


Figure 29. Zinc as a precursor run through the plasma at 700 W (top), 800 W (middle), and 900 W (bottom) at 25,000x magnification collected in the chimney

Particle size analysis was completed as described in Chapter II. The results for zinc as a precursor are displayed for particles collected in the chimney in Figures 30. Mean, median, and mode data are summarized in Table 2.

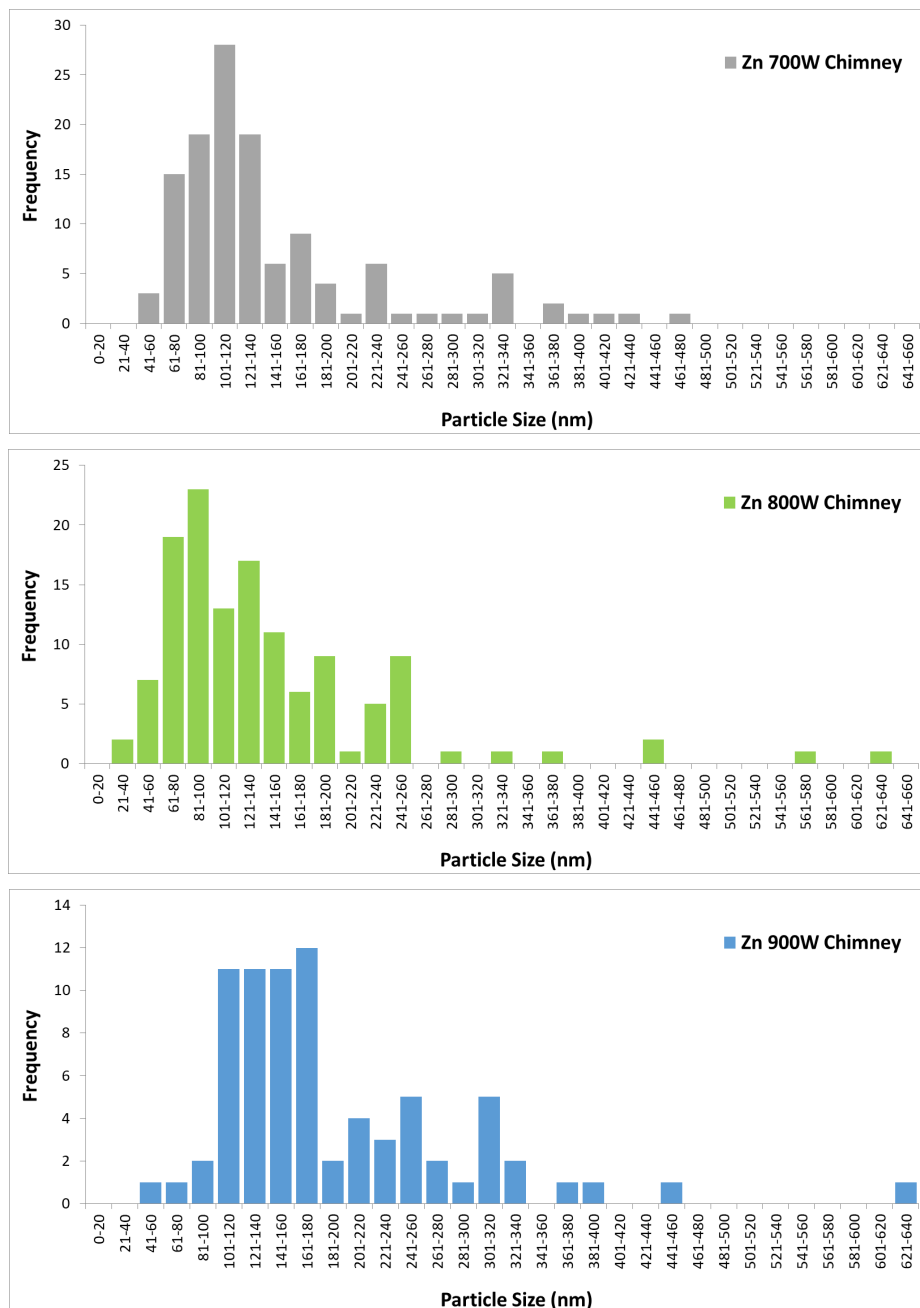


Figure 30. Particle Size distribution for zinc as a precursor collected from the chimney

The majority of particles collected in the chimney fall in the size bin of 81-140 nm for the 700 watt run, 61-120 nm for the 800 watt run and 101-160 nm for the 900 watt run.

c. Filter Particles

Figures 3—33 show the results from particles collected in the filter system. At lower magnifications, these samples exhibit the same similarities as the chimney particles do. They appear to be fine powder like substances. They appear also relatively homogenous and form soft agglomerates independent of power level in the microwave power generator. The same features that are discussed above for the chimney particles exist also in the filter particles. The same three sub-micron features are shown in Figure 33 (sphere-like shapes, needle-like rods and a combination of the two) and are circled again in red, green and blue, respectively. An additional sub-micron feature appears however in the 900 watt plasma run as shown in the bottom image of Figure 33 and circled in orange. This fourth feature appears to be large (100-300 nm) and flake-like.

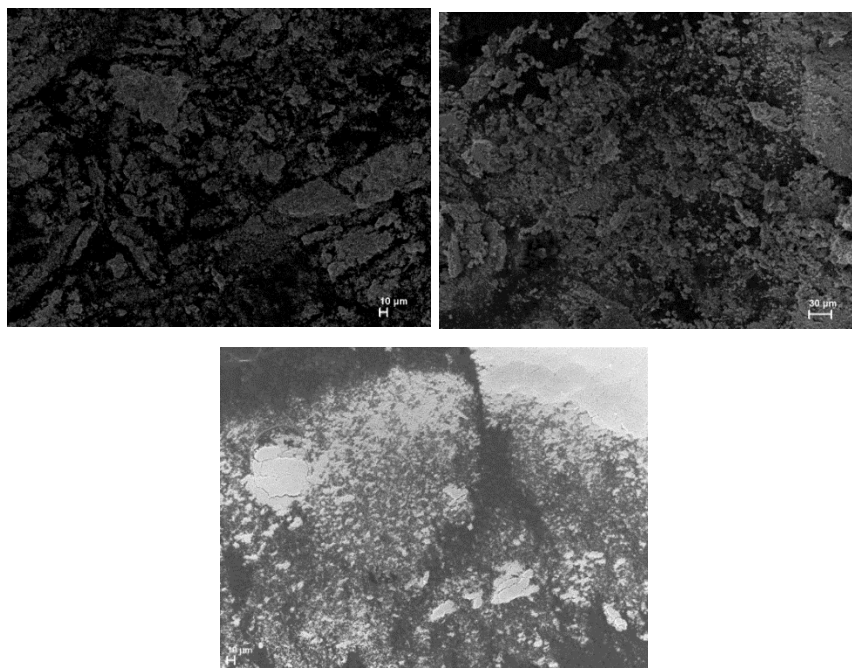


Figure 31. Zinc as a precursor run through the plasma at 700 W (top left), 800 W (top right), and 900 W (bottom) at 200x magnification collected in the filter. Scale bar: 10 μm

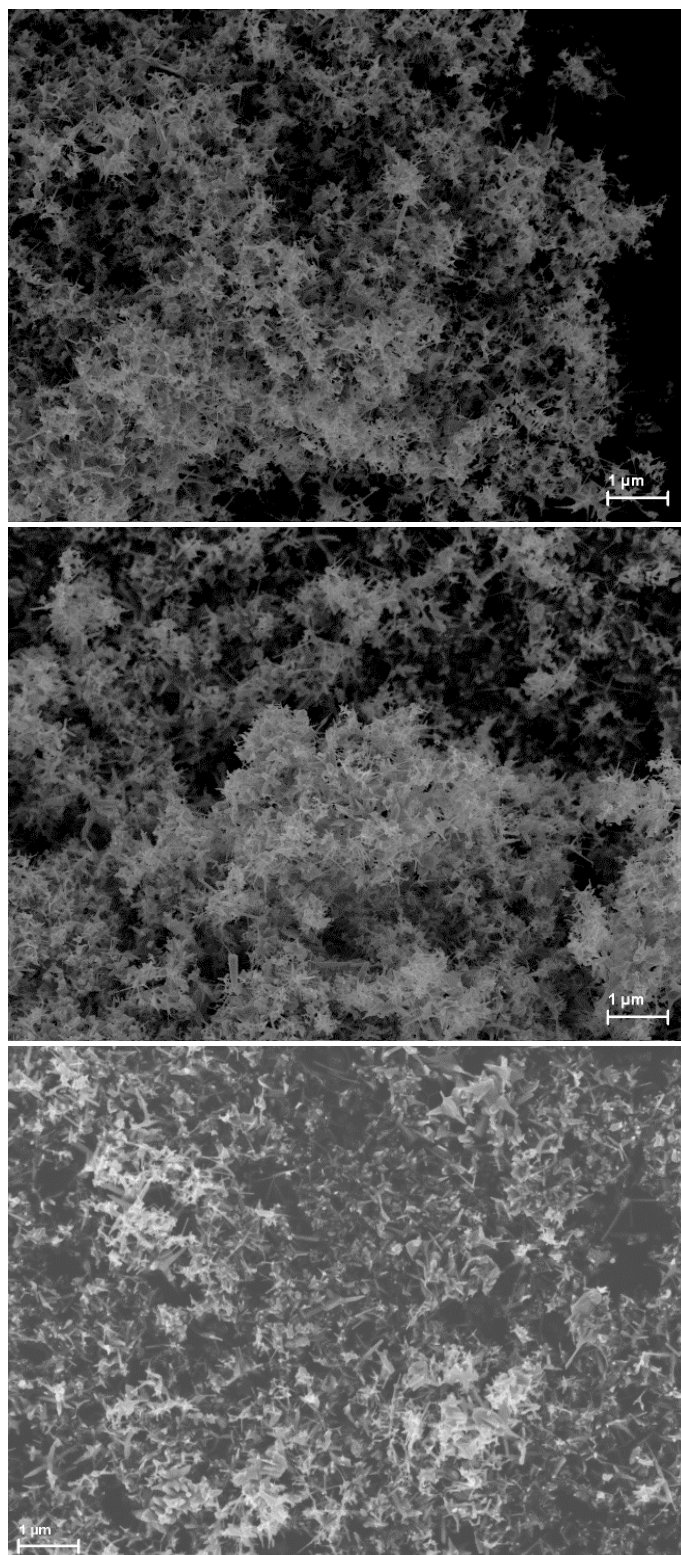


Figure 32. Zinc as a precursor run through the plasma at 700 W (top), 800 W (middle), and 900 W (bottom) at 10,000x magnification collected in the filter

