OPTIMIZING ELECTROSPUN CERAMIC NANOFIBER STRENGTH THROUGH TWO-STEP SINTERING

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by
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1 Abstract

Two-step sintering (TSS) consists of a high-temperature step and immediate cooling to a sintering temperature for an extended sintering time, where grain growth is suppressed by severe densification during the high-temperature step. TSS is adopted to enhance mechanical properties of electrospun ceramic nanofibers (CNFs), a class of porous ceramics used for environmental remediation, optoelectronics, and filtration. PVP and Ga(NO$_3$)$_3$ nanofiber mesh, provided by Lawrence Livermore National Laboratory, was shaped, oxidized, and two-step sintered to form a nanocrystalline $\beta$-Ga$_2$O$_3$ CNF tube using a high-temperature step of 1,000°C. Sintering temperatures and times varied from 625°C to 875°C for 1 hour to 4 hours. A minimum sample size of 26 tubes from each heat treatment were diametrally compressed and compared, with Weibull statistics, to isothermally sintered tubes, treated at 1,000°C for 1 hour with an average yield strength of 3.36 kPa. CNFs exhibit a pseudo-plastic transition from brittle to cellular stress-strain behavior, resulting from successive brittle fiber failures and pore crushing. TSS successfully strengthens the CNF tubes to an average yield strength of 5.72 kPa with a 2 hour, 875°C sintering. X-ray diffraction (XRD) crystallite measurements and scanning electron microscopy (SEM) showed that TSS suppressed grain growth and formed a nanocrystalline microstructure. Further SEM image processing revealed yield stress is negatively correlated with porosity, fiber diameter, and tube diameter.
2 INTRODUCTION

Lawrence Livermore National Laboratory has employed a team of student engineers from California Polytechnic State University, San Luis Obispo to facilitate automated or semi-automated tooling for electrospun polymer-ceramic nanofiber mesh manipulation. The tooling forms the mesh into tubes, specified to diameters between 6 and 12 millimeters and a length equal to 15 millimeters. During production, the mesh material consists of a polymer and a ceramic precursor. The mesh must go through a final heat treatment step to decompose present organic matter and oxidize the ceramic precursor to form the ceramic oxide; this is calcination, or heating at an elevated temperature for a specified time in air, and fiber properties are determined by the degree of sintering and the resulting microstructure. This report deals with sintering optimization for the strongest ceramic nanofiber tube given a 12 millimeter diameter, 15 millimeter tall precursor mesh tube.

2.1 Problem Statement

LLNL is sponsoring an investigation into optimizing sintering parameters for strength in electrospun beta gallium (III) oxide [$\beta$-Ga$_2$O$_3$] nanofiber tubes from the polymer-ceramic precursor, polyvinylpyrrolidone [PVP] and gallium nitrate [Ga(NO$_3$)$_3$]. Maximum mesh strength will be achieved through defect removal, minimizing grain growth, and maximizing densification. Conclusions will be drawn by statistically modeling strength as a function of sintering temperature and time using Weibull statistics.

2.2 Stakeholders

Ceramic nanofiber electrospinning, shaping, and sintering is slow, taking upwards of 16 hours to process a single mesh. The experiment should cater to the needs of LLNL by refining production efficiency and elucidating processing and strengthening relationships. Any producer of these materials can benefit from the automated tooling, given a tubular geometry requirement. The connection between ceramic nanofiber sintering characteristics and strengthening will be valuable to producing implementable materials given a design strength criteria. The Materials Engineering Department at Cal Poly welcomes involvement in cutting-edge, nanotechnology research and a working relationship with Lawrence Livermore National Laboratory.
3 BACKGROUND

Ceramics are inorganic and non-metallic, crystalline materials, characterized by high strength, brittleness, and temperature resistance. Silica [SiO$_2$], or sand, is a ceramic and one of the most abundant materials on Earth. It is the building block of glassy materials and many precious gemstones like quartz, olivine, and garnet. Other non-technical ceramic materials have been used for thousands of years in the form of pottery and other whiteware like porcelain, while technical ceramics find uses ranging from furnace linings to turbocharger rotors to composite fibers. Technical ceramic fibers are strong, stiff, and corrosion resistant at high temperatures, but suffer from low strain-to-failure due to crystalline imperfections such as pores, impurities, and electrical defects [1]. Many processing techniques exist for producing ceramic fibers with diameters on the micron scale, such as chemical vapor deposition (CVD) for silicon carbide [SiC] integrated circuitry, melt spinning for insulating wool used in petrochemical and automotive industries, and sol-gel methods for alumina [Al$_2$O$_3$] composite fibers [2-4]. Large diameter ceramic fibers are easily fractured and potentially hazardous when unbound. Safety precautions and exposure limits are set in place when fabricating and characterizing such materials. Electrospinning and subsequent thermal treatment is the simplest procedure for open-cell structured and bounded ceramic nanofiber (CNF) mesh production [5]. With high surface to volume ratios, aspect ratios greater than 1,000, and fiber diameters less than 100 nm, CNFs have unique properties catered to nanoscale engineering applications in microelectromechanical systems (MEMS), fluid and gas purification, biological scaffolding, and drug delivery devices [6].

3.1 Electrospun Ceramic Nanofibers

Ceramic materials are refractory, with melting temperatures greater than 1,000°F. To spin a fiber, the material must be viscous enough to be extruded through a syringe or spinneret. Because ceramic materials are only viscous at severe temperatures, achieving sub-micron ceramic fiber diameters requires a roundabout processing technique involving electrospinning a viscous polymer, solvent, and ceramic precursor solution and subsequent thermal conversion to decompose the organic polymer and transform the ceramic precursor to a nanocrystalline ceramic material.
3.1 Electrospun Ceramic Nanofibers

3.1.1 Processing

Electrospinning is a simple, yet power-intensive and slow process to fabricate nanofiber meshes. An electrospinning apparatus consists of a power supply, a pump dispensing the polymer-solvent-precursor solution, an extruding needle or syringe, and a collector plate or drum (Figure 1).

Figure 1: Schematic drawing of an electrospinning experimental set-up [6].

An electric potential (∼10s of kV) is applied to a ceramic-polymer-solvent solution, producing strong molecular repulsion. Using a pump with a flow rate on the order of microliters per hour, solution is drawn out of a syringe tip into an electric field between the grounded or negatively charged collector plate and biased solution. The solvent evaporates from the solution until landing on the collector in fibrous form. The result is a pre-ceramic polymer nanofiber mesh which takes about 8 hours to produce one sheet of material. There are many advantages to electrospinning, mainly the flexibility of synthesizing a variety of different fiber solutions. If the solution is a compatible ceramic-polymer-solvent system and has an ideal viscosity, the solution can be spun. This is especially convenient when designing complex materials that include multiple precursors or dopants [6].

Electrospun nanofibers with ceramic precursor materials must undergo a secondary, post-electrospinning thermal conversion to transform the fiber material into a ceramic material. Ceramic precursor materials are typically inorganic salts, consisting of the desired ceramic cation and an acetate, nitrate, or carbonate [7]. The thermal conversion of the precursor is carried out at high temperatures to burn off the polymeric binder, nucleate ceramic crystals, and coalesce the nanocrystalline ceramic. This thermal conversion is called calcination when the precursor is oxidized, or nitridation when the desired ceramic is a nitride. Other electrospun ceramics include carbides, borides, silicides, and sulphides [6]. Choice of atmosphere
plays a role in crystallization kinetics of ceramic materials, particularly rare-earth metals [8]. Depending on the polymer, ceramic, and desired performance, different thermal processing is required. The polymer binder is typically decomposed at its glass transition temperature, while ceramic nucleation begins at a lower temperature before measurable coalescence occurs [9, p. 784]. CNFs are advantageous to polymeric nanofibers for particular applications due to their high temperature resistance, crystalline microstructure, and strength.

### 3.1.2 Structure

The ability to customize fiber structure is a function of solution properties and electrospinning variables. Relevant electrospinning parameters are included in Table I from Panda (2007) and references therein, summarizing their effects on fiber morphology.