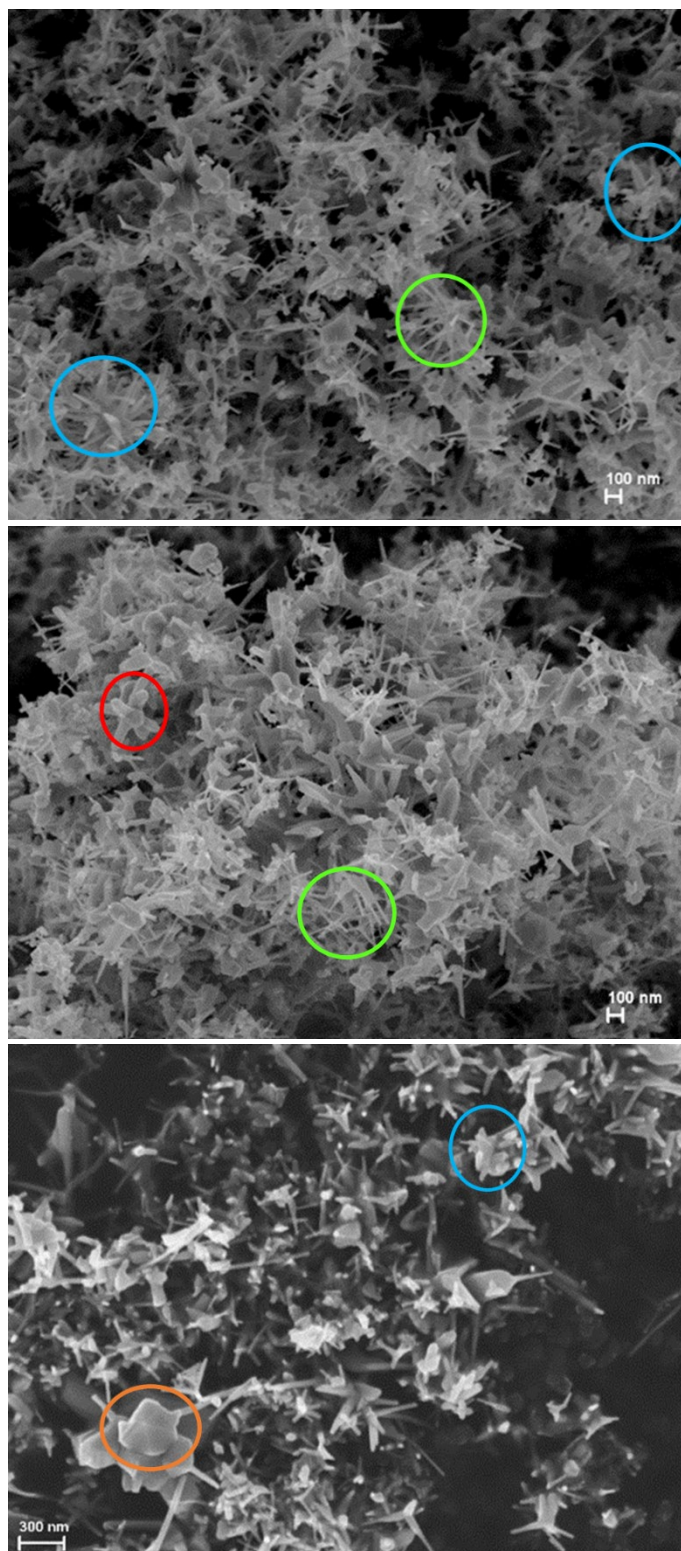


Figure 33. Zinc as a precursor run through the plasma at 700 W (top), 800 W (middle), and 900 W (bottom) at 25,000x magnification collected in the filter

Figure 34 shows the particle size distribution for the particles collected in the filter.

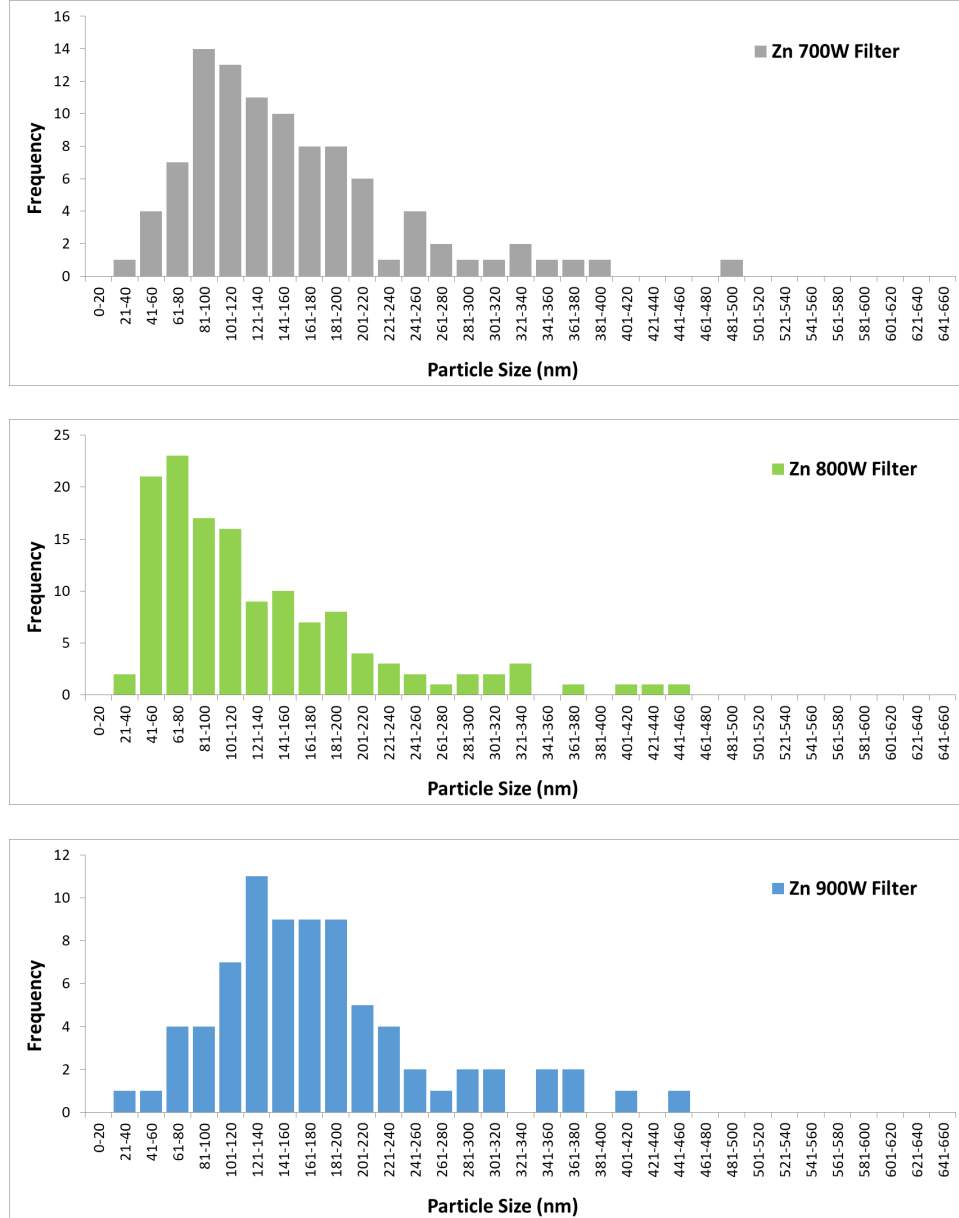


Figure 34. Particle Size distribution for zinc as a precursor collected from the filter

The particles collected in the filter exhibit a majority in the size bins of 81-140 nm, 41-100 nm, and 121-180 nm for the 700, 800, and 900 watt runs, respectively. Table 2 shows the mean, median and mode for the particle size analysis for all of the plasma runs completed for the zinc precursor at diverse conditions.

Table 2. Zinc as a precursor particle size analysis summary

	Mean (nm)	Median (nm)	Mode (nm)
700W Chimney	148.37	115.90	105.33
700W Filter	156.56	137.86	106.75
800W Chimney	142.73	120.05	91.60
800W Filter	131.27	106.57	77.11
900W Chimney	209.69	185.38	148.23
900W Filter	180.40	169.26	194.92

3. Summary of Using Zinc as a Precursor

Using zinc powder as a precursor for the A-T-P method was feasible as long as the particle size of the precursor powder was reduced in size below 100 microns, achieved by cryo-milling in this work. In the plasma, the zinc was converted to ZnO particles of four distinct shapes. Seen in the results were spheres, needle-like rods, spheres with needle-like growths outward, and large flakes. Particles were able to be collected in the filter and in the chimney systems of the plasma apparatus. The particles in the chimney exhibited larger size than those collected in the filter. For the 800 watt and 900 watt runs the average particle size was 142.73 nm and 209.69 nm, respectively for the chimney particles compared to 131.27 nm and 180.40 nm for the filter particles also for 800 watts and 900 watts, respectively. Overall, the power level of 800 watts had the smallest average particle size (131.27 nm in the filter and 142.73 nm in the chimney). Furthermore, the SEM results for 800 watts showed evidence of spherical particles. Any needle-like rods that appeared for this run also appeared as spherical centers with needle-like growths outward and not stand alone needle-like rods.

B. ZINC NITRATE AS A PRECURSOR

Presented below are results regarding plasma runs and characterization of zinc nitrate as a precursor in the A-T-P method. For the SEM images and the particle size analysis, only results from the filter are presented as the yield from the chimney was not significant to conduct complete characterization for every experiment.

1. Raw Material

Initially zinc nitrate, $\text{Zn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, obtained from Fisher Scientific Z45-500, as ACS Certified, was used as a precursor. This sample, however, was stored in powder form and exhibited extreme hygroscopic properties. In the beaker it would absorb moisture and form large agglomerates too heavy for the carrier gas to pick up. In order to overcome this, new zinc nitrate stock was obtained from Sigma-Aldrich and used ($\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ having a 99.999% trace metal basis). This second sample was stored in crystalline form and was more stable in the storage container. Before using the zinc nitrate as a precursor, it was ground into a fine powder via mortar and pestle and then quickly transferred to the precursor beaker and hermetically sealed. The changing of the zinc nitrate stock allowed for subsequent successful runs and the ability to vary parameters such as power level from the microwave generator and flow rate of the aerosol gas.

In the plasma, the zinc nitrate was expected to fully decompose and form ZnO . Figure 35 shows the natural decomposition of the raw material in the STA.

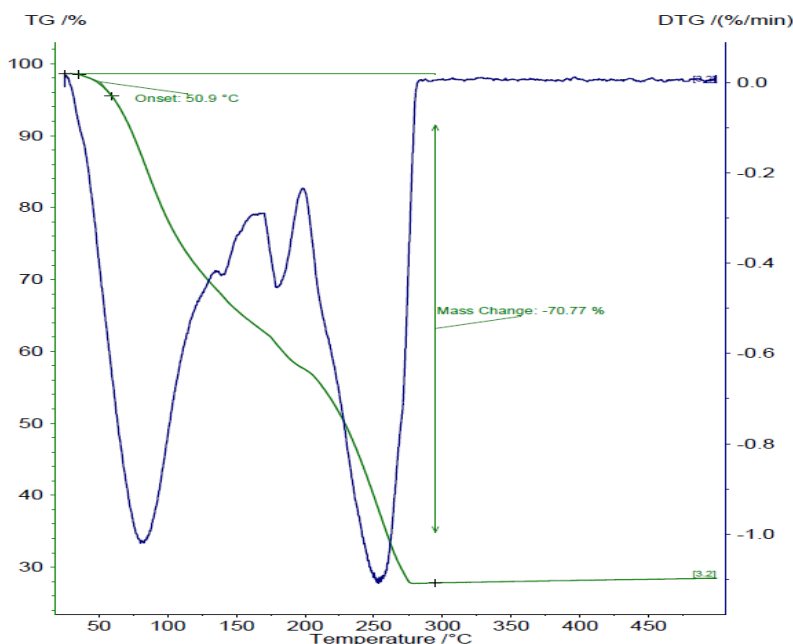


Figure 35. Zinc nitrate decomposition in the STA

The total mass loss of 70.77% corresponds to removal of the 5 H₂O molecules which begins at 50.9°C and is complete at 100°C. Following the removal of water is a period of volatility as the NO₃ begins to decompose and simultaneously the zinc oxidizes and becomes ZnO. This process fully completes by 300°C. The hot zone of the plasma reaches temperatures upwards of 3200°C [10] and thus easily and rapidly decomposes zinc nitrate into ZnO and, as indicated by the results below, has potential to be tailorable.

The XRD pattern for zinc nitrate as acquired is shown in Figure 36, and the XRD pattern for zinc nitrate decomposed by the STA, as shown in Figure 37, indicates that the sample fully converts to hexagonal wurtzite ZnO (PDF card 00-036-1451).

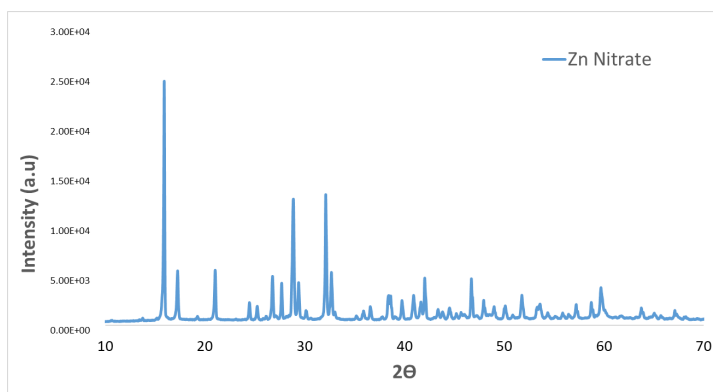


Figure 36. Zinc Nitrate XRD response prior to A-T-P

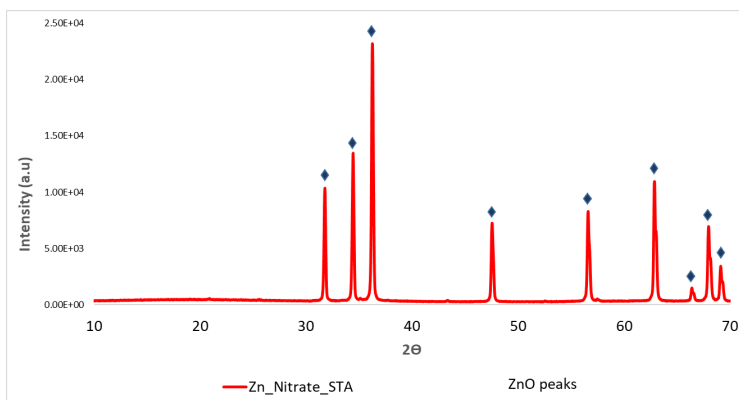


Figure 37. XRD pattern for zinc nitrate decomposed in the STA

2. Plasma Products

a. XRD Results

XRD results are shown in Figure 38 for zinc nitrate as a precursor passed through the plasma. Also, overlaid in the plot is the data for zinc as a precursor. As shown, the difference of using zinc versus zinc nitrate is that the former presents still a few peaks that correspond to zinc metal while the nitrate precursor renders only ZnO. The zinc nitrate seems to have completely oxidized and changed to hexagonal wurtzite ZnO (PDF card 00-036-1451).

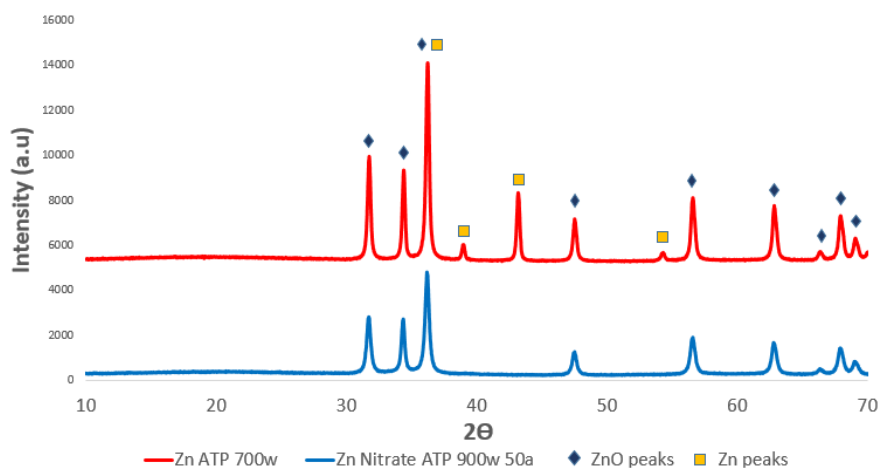


Figure 38. XRD results for zinc nitrate as a precursor run through the plasma at 900 W shown with ZnO and zinc peaks as well as zinc as a precursor

b. Effect of Power Level in Microwave Generator

Figures 39-41 show images captured at 200x, 10,000x, and 25,000x magnification for plasma runs at power levels of 700, 800 and 900 watts. Similar to the results seen with zinc as a precursor, at 200x magnification all of the images exhibit a fine and mostly homogenous powder. In contrast, from the zinc as a precursor however, spherical particles of size from 20-40 microns appear in the 800 and 900 watt runs.

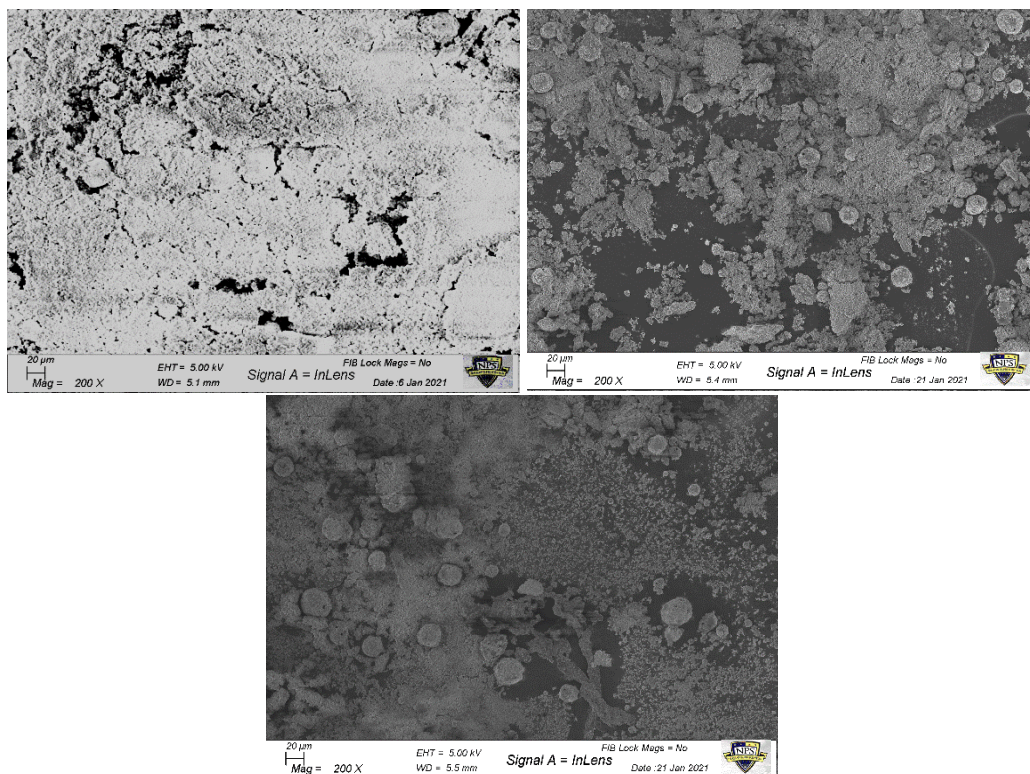


Figure 39. Zinc nitrate as a precursor run through the plasma at 700 W (top left), 800 W (top right), and 900 W (bottom) at 200x magnification collected in the filter

Upon increasing the magnification to 10,000x, it is evident that the particles from the 700 watt run become entirely flake-like similar to the flakes seen when zinc was the precursor. In the samples from the 800 and 900 watt runs nanometric particles can be seen as well as agglomerates of them. Further increasing of the magnification to 25,000x reveals that the spheres seen at 200x magnification are agglomerates of nanometric spherical particles. There is little to no evidence of the needle-like rods or combinations of needle-like rods and spherical particles such as in the zinc precursor results, and all of the particles appear to be smooth objects of nanometric size randomly agglomerated or agglomerated into large spheres. Circled in purple is proof of the hypothesis that via the A-T-P method nanometric sized spheres of ZnO could be produced (Figure 41).