**Table I: Electrospinning Process Parameters Influencing Fiber Morphology** [7]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influence</th>
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<td><strong>Solution Properties</strong></td>
<td></td>
</tr>
<tr>
<td>Polymer Concentration</td>
<td>Direct, power law, cubed, and parabolic proportion to fiber diameter for different systems</td>
</tr>
<tr>
<td>Ionic Strength</td>
<td>Proportional to charge density, inversely proportional to beading</td>
</tr>
<tr>
<td>Solvent</td>
<td>Directly related to evaporation and solidification rate</td>
</tr>
<tr>
<td>Temperature</td>
<td>Inversely proportional to viscosity and beading</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Parabolic relationship to fiber diameter and spinning ability</td>
</tr>
<tr>
<td><strong>Electrospinning Variables</strong></td>
<td></td>
</tr>
<tr>
<td>Voltage</td>
<td>Direct effect on bead formation, inversely proportional to fiber diameter and surface charge density</td>
</tr>
<tr>
<td>Collector Distance</td>
<td>Inversely proportional to bead formation density, electric field strength, and fiber diameter, exponentially inversely proportional to volume charge density</td>
</tr>
<tr>
<td>Flow Rate</td>
<td>Proportional to electric current and fiber diameter, inversely proportional to surface and volume charge density</td>
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Fiber structure is influenced by solution surface tension, viscoelastic properties, and conductivity, as well as electrospinning variables like applied potential, fiber travel distance, and solution flow rate. Additives, such as surfactants and dopants, can be implemented to control solution properties like charge density and the dielectric constant. Structural defects, such as beading and ribboning, can occur as a result of non-ideal processing parameters.
3.1 Electrospun Ceramic Nanofibers

(Figure 2). The as-spun fiber diameter, typically on the order of ∼100s of nanometers, arises from a balance between surface tension and solution electrostatic repulsion. Electrospun nanofibers are not oriented in a particular direction; however, alignment can be achieved through metal frameworks attached to the collector [7].

Figure 2: Scanning electron microscope images of (a) polyvinyl alcohol [PVA] nanofibers, (b) beading structural defects, and (c) an example of a collector drum modification to achieve fiber alignment [7].

The isotropic open-celled structure of an electrospun mesh is ideal for many applications; ceramic precursors are evenly spread through the polymer fiber structure, major porosity is observed, and a high surface to volume ratio is achieved.

Upon thermal treatment, electrospun nanofibers undergo severe volumetric shrinkage (∼50-90%) while retaining their porous and fibrous structure. Depending on the original electrospinning conditions, dopant concentration, and subsequent thermal treatment, the possible CNF structures can range from smooth to irregular and hollow to dense [10]. The fiber diameter distribution is reduced upon thermal treatment, and the average fiber diameter is often less than 100 nm.

### 3.1.3 Properties and Performance

Mesh porosity and high surface-to-volume ratios are attractive physical properties for many polymeric and composite nanofiber applications for biomedical, environmental remediation, and sensing applications [10]. Electrospinning polymeric materials allows for mechanical property, compositional, and structural engineering such that biological vessels can mimicked to a large degree. Biomaterial-based nanofiber membranes are currently being studied for vascular grafting, DNA and drug-delivery systems, and nerve guidance conduits, where particular advancements in structural integrity and biocompatibility with endothelial
and smooth muscle cells of electrospun collagen, elastin, and poly(D,L-lactide-co-glycolide) [PLGA] membranes has shown promise for native artery scaffolds in humans and animals [11]. Cellulose membranes are being used as adsorptive materials for protein purification and toxin removal. Surface functionalization with ligands or ceramic ions electrostatically attract pollutants and purify water by removing or recycling trace amounts of heavy metal such as cadmium [Cd], lead [Pb], and arsenic [As] [12]. Polymeric composite nanofibers are used to detect or sense biomolecules and hazardous gases. Nanofiber conductivity is directly proportional to the concentration of gas analytes adsorbed to its surface. For example, polypyrrole [PPy] fibers functionalized with the protein avidin can detect biotin-labeled molecules, such as DNA, in biosensors. Nanofibers functionalized with semiconducting ceramic oxides are sensitive to toxic gases like ammonia and nitroxide and sense based on measurable changes in material resistivity [12].

CNFs are a growing field in materials science, being used for a wide array of nanoscale engineering applications such as piezo- and ferroelectric devices, thermovoltaic emitters, particulate filtration, transport media, and fuel cells due to their surface to volume ratio, thermal resistivity, and conductivity. Ceramics such as magnesium titanate [MgTiO$_3$], nickel titanate [NiTiO$_3$], and lead zirconate titanate [PZT] are utilized for electronic and power generation applications, while ceramic oxides like zinc oxide [ZnO], zirconia [ZrO], and titania [TiO$_2$] are used widely in sensing, environmental remediation, and electro-optical devices [7]. The ceramic oxides mentioned exhibit photocatalytic properties, advantageous for water purification. When exposed to a particular frequency of light, photocatalysts are electromagnetically excited, producing free electrons that reduce water molecules to hydroxyl radicals [OH$^-$]. The hydroxyl radicals have the capacity to oxidize and destroy organic pollutants adsorbed to the CNF surface [13].

CNF meshes are an implementable technology that can lead to a better standard of living where access to clean water is a luxury and not a right. Economically, electrospinning is a viable process for producing effective filters, despite the slow fabrication rate. Nanofiber meshes are highly porous and require less material to produce and, therefore, cheaper than commercial filters installed in major pipelines. However, ceramic strength is negatively correlated with porosity and pore volume [14, 15]. To ensure safety and preserve the unbound nature of the electrospun mesh, the nanofibers should be strengthened such that fracture and subsequent nanoparticle dispersion is limited. Ceramic materials have much higher compressive strengths than tensile strengths.
3.2 Ceramic Nanofiber Strength

The strength of ceramic materials is dependent on the size distribution of microstructural defects, including cracks, pores, and inclusions [16]. Nanofibrous materials are considered open-celled and highly porous, where pores are the major flaw type in the microstructure. The pore size distribution and the porosity within the ceramic nanofiber material will determine its strength [15]. Typically, ceramic materials are linear elastic to failure, where stress and strain are linearly related by the elastic modulus according to Hooke's law until yielding occurs; however, the microstructure of a CNF mesh will lead to variable stress-strain behaviors. When a brittle, or linear elastic, material is stressed in compression, fracture occurs once the material is crushed when the yield strength is reached and a critical flaw size is reached (Figure 3). The compressive strength of a ceramic is determined by the average flaw size, whereas the tensile strength is determined by the largest flaw size [16].

![Figure 3: Crack nucleation and propagation in ceramic materials stressed in compression [16].](image)

As opposed to highly dense ceramics, CNF stress-strain behavior is not completely linear elastic and may continue into the plastic region of deformation. CNF meshes may be modeled as cellular materials, which have differing mechanical properties and fracture mechanics compared to fully dense ceramics, though the same strengthening mechanisms exist including reducing flaw size and porosity. CNFs, due to their inherent porosity, tend to be much weaker than dense ceramics in both compression and tension, and may introduce much more scatter into their strength measurements which hampers accurate representation and reporting. Accurate strength measurements are, again, dependent on porosity and pore size.
3.2 Ceramic Nanofiber Strength

3.2.1 Porous Ceramic Fracture Mechanics

Pores are a major flaw type in nanofibrous materials. When a crack begins to propagate through a nanofibrous material, the crack will initiate through a fiber. The crack can propagate through a polycrystal (i.e. a grain) or an interface between polycrystals (i.e. a grain boundary). Once a crack reaches a major pore, the crack propagation is blunted. The crack is unable to traverse the pore and continue propagating to the next fiber, requiring additional stress to nucleate an additional crack in the next fiber. The pores in a porous ceramic may be modeled as pre-existing cracks and points of stress concentration, which increase the nucleation energy for crack propagation under stress. Thus, unlike typically brittle materials and dense ceramics, CNFs and porous ceramics experience an increase in fracture toughness with increasing strength, as well as exhibit pseudo-plastic stress-strain behaviors at high porosities [17]. As opposed to low porosity ceramics, where a single macrocrack fractures the material, highly porous ceramics fracture from many microcracks that localize to form a macrocrack and pore crushing. CNF meshes behave as cellular materials, where fracture begins in the solid walls between pores and failure occurs due to damage accumulation from multiple fractures [15]. Once a ceramic reaches a threshold porosity (~50%), the stress-strain behavior transitions from linear elastic to "pseudo-plastic," due to the multiple microcracks and fractures formed during loading (Figure 4).