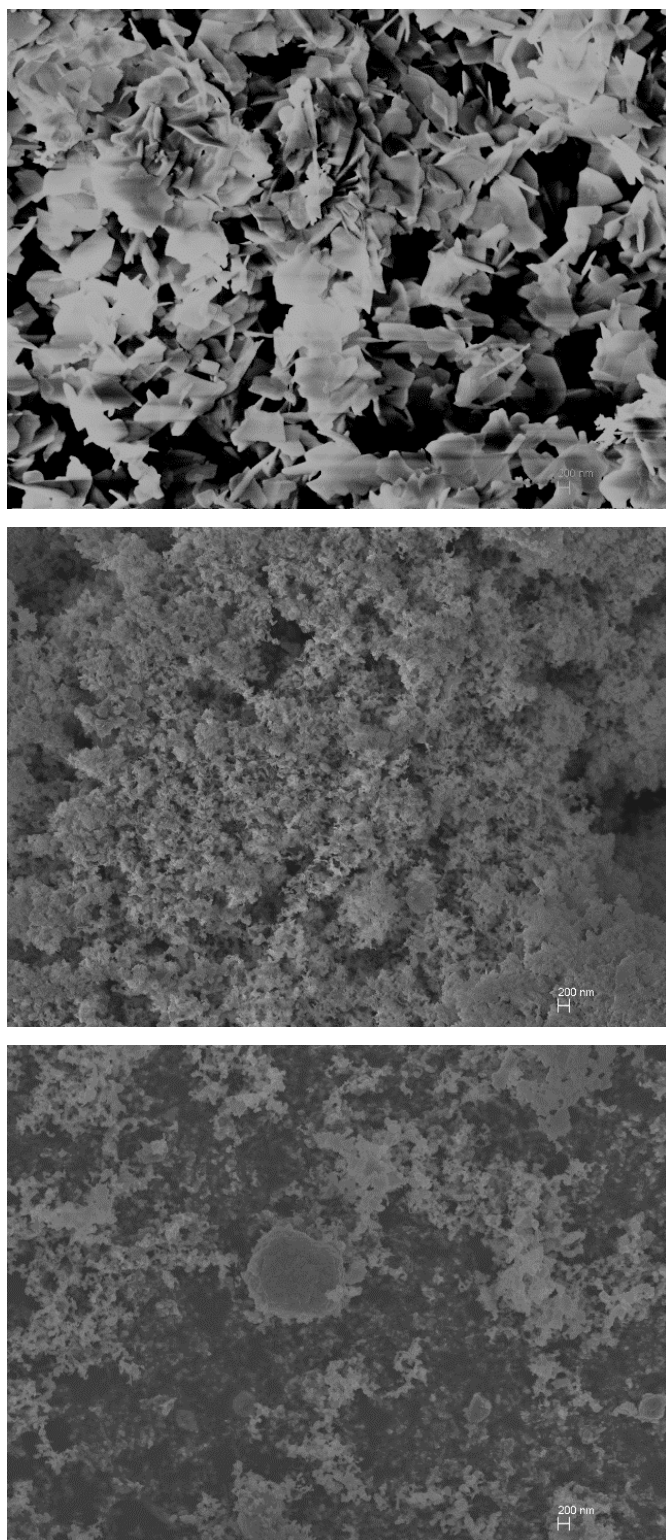


Figure 40. Zinc nitrate as a precursor run through the plasma at 700 W (top left), 800 W (top right), and 900 W (bottom) at 10,000x magnification collected in the filter

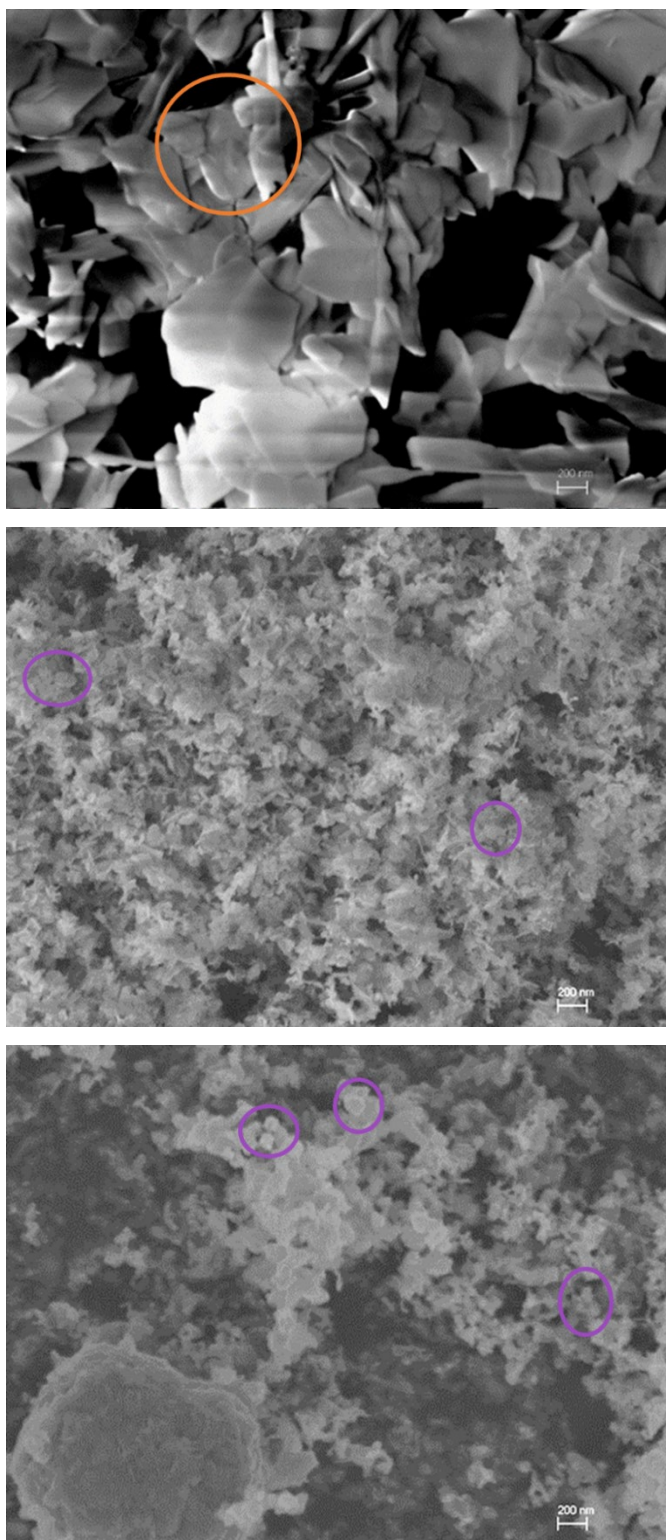


Figure 41. Zinc nitrate as a precursor run through the plasma at 700 W (top), 800 W (middle), and 900 W (bottom) at 25,000x magnification collected in the filter

Particle size distributions for 700, 800, and 900 watts are shown in Figure 42.

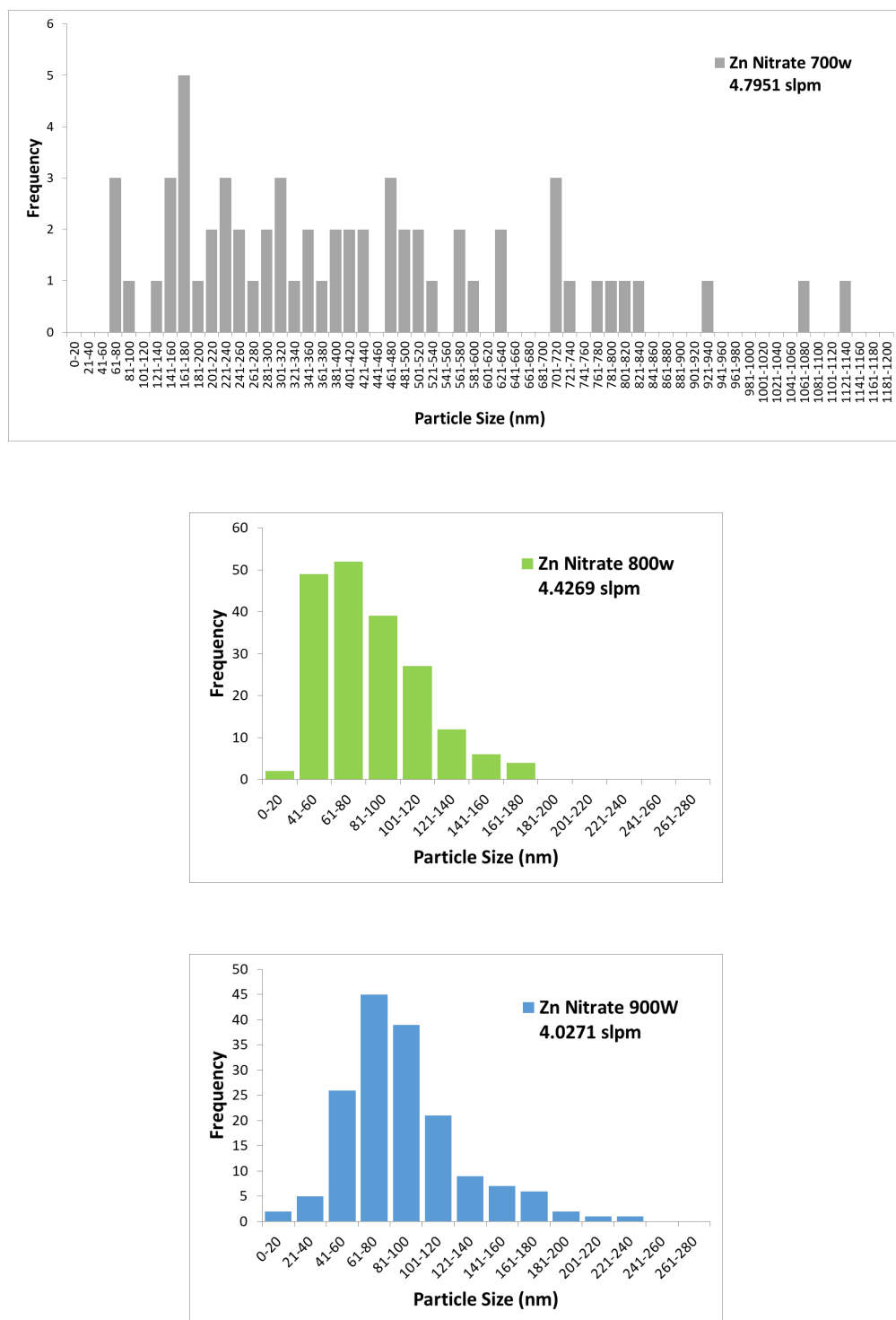


Figure 42. Particle Size distribution for zinc nitrate as a precursor collected from the filter

The mean, median and mode for these experiments are provided in Table 3.

Table 3. Zinc nitrate as a precursor particle size analysis summary

	Mean (nm)	Median (nm)	Mode (nm)
700 W (4.7951 slpm) Chimney			
700 W (4.7951 slpm) Filter	414.23	370.37	None
800 W (4.4269 slpm) Chimney	69.76	63.64	55.04
800 W (4.4269 slpm) Filter	77.76	72.47	54.86
900 W (4.0271 slpm) Chimney			
900 W (4.0271 slpm) Filter	88.22	82.23	84.13
900 W (2.6463 slpm) Filter	51.09	45.69	48.40

c. Influence of Flow Rate

Zinc nitrate as a precursor produced promising results such as nanometric spheres. The plasma runs at 900 watts for zinc nitrate as a precursor also appeared to completely eliminate any needle-like rod growth and thus zinc nitrate at 900 watts became the subject of further parametric studies including the variation of aerosol flow rates. To alter the aerosol flow rates the argon gas flow was changed on the flowmeter after stability was reached in the plasma system. Shown in Figures 43-45 are SEM images of plasma runs for 900 watts at 2.6463 slpm and 4.027 slpm at 200x, 10,000x, and 25,000x magnification. At 200x magnification (Figure 43), more micron sized spheres appear with a higher flow rate.

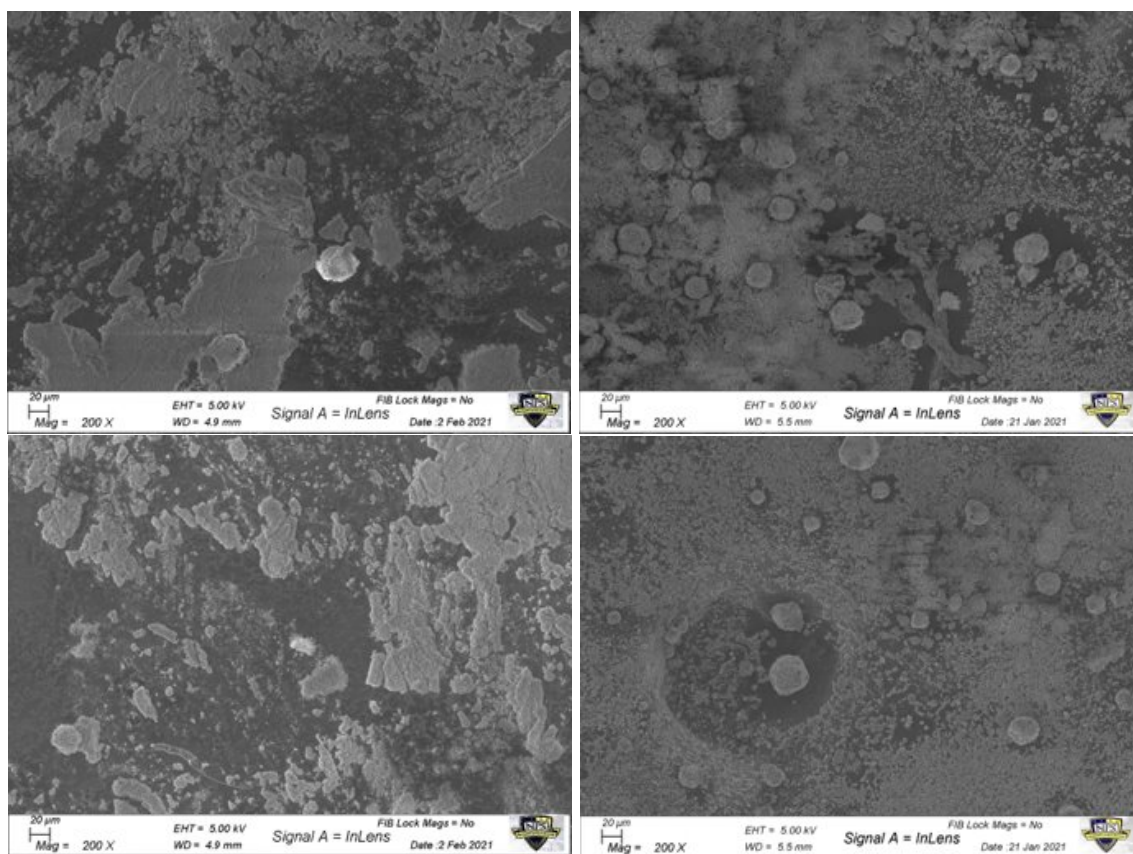


Figure 43. Zinc nitrate as a precursor at 900 W at aerosol flow rates of 2.6463 slpm (left) and 4.0271 slpm (right) at 200x magnification

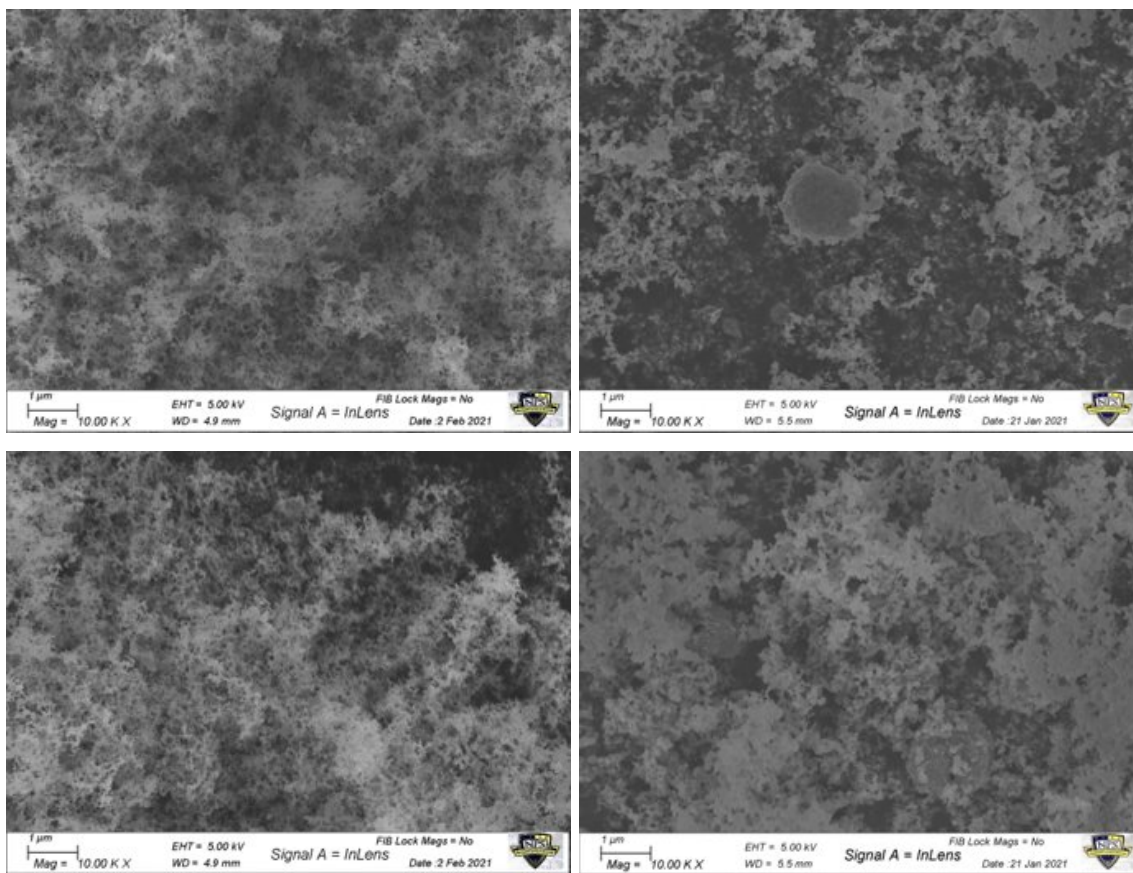


Figure 44. Zinc nitrate as a precursor at 900 W at aerosol flow rates of 2.6463 slpm (left) and 4.0271 slpm (right) at 10,000x magnification

The lower aerosol flow rate has lower particle size evidenced also by the particle size analysis later mentioned. However, the particles are not easily distinguishable from one another and the evidence of more spheres appears in the higher flow rate.