Figure 4: Load-displacement curves for (a) typically brittle, linear elastic materials, such as dense ceramics, and (b) "pseudo-plastic" materials, such as high porosity ceramics [15].

The transition between brittle fracture and pseudo-plastic fracture is explained by the solid media through which cracks propagate; dense ceramics are considered uniform solid media through which mechanical properties are controlled by the presence of isolated pores, whereas highly porous ceramics are considered cellular and are made up of a network of
3.2 Ceramic Nanofiber Strength

pores and a distribution of solid media of which mechanical properties are controlled [15, 17]. As porosity increases, the wall thickness between pores decreases, leading to cracking and pore linkage. The sample does not fracture here but fractures after continuous damage accumulation and multiple wall failures, leading to pseudo-plastic fracture behavior. As porosity decreases, wall thickness between pores increases, leading to the formation of cracks large enough for brittle fracture behavior. Nanofiber mechanical properties are also directly influenced by connectivity between fibers; the more fibers that are connected, the more distributed a load will be [17].

3.2.2 Statistical Modeling: The Weibull Distribution

Vacancies in ceramic materials are statistical in nature. Every crystalline material will have an equilibrium concentration of vacancies at a given temperature in order to lower the free energy of the crystal. Each vacancy increases the entropy of the crystal and requires an activation enthalpy of formation. The concentration of vacancies in a crystal is given by an Arrhenius relationship, depending on the Gibbs energy, $G_f$, the temperature, and the ideal gas constant, $R$, in Equation 1. Because ceramic strength is a function of statistically distributed microstructural defects, ceramic strength is variable and modeled by a statistical distribution, known as the Weibull distribution.

$$c_v = \exp \left( \frac{-G_f}{RT} \right)$$  \hspace{1cm} (1)

The Weibull probability distribution relates a specimen's probability of failure, $p$, in a given sample size, $V_o$, with an applied stress, $\sigma$ (Equation 2). A characteristic stress, $\sigma_o$, is determined as the applied stress at which a specimen in a given sample has a $\sim 37\%$ chance of surviving. The scatter presented in the strength data of a given sample size is represented by the Weibull modulus, $m$, where a large Weibull modulus means there is less scatter and a small Weibull modulus means there is more scatter.

$$p(V_o) = 1 - \exp \left[ -\left( \frac{\sigma}{\sigma_o} \right)^m \right]$$  \hspace{1cm} (2)

When analyzing ceramic strength data, a Weibull plot is constructed, where the double natural logarithm of one over the probability of survival (i.e. $1 - p$) is plotted on the y-axis against the natural logarithm of the fracture stress on the x-axis. For brittle materials, such as ceramics, a linear plot is formed, where the slope is the Weibull modulus and the x-intercept is
the characteristic stress (Figure 5). Ductile materials, however, do not follow Weibull statistics because there is not as much statistical scatter in strength data compared to brittle materials.

![Weibull plot showing probability of survival as a function of fracture stress](image)

**Figure 5**: Weibull plot showing probability of survival as a function of fracture stress [16].

In addition to inherent scatter in strength data, porosity directly influences porous ceramic strength scatter. As porosity increases, scatter in strength decreases, corresponding to a larger Weibull modulus [15]. The scatter in ceramic strength data is an insight into the flaw size distribution within the microstructure.

[talk about other distributions]

### 3.2.3 Strengthening Mechanisms

Polycrystalline materials are strengthened by minimizing porosity (i.e. maximizing densification), minimizing grain size, and, in the case for fibers, minimizing fiber diameter [16]. CNF meshes will inherently be up to ~90% porous, but the resulting nanofiber diameter and polycrystalline grain size may be controlled through mindful heat treatment.

Reducing the nanofiber diameter reduces the probability of a large defect being present in the microstructure, thus strengthening the fiber [19]. Ceramic strength is a function of the defect size distribution and the volume of the ceramic. As the ceramic volume decreases, the average flaw size decreases, so smaller ceramic components tend to be stronger than large ceramic components in compression.
Grain boundary strengthening is a mechanism for polycrystalline materials. Given by the Hall-Petch relationship in Equation 3, the yield strength of a polycrystalline material, $\sigma_y$, can be influenced by the inverse square root of the grain size, $d$, and a material specific constant, $k$. A small grain size increases the number and volume of grain boundaries, or interfaces between polycrystals, which hinder dislocation motion. Dislocations are a one-dimensional microstructural defect through which materials fracture. Grain boundaries impede the onset of plasticity, increasing the yield strength of a polycrystalline material. Many more dislocations pile up in larger grains, requiring less force to move to another grain. Thus, smaller grains, which can not store many dislocations, require more force for dislocation motion between grains. Porous ceramics with a high volume of grain boundaries and small particle sizes distribute a load much more uniformly than a porous ceramic with few grain boundaries and large grains [20, 21].

$$\sigma_o = \sigma_y + \frac{k}{\sqrt{d}}$$

An inverse Hall-Petch relationship has been observed for nanocrystalline materials with grain size is smaller than a threshold diameter below a few tens of nanometers. Grain boundaries no longer strengthen the material as a new yielding mechanism, known as grain boundary sliding, presents itself. With nanocrystalline ceramics, there are many more triple junctions, or points where three adjacent grains meet. Triple junctions are points of high strain between misoriented grains in the microstructure and can lead to the formation of nanocracks, or flaws that can initiate fracture [22]. Proper sintering must be employed to engineer a strong ceramic with appropriate grain size, minimized fiber diameter, and maximized density.

### 3.3 Nanocrystalline Sintering

Sintering is the process of coalescing particles into a larger solid or porous mass through heat treatment. The process of sintering controls microstructural densification and grain growth, where both mechanisms are dependent on temperature and grain size. Through sintering, a desired ceramic microstructure with tailored mechanical properties can be formed by controlling process parameters such as heating rate, temperature, and applied pressure [9, p. 425]. Because the properties of a material are largely dependent on the material’s microstructure, sintering directly affects the performance of a material for a given application. CNFs are typically solid-state sintered as opposed to liquid sintering due to the severe
melting temperatures of ceramic materials; however, the high surface to volume ratio of nanoparticles results in a reduced material melting temperature. This effect must be taken into account when sintering nanocrystalline materials, leading to reduced sintering times and temperatures [23]. CNFs are typically sintered without pressure to preserve inherent porosity. Densification is a much slower process without applied pressure, but an engineered heat treatment can take advantage of multiple sintering mechanisms to produce a nanofiber microstructure that is adequately dense, with minimally grown grains and without eliminating mesh porosity.