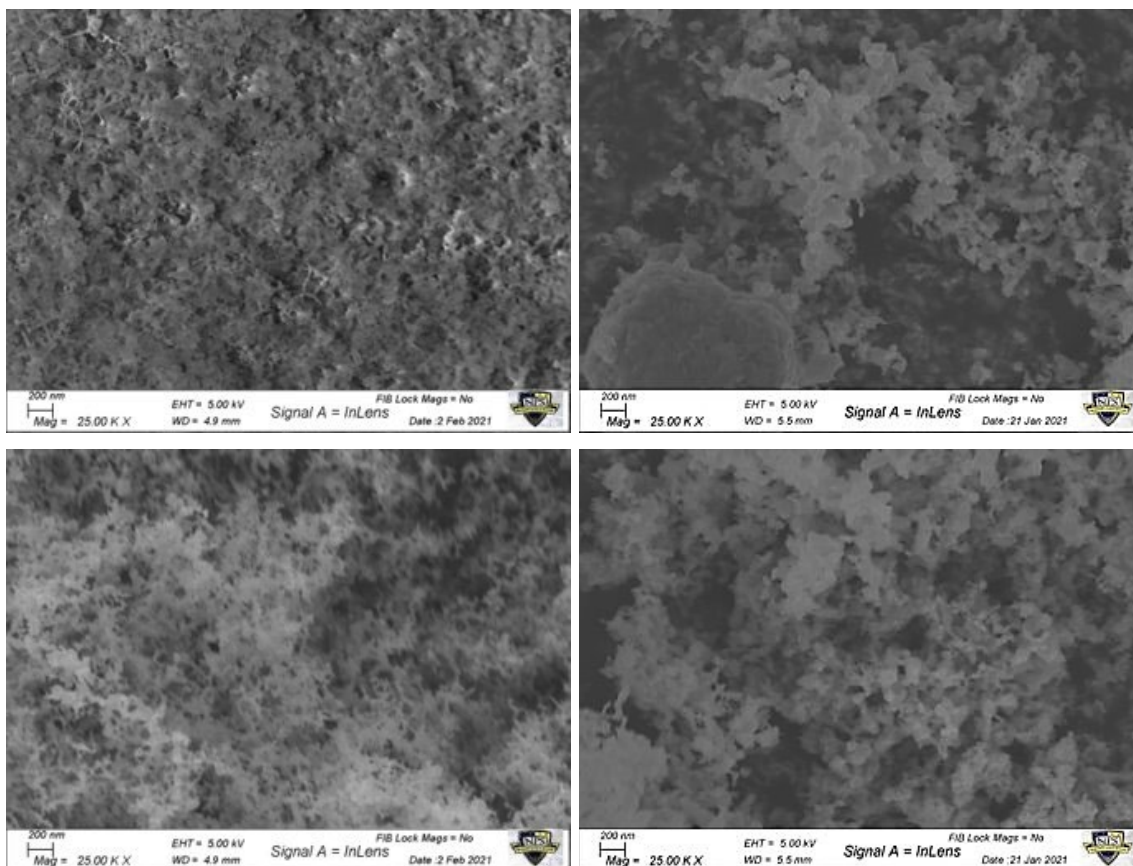


Figure 45. Zinc nitrate as a precursor at 900 W at aerosol flow rates of 2.6463 slpm (left) and 4.0271 slpm (right) at 25,000x magnification

Figure 46 displays the results for the particle size distribution for the varying flow rates at 900 watts. In support of the SEM images, the particle size analysis shows that the lower aerosol rate had a reduced particle size. However, there were less distinguishable spheres, which suggests that there could be a flow rate in between 2.6463 slpm and 4.0271 slpm where smaller yet, distinguishable nanometric spheres could be produced.

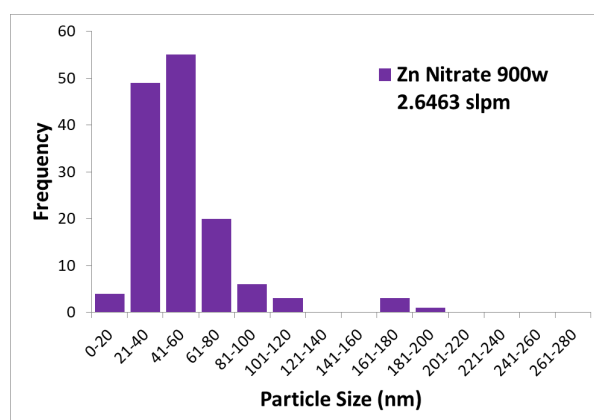
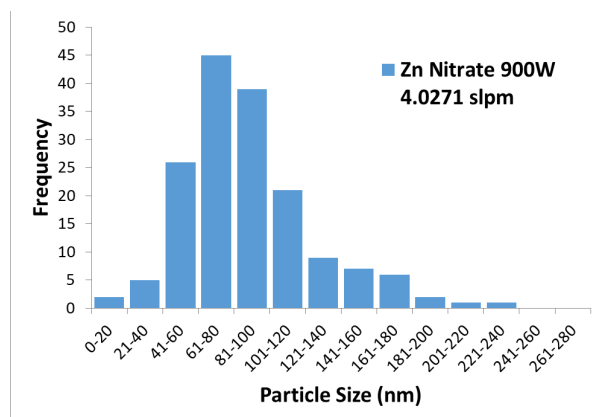


Figure 46. Particle Size breakdown for zinc nitrate as a precursor collected from the filter

d. Additional Evidence of Spherical Particles

The plasma run with the strongest evidence of affirming the hypothesis had the following parameters: zinc nitrate as a precursor, run at 800 watts with an aerosol flow rate of 4.4269 slpm. These particles were collected in the chimney. Figures 47 and 48 show the SEM images at a 200x magnification and at a 25,000x magnification, respectively. Figure 48 shows that the spheres of sizes 5-15 microns seen at low magnification are agglomerates and the result of sintering nanometric spheres of sizes 10-100 nm.

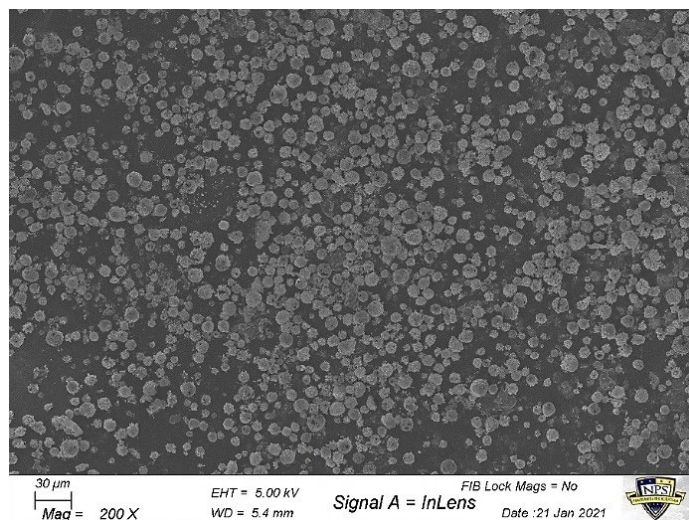


Figure 47. Zinc nitrate as a precursor at 800 W, 4.4269 slpm aerosol flow collected in the chimney. Evidence of spherical particles captured at lower magnification

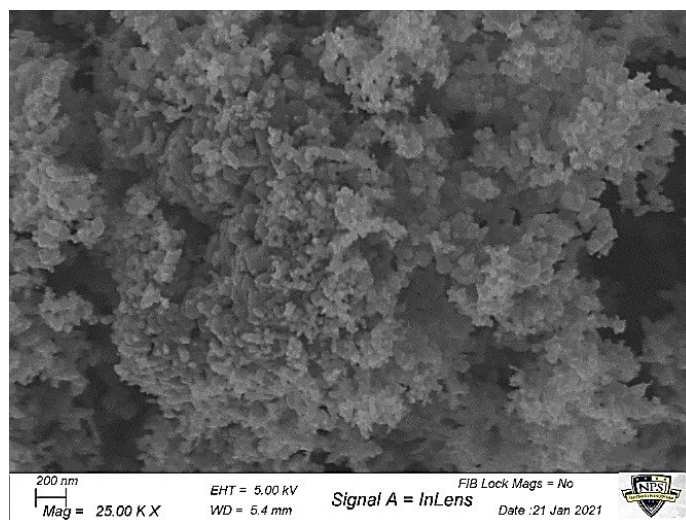


Figure 48. Zinc nitrate as a precursor at 800 W, 4.4269 slpm aerosol flow collected in the chimney at higher magnification showing agglomerates of nanometric spheres

3. Summary of Using Zinc Nitrate As a Precursor

Zinc nitrate was a feasible precursor for the A-T-P method if the sample had not absorbed too much moisture and was ground into a powder. In the plasma the powder fully decomposes into ZnO. Three distinct shapes appeared when zinc nitrate was used: flakes,

spheres or spherical growths with needle-like growths outward. These shapes were similar to those that appeared for zinc as a precursor, however, the stand alone needle-like rods were not present and the outward growths were much less drastic ranging only a few nanometers in length compared to 100-350 nm lengths present with zinc. The spheres that were seen were of nanometric size as small as 20 nm. Larger spheres as large as 8 microns were agglomerates of smaller spheres.

Overall, the particle size for plasma products of zinc nitrate as a precursor were smaller than that of zinc. For a power level of 800 watts the average particle size was 77.76 nm for particles collected in the filter compared to 131.27 nm for zinc for the same power level. For a power level of 900 watts a similar result was seen with an average of 88.22 nm for filter particles with zinc nitrate as a precursor and 180.40 nm for zinc as a precursor.

Varying the flow rates of the aerosol stream resulted in a lower average particle size (51.09 nm compared to 88.22 nm) for the lower flow rate. However, the higher flow rate produced more easily distinguishable spheres.

C. ADDITIONAL PRECURSORS OF INTEREST

In addition to the zinc powder and zinc nitrate powder precursors used, the sponsor of this work provided five additional precursors for future work: calcium sulfate, calcium nitrate, calcium lanthanum sulfide, lanthanum nitrate, and zinc sulfide. These were all solid powder or small crystalline samples.

XRD analysis was performed on these samples as a baseline for future plasma synthesis using them as precursors.

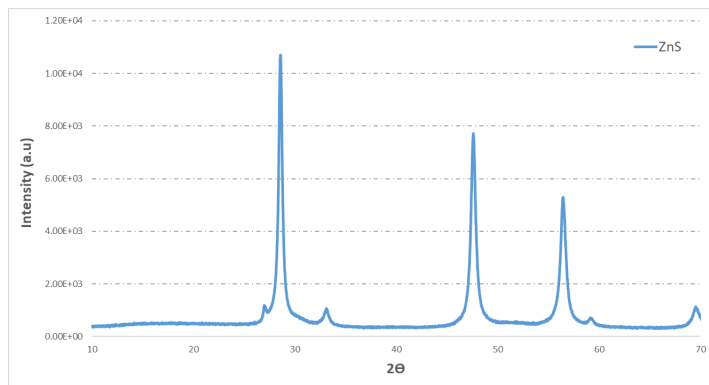


Figure 49. XRD results for ZnS

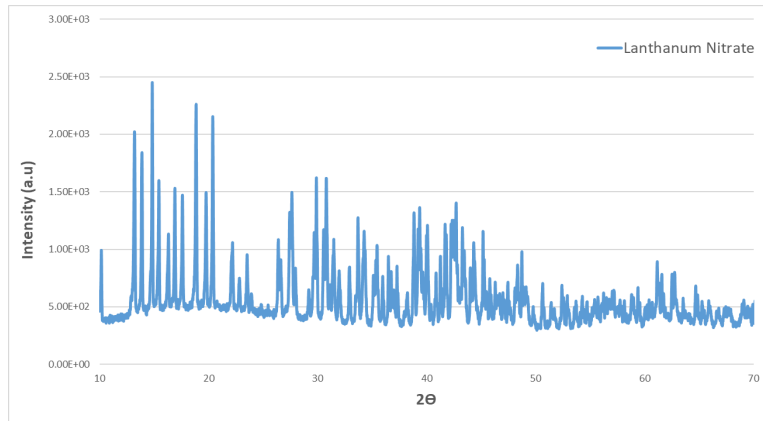


Figure 50. XRD results for lanthanum sulfide

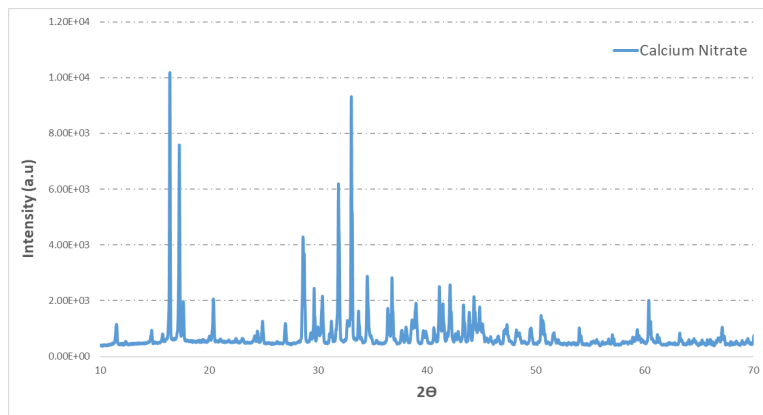


Figure 51. XRD results for calcium nitrate

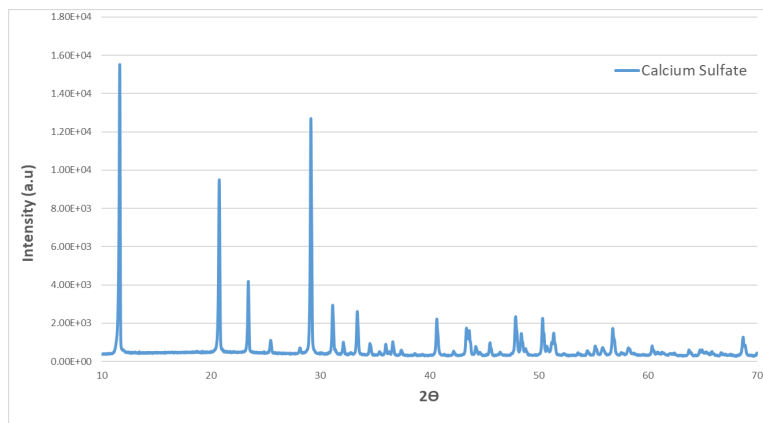


Figure 52. XRD for calcium sulfate

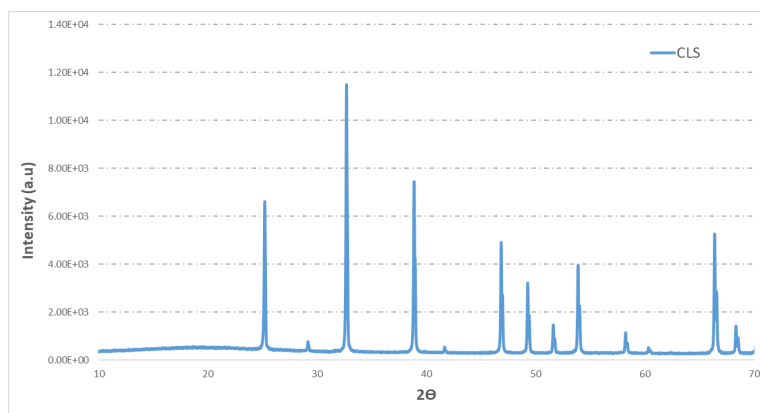


Figure 53. XRD results for CaLa₂S₄

This diffraction data will act as the baseline for the precursor powders. With the achievement of being able to produce spherical ZnO, the process can continue to be refined to produce more uniform yields, larger yields and spheres of desirable size. Then, work could be done to move on from ZnO to materials that could exhibit better material and mechanical properties for the same applications but that would also require nanometric spheres.

D. DISCUSSION OF LITERATURE

ZnO can be produced by a multitude of different methods to include hydrothermal decomposition, solid-state pyrolytic reactions, precipitation, aerosol spray pyrolysis, microwave and ultrasonics combined, and thermal decomposition of zinc acetate [7, 8, 21, 22]. These other methods compared to the A-T-P method implemented in this thesis work exhibit the same advantages however can be subjected to certain disadvantages not experienced through the A-T-P method. The particles produced from zinc as a precursor (spheres, needle-like rods, a combination of the two and flake like particles) and from zinc nitrate as a precursor (nanometric and micron spheres, combinations of spheres with needle-like growths, and flakes) are seen in other production methods as well [8, 9, 22]. In some of these methods, such as solid-state pyrolytic reaction, microwave-hydrothermal processes, and facile microwave/ultrasonic fabrication, the synthesis techniques are tailorable to achieve specific shapes and sizes [8, 21, 9]. In other techniques, such as

standard or traditional high temperature solid state methods [7], spray pyrolysis, and standard hydrothermal methods [21], the final form of the ZnO particles is less tailorable.

By manipulating parameters of the A-T-P method, changes in particle size and shape were observed. The ability to control operating parameters such as the precursor used, the power level of the microwave generator, the flow rate of the aerosol gas and plasma gas, and the type of carrier gas implemented to create the aerosol stream will enable the tailor-ability of shape, size and composition as evidenced by the results in this thesis. The needle-like rods and growths observed in this work may not have immediate application in the sulfurizing and subsequent sintering of the ceramic particles; however, there could be various other applications such as explored by the work of Li et al. [9]. The nanometric and micron spheres produced in this work confirm the hypothesis and could easily be sulfurized and subsequently sintered and processed to bulk form for forward looking infrared optics and transparent ceramic windows [1].

IV. CONCLUSIONS

In this thesis an A-T-P method was used to take zinc and zinc nitrate, decompose and oxidize them into ZnO. The post plasma products were then characterized by XRD to confirm that hexagonal wurtzite ZnO was formed. The plasma products were also characterized in the SEM to analysis shape and size. A study was completed comparing power levels for each precursor. An additional study was completed to look at the effect of aerosol flow rate for the zinc nitrate precursor.

In sum, XRD patterns of the post plasma products showed that hexagonal wurtzite ZnO was formed for both precursors. The zinc precursors had XRD patterns with residual zinc that did not oxidize; however, the zinc nitrate precursor had fully converted to ZnO and exhibited no additional diffraction peaks. Other parameters such as aerosol flow rate nor power level had an impact on the XRD pattern of the plasma products for either precursor.

Using zinc powder as a precursor for the A-T-P method was feasible as long as the particle size of the precursor powder was reduced. In the plasma, the zinc was converted to ZnO particles of four distinct shapes: spheres, needle-like rods, spheres with needle-like growths outward, and large flakes. Of the three power levels run for zinc the power level of 800 watts had the smallest average particle size (131.27 nm in the filter and 142.73 nm in the chimney). Furthermore, the SEM results for 800 watts showed evidence of spherical particles, or spherical particles with growths; however, there was little to no indication of single needle-like rods.

Zinc nitrate was also a feasible precursor for the A-T-P method if the sample had not absorbed too much moisture and was ground into a powder. Three distinct shapes appeared when zinc nitrate was used: flakes, spheres or spherical growths with needle-like growths outward. The needle-like outward growths seen were much less drastic than the zinc plasma products ranging only a few nanometers in length compared to 100-350 nm lengths present with zinc. Micron and nanometric spheres were seen for power levels of 800 and 900 watts. Overall, the particle size for plasma products of zinc nitrate as a

precursor were smaller than that of zinc. Varying the flow rates of the aerosol stream resulted in a lower average particle size (51.09 nm compared to 88.22 nm) for the lower flow rate. However, the higher flow rate produced more easily distinguishable spheres.

ZnO is an invaluable material used in a multitude of different applications. Many production methods exist to produce ZnO with ideal geometries, sizes, material and mechanical properties for specific applications. Sulfurization of ZnO into ZnS in order to create transparent windows and domes with desirable transmission and mechanical properties is one application with ongoing research efforts. This research sought to find a production method for spherical and nanometric ZnO that could easily be sulfurized and then sintered into such windows and domes. This thesis confirms the hypothesis that the use of an Aerosol-Through-Plasma method, adequate precursors, and appropriate parameters will allow for the synthesis of nanometric and spherical ZnO particulates.