3.3.1 Densification and Grain Growth

Sintering activity is a function of heat treatment time and temperature, where the amount of crystalline coalescence is dependent on mass diffusion given by an Arrhenius relationship in Equation 4, where mass transport rate is determined by the maximal diffusion coefficient, \( D_0 \), the activation energy for diffusion \( E_A \), the ideal gas constant, and temperature. Diffusion is the mechanism by which all sintering mechanisms are thermally activated, and its driving force is the gradient of chemical potential energy in the microstructure.

\[
D = D_0 \cdot exp\left(\frac{-E_A}{RT}\right)
\] (4)

The driving force for sintering is the reduction of interfacial free energy by replacing grain surfaces with grain boundaries through densification and reducing interfacial grain boundary area per volume of grains through grain growth [24]. To strengthen a porous ceramic, maximum densification with minimal grain growth is required. Ceramic densification rate is a function of temperature and grain size (Equation 5). Densification rate, \( \rho \), is enhanced by smaller grain sizes, \( d \), and higher temperatures, as grain boundary diffusion, \( D_{gb} \), is related to temperature through the Arrhenius relationship in Equation 4 [23].

\[
\dot{\rho} \propto \frac{D_{gb}}{T d^4}
\] (5)

Grain growth, otherwise known as grain coarsening, arises from misorientation between grains. The driving force for grain growth is proportional to the thermally activated migration of grain boundaries, \( M \), rather than crystal coalescence [25, p. 93]. The grain boundaries between misfitted grains are in a much higher energy state, causing accelerated atomic diffusion. Striving to minimize free energy, the grains will grow larger in order to minimize
3.3 Nanocrystalline Sintering

Grain growth can either be normal, meaning the resulting grain size distribution is narrow, or abnormal, where exceptionally large grains grow among many fine grains. Normal grain growth, given by Equation 6, is proportional to the square root of the sintering time, so longer sintering times yield larger grains. Grain growth is also dependent on the initial grain size, \(d_0\), but to a much lesser extent than the dependence on sintering time and temperature.

\[
d^2 - d_0^2 \propto M t
\]  

Grain growth works in opposition to densification, since these phenomena are competing in the balance of free energy [9, p. 545]. The densification curve, plotting relative density versus sintering time, illustrates the dominant mechanisms in different stages of sintering Figure 6. The initial and intermediate sintering stages are characterized by rapid densification, while the final stage is characterized by grain growth. Grain coarsening still occurs in the first sintering stages, but microstructural evolution is dominated by densification.

![Densification Curve](image)

**Figure 6**: Densification curve of a powder compact, showing the stages of sintering [24, p. 40].

When constructing a sintering profile for nanocrystalline ceramic strength, variables controlled for are initial grain size, sintering temperature, and sintering time. Nanoparticles are susceptible to differential densification and abnormal grain growth at high temperatures due to their high surface to volume ratio. Additionally, nanocrystalline melting temperatures tend to be lower than their bulk counterparts, resulting in reduced sintering parameters [23].
3.3 Nanocrystalline Sintering

3.3.2 Isothermal vs. Two-Step Sintering

There are two approaches to sintering ceramic materials in the literature; isothermal sintering and two-step sintering (TSS). The sintering parameters vary for each approach, producing variable microstructures with subsequent mechanical properties (Figure 7).

![Figure 7: The isothermal and two-step sintering profiles, with respective microstructural evolution from densification and grain growth [26].](image)

Isothermal sintering is the convention for ceramic processing, consisting of three process variables; heating rate, sintering temperature, and sintering time. Heating rate is dependent on part geometry and whether crystallization of a new phase occurs. Generally, sintering temperature is greater than the ceramic operating temperature and sintering time is longer than heat-up time. Cooling rate is controlled to prevent thermal stress in the microstructure through annealing. Thermal stressing is a function of the thermal gradient across a component, so annealing is unnecessary for small components [9, p. 787]. Isothermal sintering produces ceramics with large grains (i.e. $d > 1 \mu$m) because of unsuppressed grain growth during the dwell. Nanocrystalline ceramics are nearly impossible to produce isothermally without the aid of applied pressure. CNF fiber diameter and grain size must be on the nanoscale to preserve the high surface to volume ratio and porosity.

TSS was pioneered by Chen and Wang to suppress grain growth and sinter fully dense nanocrystalline yttria ($Y_2O_3$) without applied pressure [27]. TSS heats a ceramic to a much greater temperature and immediately cools to the sintering temperature for an extended dwell time. With rapid densification in initial stage sintering, the high-temperature step diffuses crystals together without allowing enough time for any meaningful grain growth.
The immediate reduction to the sintering temperature is where grain growth should occur; however, the formation of many triple junctions, as discussed in Section 3.2.3, during the high-temperature step suppresses grain boundary mobility and not grain boundary diffusion, essentially freezing out grain growth but not densification [27, 28]. Because kinetics are slow, TSS reduces differential densification through the elimination of fine particles from enhanced in the initial stage of sintering, and delays pore elimination to the final stages [29].

TSS is advantageous for sintering nanocrystalline ceramics. Grain growth is unsuppressed during isothermal sintering. CNF fiber diameter is $\sim 100$ nm, so the grains must be nanocrystalline to strengthen a fiber. If sintered too hot and too long, the grains grow unchecked and de-sinter, causing morphological instability.

### 3.3.3 De-Sintering

When grains grow while constrained from shrinking, de-sintering occurs, breaking up a fiber of truncated grains into isolated spheres. This phenomenon arises from reduction of the surface energy to grain boundary area ratio; once reaching a critical grain size aspect ratio, a spherical grain has the lowest surface energy and is favorable to high interfacial surface energy grain boundaries (Figure 8).

![Figure 8](image.png)

Figure 8: Evolution of fiber (a) with unconstrained grains (b, c) and constrained grains (b', c') [30].

The reduction of free energy is concurrent with a decrease in the dihedral angle, $\psi$, which is the angle between adjacent grains. The energy reduction due to sintering of a crystalline fiber is the ratio of the free energy of the unconstrained fiber, $E_u$, to the free energy of the constrained fiber, $E_c$ [30]. Given an equilibrium dihedral angle, $\psi_e$, dependent on the grain aspect ratio and the free energy of a grain, the reduction in free energy is expressed
through Equation 7. A de-sintered constrained fiber is more energetically unfavorable than an unconstrained fiber [30].

\[
\frac{E_u}{E_c} = \left[ \frac{1}{2} \cos \frac{\psi_e}{2} \left( 3 - \cos^2 \frac{\psi_e}{2} \right) \right]
\]  

(7)

Constraints in powder compacts are due to a wide grain size distribution from differential densification, a common problem when isothermally sintering nanocrystalline ceramics. TSS reduces differential densification through grain boundary diffusion of finer particles into coarser grains, resulting in a narrower grain size distribution.

### 3.4 β-Ga₂O₃ Nanostructures

This paper is investigating the sintering characteristics and mechanical performance of a beta gallium (III) oxide [β-Ga₂O₃] CNF tube calcined from an electrospun polyvinylpyrrolidone [PVP] and gallium nitrate [Ga(NO₃)₃] nanofiber mesh. PVP is a water-soluble thermoplastic polymer used for glues, surfactants, and binders due to its adhesive properties. Ga(NO₃)₃ is the ceramic precursor used to form β-Ga₂O₃, and it is used to treat hypercalcemia, a condition secondary to cancer. Gallium (III) oxide is a polymorphic material, and the specific crystal structure investigated is β-Ga₂O₃.

#### 3.4.1 Material Properties and Applications

β-Ga₂O₃ is the most stable gallium(III) oxide polymorph, being a monoclinic structured ceramic oxide semiconductor, with gallium cations occupying the octahedral and tetrahedral interstitial sites in a distorted oxide anion cubic structure. Both the crystal structure and X-ray diffraction pattern are simulated using VESTA in Figure 9 [31]. The β-Ga₂O₃ unit cell consists of 10 atoms, and dimensions used for simulation are found in literature [32, 33]. The simulated pattern 2θ values match well with the JCPDS reference pattern, with major peaks occurring at 2θ = 30.4, 31.8, 35.3, and 64.1°, corresponding to the (4 0 1), (0 0 2), (1 1 1), and (5 1 2) planes, respectively [34].

β-Ga₂O₃ has a bulk density of 5.88 g/cm³ and a melting temperature of 1,725°C. High-temperature gas sensing applications rely on oxygen vacancies in the crystal structure to donate electrons to produce noticeable capacitance variations when exposed to reducing gases. β-Ga₂O₃ nanowire gas sensing can occur at room temperature and be finely tuned to analytes such as toluene, acetone, and methanol [35].
Figure 9: VESTA simulated a) $\beta$-$\text{Ga}_2\text{O}_3$ crystal structure and b) X-ray diffraction pattern [31-33]. Major peaks occur at c) $2\theta = 30.4, 31.8, 35.3$, and $64.1^\circ$, corresponding to the (4 0 1), (0 0 2), (1 1 1), and (5 1 2) planes, respectively, for $\beta$-$\text{Ga}_2\text{O}_3$ calcined at 800 and 1,000°C [34].

With a band gap of 4.9 eV, bulk $\beta$-$\text{Ga}_2\text{O}_3$ is optically transparent. However, $\beta$-$\text{Ga}_2\text{O}_3$ nanofibers of variable crystallinities based on heat treatment exhibit tunable blue and yellow photoluminescence [36-38]. When doped with a concentration of lanthanides and actinides, $\beta$-$\text{Ga}_2\text{O}_3$ nanofiber photoluminescent properties can be further tuned to green and red, covering all primary colors, which is attractive for optoelectronic and flat panel display technologies [39-41].

$\beta$-$\text{Ga}_2\text{O}_3$ nanowires exhibit excellent thermal stability and photocatalytic properties when exposed to UV light due to the oxidative nature of its crystal structure. Photocatalytic properties for Rhodamine B [RhB] degradation was susceptible to differing nanostructure sizes and morphology [42]. The $\beta$-$\text{Ga}_2\text{O}_3$ nanostructure is highly adsorptive [43]. $\beta$-$\text{Ga}_2\text{O}_3$ nanostructures are also excellent catalysts, and have been embedded in alumina to grow gallium nitride [GaN] nanowires with 50 nanometer fiber diameters [44].

$\beta$-$\text{Ga}_2\text{O}_3$ has been investigated for electronic applications such as metal oxide field-effect transistors (MOSFET), Schottkey diodes, and metal insulator semiconductors (MIS) [35]. GaN is a common dielectric material and is known to grow $\beta$-$\text{Ga}_2\text{O}_3$ at a rate of 25 nanometers per minute in dry oxygen at 900°C [45]. The $\beta$-$\text{Ga}_2\text{O}_3$/GaN dielectric layer is advantageous due to minimized current leakage. GaN nanowire oxidation has also been observed and can be implemented as a protective coating for MOSFET devices [46].

Lawrence Livermore National Laboratory is using $\beta$-$\text{Ga}_2\text{O}_3$ CNFs to form low pressure media for high-temperature, high-efficiency particulate air (HEPA) filters used in nuclear facility ventilation systems [47]. Compared to commercial HEPA borosilicate glass filtration membranes, the tubular CNFs desirably yield much lower pressure drops across the filter;
however, when compared to as-spun nanofiber membranes, CNF tubes produced higher pressure drops (Figure 10). Depending on tube geometry, desired performance is still feasible. The rupture strength and directional strength are important properties when determining filter lifetime. Stronger filtration media are replaced less often and more reliable.

![Figure 10: Comparison of pressure drop between traditional HEPA membranes, polymer nanofiber membranes, and CNF tubes [47].](image)

Growth conditions directly influence the size, morphology, and properties of nanostructured $\beta$-Ga$_2$O$_3$. The kinetic behavior and transformation of the precursor material must be understood to properly evolve a $\beta$-Ga$_2$O$_3$ microstructure.

### 3.4.2 Decomposition and Kinetic Behavior

Gallium(III) oxide exists with many possible crystal structures depending on precursor materials used and thermal processing (Figure 11). $\beta$-Ga$_2$O$_3$ is the most stable polymorph, and at elevated temperatures, all other gallium(III) oxide crystal structures transform to the monoclinic orientation. It is possible with low processing temperatures to form the $\delta$- and $\epsilon$-Ga$_2$O$_3$ phases in conjunction with $\beta$-Ga$_2$O$_3$, which may influence lattice parameters and mechanical properties through the introduction of lattice strain. For $\beta$-Ga$_2$O$_3$ nucleation from an anhydrous Ga(NO$_3$)$_3$ precursor material, the processing temperature must exceed at least 870°C.
3.4 \( \beta \)-Ga\(_2\)O\(_3\) Nanostructures

PVP decomposes at its glass transition temperature, \( T_g \), of about 450°C. The provided nanofiber meshes are mostly PVP, resulting in severe shrinkage upon thermal treatment. Typically a binder burnout step is added to a sintering profile to fully decompose the polymer and prevent bubbling to preserve the structure. The necessity of a binder burnout step is determined by off-gassing during decomposition. Anhydrous Ga(NO\(_3\))\(_3\) is not thermodynamically stable, releasing water vapor and N\(_2\)O\(_5\) throughout its decomposition, and depending on heating rate, Ga(NO\(_3\))\(_3\) decomposes to many intermediate compounds before transforming to \( \beta \)-Ga\(_2\)O\(_3\) [49]. Faster heating rates (i.e. greater than 5°C/min) were found to result in less decomposition intermediates than slower heating rates, meaning faster heating rates are optimal for \( \beta \)-Ga\(_2\)O\(_3\) formation. With faster decomposition heating rates, there is less off-gassing, so a binder burnout step is unnecessary to include if a heating rate of 5°C/min is chosen. Regardless of the heating rate, \( \beta \)-Ga\(_2\)O\(_3\) begins nucleating forms at around \( \sim \)600°C. The inclusion of a nucleation step is also negligible since any step which grows \( \beta \)-Ga\(_2\)O\(_3\) crystals is not preferred. Fine \( \beta \)-Ga\(_2\)O\(_3\) crystals should nucleate during the TSS high-temperature step regardless.

### 3.4.3 Sintering Characteristics

Sintering activity has been monitored for micro-sized \( \beta \)-Ga\(_2\)O\(_3\) particles sintered at variable temperatures from 900°C to 1,550°C for 1 hour [50]. The morphology of the initial \( \beta \)-Ga\(_2\)O\(_3\) particles directly influenced their sintering characteristics. Particles with elliptic
or rod-like structures experienced maximum densification at \( \sim 1,200^\circ C \), while monoclinic particles densified severely at \( \sim 1,400^\circ C \). However, nanocrystalline materials sinter at lower temperatures than bulk materials. Table II provides a summary of nanocrystalline \( \beta\)-Ga\(_2\)O\(_3\) heat treatments found in the literature.

**Table II**: Nanostructured \( \beta\)-Ga\(_2\)O\(_3\) Calcining Conditions From Literature

<table>
<thead>
<tr>
<th>Reference</th>
<th>Temperature</th>
<th>Time</th>
<th>Influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>[36]</td>
<td>700, 800(^\circ)C</td>
<td>1 hour</td>
<td>Crystallite size of 20 nm</td>
</tr>
<tr>
<td>[37]</td>
<td>750, 850, 950, 1,050(^\circ)C</td>
<td>N/A</td>
<td>Increasing crystallinity with temperature</td>
</tr>
<tr>
<td>[38]</td>
<td>550, 600, 650, 700, 750(^\circ)C</td>
<td>2, 4, 6, 8 hours</td>
<td>Increasing crystallinity with temperature and time</td>
</tr>
<tr>
<td>[39]</td>
<td>900(^\circ)C</td>
<td>6 hours</td>
<td>Fiber diameter of 55 nm</td>
</tr>
<tr>
<td>[40, 41]</td>
<td>900(^\circ)C</td>
<td>3 hours</td>
<td>Fiber diameter between 100 nm and 300 nm</td>
</tr>
<tr>
<td>[42]</td>
<td>900(^\circ)C</td>
<td>3 hours</td>
<td>Grain size around 200 nm</td>
</tr>
<tr>
<td>[43]</td>
<td>900(^\circ)C</td>
<td>2 hours</td>
<td>Crystallite size of 50 nm</td>
</tr>
</tbody>
</table>