For follow on research, results suggest that zinc nitrate is an adequate precursor and that there is potentially a balance between power and aerosol flow rate to achieve the correct size and shape particles. When the formation of nanometric spherical ZnO is refined enough, attempts could be to introduce sulfur into the environment. This could be in a furnace after the ZnO has been produced via the A-T-P method or directly in the A-T-P method as the carrier gas combining with the precursor to form the aerosol. For the objective applications, ZnS is the current industry standard [1]; however, one question for future work would be if sulfur is introduced into the A-T-P method are the resulting particulates produced still spherical and of the same size as seen in this thesis work? Furthermore, are they purged of the oxygen and ZnS is present vice ZnO? Moreover, attempts could be made to oxidize the additional precursors listed in Chapter III and investigate the shapes caused by the A-T-P method.

APPENDIX A. SOP FOR THE PLASMA SYSTEM

Operation of the plasma system requires the use of ultraviolet protective glasses, high temperature gloves or mittens to handle the chimney and any tasks near the hot zone, a lab coat and ear plugs. The following procedure was followed for each plasma run.

- a. *The chiller was powered on and set to 10°C*
- b. *The MKS pressure controller, vibration source, and vacuum pump, were powered on.*
- c. *Start the plasma gas flow. For this thesis, UHP argon gas was used for the plasma flow. The flow was adjusted to about 20 psi and then controlled by a Matheson Gas rotameter flow meter (604) shown in Figure 54*



Figure 54. Analog flow meter controls

- d. *The fume hood was powered on*
- e. *The microwave power generator was powered on*
- f. *The plasma was started (via striking with a metal tip if necessary)*
- g. *The smart match interface was used to reduce the reflected watts to minimum accepted values*

- h. The chimney was directed to the filter assembly and slowly closed as the MKS controller approaches a pressure near (10 psi below) atmospheric pressure*
- i. With the plasma system stable the aerosol flow is opened and adjusted using a flowmeter (603) shown in Figure 54*

In order to turn off the plasma system:

- j. The vibration source, and the aerosol gas were powered off*
- k. The chimney was opened*
- l. The MKS controller was set to close*
- m. The power generator was turned off, the system was allowed to cool for 15 minutes*
- n. Lastly the plasma gas, chiller, fume hood, and vacuum pump were turned off*

APPENDIX B. MATHESON ROTAMETER CALIBRATION DATA

For a complete library of rotameter calibration data, visit:
<http://www.matheson-gas.com/gas-handling/rotameter-FAQ>



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 Montgomeryville, PA 18936
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www.matheson-gas.com

UNITS : SLPM ARGON DATE : 02-01-79
 TUBE NUMBER : 604 (E700) STD CONDITIONS : 1 ATMOS. 670 DEG F
 SERIAL NUMBER : TYPICAL GAS TEMPERATURE : 70 DEG F
 FLOAT MATERIAL: 316 ST. STL. PRESSURE IN TUBE : 20 PSIG

E703AR20.DAT

SCALE READING	FLOW RATE	SCALE READING	FLOW RATE	SCALE READING	FLOW RATE	SCALE READING	FLOW RATE
150.0	22.09	110.0	16.44	70.0	10.44	30.0	4.41
149.0	21.96	109.0	16.29	69.0	10.29	29.0	4.26
148.0	21.83	108.0	16.14	68.0	10.14	28.0	4.11
147.0	21.69	107.0	16.00	67.0	9.99	27.0	3.96
146.0	21.56	106.0	15.85	66.0	9.84	26.0	3.80
145.0	21.43	105.0	15.70	65.0	9.69	25.0	3.65
144.0	21.29	104.0	15.55	64.0	9.54	24.0	3.50
143.0	21.16	103.0	15.40	63.0	9.39	23.0	3.35
142.0	21.02	102.0	15.25	62.0	9.24	22.0	3.19
141.0	20.89	101.0	15.10	61.0	9.09	21.0	3.04
140.0	20.75	100.0	14.95	60.0	8.94	20.0	2.89
139.0	20.61	99.0	14.80	59.0	8.79	19.0	2.73
138.0	20.47	98.0	14.65	58.0	8.64	18.0	2.58
137.0	20.33	97.0	14.50	57.0	8.49	17.0	2.42
136.0	20.20	96.0	14.35	56.0	8.34	16.0	2.27
135.0	20.06	95.0	14.20	55.0	8.19	15.0	2.12
134.0	19.92	94.0	14.05	54.0	8.03	14.0	1.96
133.0	19.78	93.0	13.90	53.0	7.88	13.0	1.80
132.0	19.63	92.0	13.75	52.0	7.73	12.0	1.65
131.0	19.49	91.0	13.60	51.0	7.58	11.0	1.49
130.0	19.35	90.0	13.45	50.0	7.43	10.0	1.34
129.0	19.21	89.0	13.30	49.0	7.28	9.0	1.18
128.0	19.07	88.0	13.15	48.0	7.13	8.0	1.02
127.0	18.92	87.0	13.00	47.0	6.98	7.0	0.87
126.0	18.78	86.0	12.85	46.0	6.83	6.0	0.71
125.0	18.64	85.0	12.70	45.0	6.68	5.0	0.55
124.0	18.49	84.0	12.55	44.0	6.53		
123.0	18.35	83.0	12.40	43.0	6.38		
122.0	18.20	82.0	12.25	42.0	6.23		
121.0	18.06	81.0	12.10	41.0	6.08		
120.0	17.91	80.0	11.95	40.0	5.93		
119.0	17.77	79.0	11.80	39.0	5.78		
118.0	17.62	78.0	11.65	38.0	5.62		
117.0	17.47	77.0	11.50	37.0	5.47		
116.0	17.33	76.0	11.35	36.0	5.32		
115.0	17.18	75.0	11.20	35.0	5.17		
114.0	17.03	74.0	11.04	34.0	5.02		
113.0	16.88	73.0	10.89	33.0	4.87		
112.0	16.74	72.0	10.74	32.0	4.72		
111.0	16.59	71.0	10.59	31.0	4.56		

For a complete library of rotameter calibration data, visit:
<http://www.mathesongas.com/gas-handling/rotameter-FAQ>



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UNITS	: SLPK ARGON	DATE	: 12-12-1991
TUBE NUMBER	: 603(E500) TYPICAL	STD CONDITIONS	: 1 ATMOS. & 70 DEG F
FLOAT NUMBER	: 002	GAS TEMPERATURE	: 70 DEG F
FLOAT MATERIAL	: 316 ST. STL.	PRESSURE IN TUBE	: 20 PSIG

SCALE READING	FLOW RATE	SCALE READING	FLOW RATE	SCALE READING	FLOW RATE	SCALE READING	FLOW RATE
150.0	6.2883	110.0	5.1334	70.0	3.5956	30.0	1.6149
149.0	6.2608	109.0	5.1008	69.0	3.5507	29.0	1.5622
148.0	6.2334	108.0	5.0679	68.0	3.5056	28.0	1.5095
147.0	6.2061	107.0	5.0348	67.0	3.4602	27.0	1.4567
146.0	6.1787	106.0	5.0014	66.0	3.4144	26.0	1.4039
145.0	6.1514	105.0	4.9678	65.0	3.3684	25.0	1.3512
144.0	6.1241	104.0	4.9338	64.0	3.3221	24.0	1.2984
143.0	6.0968	103.0	4.8995	63.0	3.2755	23.0	1.2456
142.0	6.0695	102.0	4.8650	62.0	3.2287	22.0	1.1929
141.0	6.0422	101.0	4.8302	61.0	3.1815	21.0	1.1402
140.0	6.0148	100.0	4.7951	60.0	3.1341	20.0	1.0875
139.0	5.9873	99.0	4.7596	59.0	3.0864	19.0	1.0349
138.0	5.9599	98.0	4.7239	58.0	3.0385	18.0	0.9824
137.0	5.9323	97.0	4.6879	57.0	2.9903	17.0	0.9299
136.0	5.9047	96.0	4.6515	56.0	2.9419	16.0	0.8776
135.0	5.8770	95.0	4.6149	55.0	2.8932	15.0	0.8253
134.0	5.8492	94.0	4.5779	54.0	2.8443	14.0	0.7732
133.0	5.8213	93.0	4.5407	53.0	2.7951	13.0	0.7212
132.0	5.7933	92.0	4.5031	52.0	2.7457	12.0	0.6694
131.0	5.7651	91.0	4.4652	51.0	2.6961	11.0	0.6177
130.0	5.7369	90.0	4.4269	50.0	2.6463	10.0	0.5662
129.0	5.7085	89.0	4.3884	49.0	2.5962	9.0	0.5148
128.0	5.6799	88.0	4.3495	48.0	2.5460	8.0	0.4637
127.0	5.6512	87.0	4.3104	47.0	2.4956	7.0	0.4128
126.0	5.6224	86.0	4.2709	46.0	2.4449	6.0	0.3621
125.0	5.5933	85.0	4.2310	45.0	2.3941	5.0	0.3116
124.0	5.5642	84.0	4.1909	44.0	2.3431		
123.0	5.5348	83.0	4.1504	43.0	2.2919		
122.0	5.5052	82.0	4.1096	42.0	2.2406		
121.0	5.4754	81.0	4.0685	41.0	2.1891		
120.0	5.4455	80.0	4.0271	40.0	2.1375		
119.0	5.4153	79.0	3.9854	39.0	2.0857		
118.0	5.3849	78.0	3.9433	38.0	2.0338		
117.0	5.3543	77.0	3.9009	37.0	1.9818		
116.0	5.3235	76.0	3.8583	36.0	1.9296		
115.0	5.2924	75.0	3.8152	35.0	1.8774		
114.0	5.2611	74.0	3.7719	34.0	1.8250		
113.0	5.2295	73.0	3.7283	33.0	1.7726		
112.0	5.1977	72.0	3.6844	32.0	1.7201		
111.0	5.1657	71.0	3.6401	31.0	1.6675		

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