Nanocrystalline \( \beta\)-Ga\(_2\)O\(_3\) is typically sintered between the crystallization temperature for \( \beta\)-Ga\(_2\)O\(_3\), 600\(^\circ\)C, and 1,000\(^\circ\)C for up to 8 hours. The optimal sintering temperature and time for maximal CNF strength should lie within these ranges. The sintering temperature and time which effectively densifies and reduces grain growth will produce the strongest \( \beta\)-Ga\(_2\)O\(_3\) CNF microstructure.
4 METHODOLOGY

Optimal TSS parameters for $\beta$-Ga$_2$O$_3$ CNF tubes are found using a $2^3$ design-of-experiment (DOE) with three sintering temperatures and three sintering times, yielding nine heat treatments (Table III). A high-temperature step of 1,000°C was chosen to compare against LLNL’s current isothermal sintering at 1,000°C for 1 hour with 5°C/min heating and cooling rates.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$t_1$</th>
<th>$t_2$</th>
<th>$t_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1$</td>
<td>625°C, 1 hour</td>
<td>625°C, 2 hours</td>
<td>625°C, 4 hours</td>
</tr>
<tr>
<td>$T_2$</td>
<td>750°C, 1 hour</td>
<td>750°C, 2 hours</td>
<td>750°C, 4 hours</td>
</tr>
<tr>
<td>$T_3$</td>
<td>875°C, 1 hour</td>
<td>875°C, 2 hours</td>
<td>875°C, 4 hours</td>
</tr>
</tbody>
</table>

4.1 Sample Preparation

Sample preparation is outlined in Figure 12. PVP and Ga(NO$_3$)$_3$ nanofiber mesh sectioned into 39 mm x 15 mm strips was shaped around a 12 mm diameter steel mandrel coated with Teflon tape and sealed using heat to produce 15 mm tall, 12 mm diameter tubes.

Figure 12: The PVP and Ga(NO$_3$)$_3$ nanofiber mesh is a) shaped into 15 mm tall and 12 mm diameter tubes, then b) calcined and sintered, forming c) highly deformed $\beta$-Ga$_2$O$_3$ specimens.
Using 5°C/min rates, the tubes were held in a round fused-quartz crucible and heat treated first to 1,000°C and second to the sintering temperature for the given sintering time in Table III. The CNF tubes were cooled in the furnace to room temperature at 5°C/min.

### 4.2 Mechanical Testing

A minimum sample size \((N)\) of 26 calcined tubes from each heat treatment were measured across the middle of their tubular cross-section and diametrally compression tested in an Instron-Mini 50 universal mechanical tester with a crosshead speed of 0.3 mm/min and a 50 N static load cell (Figure 13). Tubes isothermally sintered at 1,000°C with variable cross-sectional areas were compression tested under the same conditions.

![Figure 13: Mechanical testing experimental setup.](image)

Weibull statistics were performed for each heat treatment yield stress to determine the respective Weibull modulus. Using MiniTab, the Anderson-Darling goodness test determined the Weibull and lognormal distribution fit, and non-parametric Kruskal-Wallis tests were used to compare the isothermal and TSS strength medians.

### 4.3 Microstructural Characterization

The crushed \(\beta\)-Ga\(_2\)O\(_3\) specimens were collected for X-ray powder diffraction (XRD) to determine the phase composition, as well as crystallite size \((\tau)\) using the full-width half-maximum \((\beta)\) of the most intense peak position (Equation 8). XRD was performed on a
Siemens Diffraktometer D5000 using 0.15406 nm, Cu K-α radiation, a scan rate of 2 degrees/min from 20 to 80° 2θ, and an increment of 0.005.

\[
\tau = \frac{0.9\lambda}{\beta \cos(\theta)}
\] (8)

SEM images taken on an FEI Quanta 200 were processed to determine post-heat treatment fiber diameter, porosity, and pore size for the strongest CNF microstructures. The fiber diameter distribution is measured using ImageJ, an image processing software, at different magnifications. Porosity and pore size distributions were determined by first converting the gray-scale SEM image to a highly contrasted, or threshold, image in ImageJ and then using an app in MATLAB to calculate the size and area fraction of dark region [51]. Porosity and pore size distribution were determined for a standardized magnification of 50,000x with outputs similar to Figure 14.

Figure 14: Example output from MATLAB porosity calculations.
5 RESULTS

The sintered $\beta$-Ga$_2$O$_3$ CNF tubes severely deformed from their original cylindrical shape. The contact area between the compression platens and the CNF specimens varied between samples, which introduces systematic error into the strength measurements. Additionally, the cross-sectional area was variable across the length of the tubes and is highly porous. Porosity and wall thickness variation introduces additional scatter to the strength data.

5.1 Mechanical Properties

There are two options for defining CNF tube fracture strength; the yield stress ($\sigma_y$) and the maximum stress ($\sigma_m$). The CNF tubes exhibited two stress-strain behaviors; cellular and brittle. The dashed stress-strain curve in Figure 15 is characteristic of pseudo-plastic, cellular damage accumulation and strength loss, while the solid curve shows strengthening after brittle fracture from pore crushing and subsequent densification [52]. The yield stress is measured as the stress applied where the first significant drop, defined as a sharp 25% loss, in strength occurs. The yield stress is chosen to represent CNF tube strength to eliminate most outliers and determine where fracture begins to initiate.

![Figure 15: CNF fracture modes from fiber damage accumulation and pore crushing densification.](image-url)
CNF strength is highly influenced by component geometry (Table IV). Compared to tubes provided by LLNL with diameters equal to about 2.3 mm, the experimental geometry yields tubes of about 4.6 mm diameter that are, on average, ~87% weaker.

Table IV: Volume Effects on $\beta$-$\text{Ga}_2\text{O}_3$ CNF Isothermal Strength

<table>
<thead>
<tr>
<th>Profile</th>
<th>Average Tube Diameter (mm)</th>
<th>N</th>
<th>$\bar{\sigma}_y$ (kPa)</th>
<th>s (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso, LLNL</td>
<td>2.34</td>
<td>36</td>
<td>24.9</td>
<td>16.5</td>
</tr>
<tr>
<td>Iso, Own</td>
<td>4.62</td>
<td>26</td>
<td>3.36</td>
<td>1.61</td>
</tr>
</tbody>
</table>

The isothermally treated tube strength data fit both Weibull and lognormal distributions, characteristic of porous ceramic materials (Figure 16) [53, 54]. The Weibull fit validates the use of Weibull statistics for comparing isothermally sintered CNF strength.

![Weibull Distribution Fit](image1)

Weibull Distribution Fit

![Lognormal Distribution Fit](image2)

Lognormal Distribution Fit

![Anderson-Darling Test](image3)

Anderson-Darling Test

![Anderson-Darling Test](image4)

Anderson-Darling Test

Figure 16: Isothermally sintered CNF strength fit with a) Weibull distributions and b) lognormal distributions. The c) Weibull and d) lognormal fits confirm validity of Weibull statistics.

The average yield strength is listed for the isothermally sintered and two-step sintered specimens in Table V. Each 2 hour and 4 hour TSS profile on average produced stronger CNF tubes with increasing temperature. The strongest CNF tube produced was with a 2 hour, 875°C sintering and had an average yield stress of 5.72 kPa.
The TSS strength distributions fit Weibull and lognormal distributions, justifying Weibull statistics for reliability calculations across all CNF heat treatments (Figure 17).

Table V: Two-Step Sintering $\beta$-$\text{Ga}_2\text{O}_3$ CNF Strength

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time</th>
<th>N</th>
<th>$\bar{\sigma}_y$ (kPa)</th>
<th>s (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>625°C</td>
<td>1 hr</td>
<td>32</td>
<td>2.29</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>2 hr</td>
<td>30</td>
<td>4.54</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>4 hr</td>
<td>28</td>
<td>3.69</td>
<td>2.21</td>
</tr>
<tr>
<td>750°C</td>
<td>1 hr</td>
<td>30</td>
<td>2.47</td>
<td>1.74</td>
</tr>
<tr>
<td></td>
<td>2 hr</td>
<td>30</td>
<td>5.20</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>4 hr</td>
<td>29</td>
<td>4.13</td>
<td>2.44</td>
</tr>
<tr>
<td>875°C</td>
<td>1 hr</td>
<td>30</td>
<td>3.17</td>
<td>2.13</td>
</tr>
<tr>
<td></td>
<td>2 hr</td>
<td>30</td>
<td>5.72</td>
<td>2.89</td>
</tr>
<tr>
<td></td>
<td>4 hr</td>
<td>29</td>
<td>5.49</td>
<td>2.06</td>
</tr>
</tbody>
</table>

Figure 17: Two-step sintered CNF strength fit with a) Weibull distributions and b) lognormal distributions. The c) Weibull and d) lognormal fits confirm validity of Weibull statistics.
Each heat treatment produced unreliable and weak CNF components (Figure 18). The strength data moderately fit a single linear Weibull trendline; however, the trendline can be broken into multiple linear fits at lower and higher strengths.

![Figure 18: CNF tube strength Weibull plots for a) 1 hour TSS, b) 2 hour TSS, c) 4 hour TSS, and d) isothermal sintering.](image)

The CNF Weibull moduli are low, between 1.7 and 2.6 (Table VI). The characteristic stresses, or the stress applied where ~37% of samples in a population fail, reveal that strength is correlated with sintering temperature. The 90% confidence interval for Weibull distribution parameters is calculated from ASTM C1239 [55].
Table VI: $\beta$-Ga$_2$O$_3$ CNF Weibull Parameters

<table>
<thead>
<tr>
<th>Profile</th>
<th>Temperature</th>
<th>Time</th>
<th>N</th>
<th>$\bar{\sigma}$ (kPa)</th>
<th>$\bar{m}$</th>
<th>($\sigma_{0.05}$, $\sigma_{0.95}$)</th>
<th>($m_{0.05}$, $m_{0.95}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS</td>
<td>625°C</td>
<td>1 hr</td>
<td>32</td>
<td>2.60</td>
<td>2.09</td>
<td>(2.23, 3.04)</td>
<td>(1.58, 2.54)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 hr</td>
<td>30</td>
<td>5.14</td>
<td>2.39</td>
<td>(4.47, 5.92)</td>
<td>(1.79, 2.91)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 hr</td>
<td>28</td>
<td>4.19</td>
<td>1.77</td>
<td>(3.44, 5.11)</td>
<td>(1.31, 2.17)</td>
</tr>
<tr>
<td></td>
<td>750°C</td>
<td>1 hr</td>
<td>30</td>
<td>2.60</td>
<td>2.09</td>
<td>(2.25, 3.39)</td>
<td>(1.23, 2.00)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 hr</td>
<td>30</td>
<td>5.26</td>
<td>2.58</td>
<td>(5.15, 6.68)</td>
<td>(1.93, 3.15)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 hr</td>
<td>29</td>
<td>4.66</td>
<td>1.89</td>
<td>(3.89, 5.59)</td>
<td>(1.41, 2.31)</td>
</tr>
<tr>
<td></td>
<td>875°C</td>
<td>1 hr</td>
<td>30</td>
<td>3.57</td>
<td>1.75</td>
<td>(2.95, 4.33)</td>
<td>(1.31, 2.13)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 hr</td>
<td>30</td>
<td>6.49</td>
<td>2.20</td>
<td>(5.58, 7.57)</td>
<td>(1.65, 2.68)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 hr</td>
<td>29</td>
<td>5.58</td>
<td>2.61</td>
<td>(4.90, 6.37)</td>
<td>(1.94, 3.19)</td>
</tr>
<tr>
<td>Iso, LLNL</td>
<td>1,000°C</td>
<td>1 hr</td>
<td>36</td>
<td>27.9</td>
<td>1.58</td>
<td>(23.0, 33.8)</td>
<td>1.22, 1.90</td>
</tr>
<tr>
<td>Iso, Own</td>
<td>1,000°C</td>
<td>1 hr</td>
<td>26</td>
<td>3.85</td>
<td>1.92</td>
<td>(3.19, 4.66)</td>
<td>(1.40, 2.37)</td>
</tr>
</tbody>
</table>

For non-normal distributions, the analysis of variance between medians using the Kruskal-Wallis test is recommended. The most significantly different TSS profiles with $\alpha = 0.01$ are the 2 hour and 4 hour, 875°C and the 2 hour 750°C TSS profiles (Figure 19).

![Figure 19:](image)

Figure 19: The analysis of variance between medians yielding p-values equal to 0.002, 0.0005, and 0.0045 when the a) 750°C, 2 hour, b) 875°C, 2 hour, and c) 875°C, 4 hour TSS strength distributions were compared to the isothermal sintering strength distribution, respectively.
5.2 Microstructural Characteristics

Surface characterization was performed at 500x magnification for each of the significantly stronger CNF microstructures (Figure 20). The surface morphology is extensively flawed with macropores and cracking, and the microstructure appears to be open-celled.

![Figure 20: Surface morphology at 500x magnification of a) isothermally sintered CNFs, b) the 750°C and c) 875°C 2 hour TSS CNFs, and d) the 4 hour 875°C TSS CNFs.](image)

Higher magnification microscopy reveals fiber morphology (Figure 21). The isothermally sintered CNFs in Figure 21a are relatively thin and disperse, and grains are not visibly resolved.
The TSS CNFs are more densely packed and grains can be seen to span the fiber diameter. Slight de-sintering is observed in the 875°C micrographs (Figure 21c and d).

![Figure 21](image)

**Figure 21:** Representative SEM images at 50,000x magnification of a) isothermally sintered CNFs, b) the 750°C, and c) 875°C 2 hour TSS CNFs, and d) the 4 hour 875°C TSS CNFs.

The CNF diffraction pattern is the same shape as the reference with highly broadened peaks due to the nanocrystalline microstructure; however, the shift in diffraction angle suggests there are other Ga$_2$O$_3$ polymorphs, significant lattice strain, or displacement errors present (Figure 22). The CNF $(0 \ 0 \ 2)$ peak, located around $\sim 29.5^\circ \ 2\theta$, is shifted left by at least...
2°. Higher 2θ angles, such as the peak corresponding to the (5 1 2) plane typically located at ∼64°, are shifted even further. This may be attributed either to displacement error during measurement or inherent porosity causing lattice spacing to expand by ∼10% larger than the reference.

![Diffraction Pattern](image)

**Figure 22:** CNF diffraction pattern with significant peak displacement errors, masking peak matching with β-Ga2O3 reference pattern.

Crystallite size is determined by the (0 0 2) peak (Table VII). The isothermally sintered crystallite size is 32.2 nm, while most TSS profiles produced smaller CNF crystallites with the exception of the 750°C 4 hour profile. Although the peaks are shifted, the qualitative analysis and comparison between peak widths reveals that extended sintering times implemented through TSS suppresses grain growth and produces nanocrystalline microstructures.
### Table VII: $\beta$-$\text{Ga}_2\text{O}_3$ CNF (0 0 2) Crystallite Size

<table>
<thead>
<tr>
<th>Profile</th>
<th>Temperature</th>
<th>Time</th>
<th>$2\theta$ ($^\circ$)</th>
<th>$\beta$ (rads)</th>
<th>$\tau$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS</td>
<td>625°C</td>
<td>1 hr</td>
<td>29.515</td>
<td>6.98E-3</td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 hr</td>
<td>29.46</td>
<td>6.72E-3</td>
<td>21.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 hr</td>
<td>29.415</td>
<td>5.88E-3</td>
<td>24.4</td>
</tr>
<tr>
<td></td>
<td>750°C</td>
<td>1 hr</td>
<td>29.445</td>
<td>6.37E-3</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 hr</td>
<td>29.605</td>
<td>5.15E-3</td>
<td>27.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 hr</td>
<td>29.39</td>
<td>4.36E-3</td>
<td>32.9</td>
</tr>
<tr>
<td></td>
<td>875°C</td>
<td>1 hr</td>
<td>29.515</td>
<td>5.67E-3</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 hr</td>
<td>29.55</td>
<td>4.71E-3</td>
<td>30.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 hr</td>
<td>29.355</td>
<td>5.32E-3</td>
<td>26.9</td>
</tr>
<tr>
<td>Iso, Own</td>
<td>1,000°C</td>
<td>1 hr</td>
<td>29.31</td>
<td>4.45E-3</td>
<td>32.2</td>
</tr>
</tbody>
</table>

Using the images in Figure 21, porosity, the pore size distribution, and the fiber size distribution is determined. Porosity is directly correlated with CNF average yield stress (Figure 23). Of the significantly strengthening TSS profiles, the CNF tube with the lowest porosity or highest density was the 875°C 2 hour profile at 49%. Compared to the isothermally sintered tubes, the TSS CNFs are much denser.

![Figure 23: CNF characteristic strength, with 90% confidence, is inversely proportional to porosity.](image)

The pore size distributions are exponentially distributed and highly skewed right (Figure 24). The pore sizes are much smaller than 0.3 $\mu$m; this is advantageous because, by definition, HEPA-grade filters must be able to filter 99.97% of particulates larger than 0.3 $\mu$m.
5.2 Microstructural Characteristics

Figure 24: Pore size distribution for the a) isothermally sintered CNFs, b) the 750°C and c) 875°C 2 hour TSS CNFs, and d) the 4 hour 875°C TSS CNFs.

The fiber diameter distribution is best fit by a lognormal distribution (Figure 25). At low magnifications, there are many large fibers on the tube surface, but as magnification is increased, much smaller fibers appear within the microstructure.

Figure 25: The fiber diameter distribution fit to a lognormal distribution.
The microstructural characteristics are summarized in Tables VIII and IX. Compared to the isothermally sintered CNFs, the TSS tubes are more dense with nearly the same pore sizes ($P_r$). The fiber diameters ($f_d$) are larger at longer sintering times, similar to the crystallite size.

**Table VIII: $\beta$-Ga$_2$O$_3$ CNF Porosity Characteristics**

<table>
<thead>
<tr>
<th>Profile</th>
<th>Temperature</th>
<th>Time</th>
<th>$P_r$ (nm)</th>
<th>$s$ (nm)</th>
<th>$P_{r,\ max}$ (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS</td>
<td>750°C</td>
<td>2 hr</td>
<td>42.8</td>
<td>37.7</td>
<td>247</td>
<td>55.6</td>
</tr>
<tr>
<td></td>
<td>875°C</td>
<td>2 hr</td>
<td>42.6</td>
<td>34.1</td>
<td>251</td>
<td>49.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 hr</td>
<td>60.1</td>
<td>45.2</td>
<td>308</td>
<td>51.1</td>
</tr>
<tr>
<td>Iso, Own</td>
<td>1,000°C</td>
<td>1 hr</td>
<td>52.1</td>
<td>41.7</td>
<td>248</td>
<td>64.3</td>
</tr>
</tbody>
</table>

**Table IX: $\beta$-Ga$_2$O$_3$ CNF Fiber Diameters**

<table>
<thead>
<tr>
<th>Profile</th>
<th>Temperature</th>
<th>Time</th>
<th>$f_d$ (nm)</th>
<th>$s$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS</td>
<td>750°C</td>
<td>2 hr</td>
<td>87.9</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>875°C</td>
<td>2 hr</td>
<td>82.4</td>
<td>26.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 hr</td>
<td>104.2</td>
<td>25.1</td>
</tr>
<tr>
<td>Iso, Own</td>
<td>1,000°C</td>
<td>1 hr</td>
<td>78.4</td>
<td>20.8</td>
</tr>
</tbody>
</table>
6 Discussion

$\beta$-Ga$_2$O$_3$ CNF mechanical properties are influenced by geometrical constraints and microstructural consequences of two-step sintering. The post-sintering specimens were extremely distorted from their original tubular shape. The contact area between the compression platens and the specimen was variable as most tubes were nearly tetrahedral shaped. This undesirable geometry does not distribute loads evenly and may lead to much lower strength values than expected. The tetrahedral geometry is also undesirable for LLNL's purpose, as the cross-sections at the tube ends were elliptic rather than circular. An elliptic cross-section requires more power to force air through the tube, increasing the pressure drop and operating cost. In order to produce reliable results, tube geometry control requires refinement.

The severe volumetric shrinkage undergone during the high-temperature step determines the overall effectiveness of TSS. The high-temperature step determines the degree to which grain boundary mobility is limited and densification is maximized during the sintering dwell. Densification during the sintering dwell is the main driving force for enhancing porous ceramic strength [53]. Further investigation into the high-temperature step is required to further optimize grain growth suppression, densification, and strength. If the high-temperature step were optimized, there would ideally be no grain growth between the 2 hour and 4 hour sinterings. Because there is a slight amount of grain growth as sintering time and temperature increases, other microstructural characteristics like fiber diameter are affected. Unsuppressed grain growth may lead to fiber enlargement, de-sintering, and reduced strength. Conversely, if the sintering time is too short, the slow kinetics of densification will not produce a structure dense enough to handle any significant loading. The sintering temperature should also be high enough to densify the microstructure in a timely manner, while reducing de-sintering effects from constrained fibers.

A common theme among many of the observed distributions is their lognormal fit. Because ceramic strength is based on a distribution of flaw sizes, it is reasonable to assume the type of flaw size distribution determines the type of statistics used to evaluate the strength distribution. Weibull statistics may not be the most representative type of statistics for understanding microstructural effects on CNF strength due to their lognormal fiber diameter distribution and exponential pore size distribution. Fiber diameter is inversely proportional with strength, except in the case of the isothermally sintered tubes which were much more porous. A smaller fiber diameter can indicate a smaller volume and probability for large flaws to be present. However, this relationship between fiber diameter is not as strongly evident as
the relationship between porosity and strength.

The multiple modes of fracture and the multiple Weibull trendlines suggest there are multiple flaw distributions. The CNF tubes fracture due to defects; however, there are both surface defects and volume defects present. Large surface defects could have caused specimens to prematurely fail, skewing the strength distribution towards lower values. This can account for the lognormal fit.

The significant peak shift observed in the XRD data do not provide accurate quantitative crystallite sizes, but peak broadness may still comparable across different sintering profiles. CNF strength increased with crystallite size, except for the case of the isothermally sintered tubes which had a much higher porosity. The 875°C 4 hour sintered tubes had smaller crystallite size but lower strength. One explanation for the TSS strength and TSS crystallite size proportionality is the inverse Hall-Petch relationship; the critical crystallite size where grain boundary strengthening reaches its limit may be in the range ~30 nm.
7 CONCLUSIONS

1. With a high-temperature step of 1,000°C, two-step sintering strengthens $\beta$-Ga$_2$O$_3$ CNFs optimally with a 2 hour, 875°C sintering dwell, enhancing the average yield stress from 3.36 kPa to 5.72 kPa. However, the components are considered unreliable using Weibull statistics, yielding a Weibull modulus of 2.20.

2. Two-step sintering successfully suppresses grain growth at extended sintering times and densifies CNF microstructure at higher sintering temperatures. The minimal grain growth observed points to subprime high-temperature step parameters, where a threshold densification responsible for freezing grain boundary mobility is not reached.

3. Porosity is the major flaw type and microstructural characteristic influencing the average CNF yield stress.
8 Acknowledgements

Wholeheartedly, I would like to thank Dr. James Kelly and Dr. Jeff Haslam at Lawrence Livermore National Laboratory for providing me with a meaningful research topic in electrospun nanomaterials. I’d also like to thank my advisor and the department chair of the Materials Engineering Department at Cal Poly, Dr. Trevor Harding, for guiding me throughout my senior year. I’d like to thank Dr. Blair London and Eric Beaton for providing me with the necessary instrumentation and work space to complete this project. Finally, I’d like to thank Cassi Goldsmith for being a great department administrative coordinator.
9 References


