

Molecular Synthesis of Complex Nitrogen Defects in HPHT Nanodiamond

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Abstract

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After Antoine Lavoisier’s seminal paper demonstrating the elemental composition of diamond as exclusively carbon in 1772, much research has been devoted to the synthesis, characterization, and application of this illustrious material. By the middle of the 20th century, through the ingenuity of H. Tracy Hall, the first artificial diamond synthetic avenue was discovered; through high-pressure, high-temperature means, a micro-crystal of diamond had been made. Industrial techniques such as CVD and detonation are currently employed to fabricate diamond for commercial applications with ranging purity. Moreover, research within the last twenty years on the optically active defects, also known as color centers, within diamond have found that they hold advantageous properties for a myriad of applications like quantum processing, telecommunications, fluorescence imaging, and magnetic sensing. While much has been discovered about diamond, and the > 100 naturally occurring optically active defects within diamond, an outstanding scientific challenge remains in rationally and deterministically incorporating specific defects into synthetic diamond. Precise atomistic control over the formation of these defects remains elusive, especially so with complex heteroatomic defects like the NE8 center, whose properties align itself as an excellent defect for quantum communication applications.

In this work, we demonstrate a facile synthetic avenue to deterministically introduce desired defects into HPHT synthesized nanodiamond. The first part of the synthetic scheme

includes the selection of an appropriate small molecule that matches the stereochemistry and stoichiometry of the desired defect and incorporating the small molecule into a carbon aerogel matrix to serve as a carbonaceous precursor for the formation of nanodiamond. The second part of this process is to place these doped carbon aerogel samples into a diamond anvil cell to access pressures similar to where diamonds are formed in nature and to drive the phase transformation to diamond through photothermal heating.

Also in this work, we demonstrate for the first time the phenomenon of laser cooling at elevated pressures. By placing a rare earth doped ceramic material inside a diamond anvil cell, we leverage the phonon assisted anti-Stokes fluorescence properties of this material to locally cool the surrounding area in the diamond anvil cell chamber. We also investigate the magnitude of cooling between the lower pressure scheelite phase and the higher pressure fergusonite phase.

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GLOSSARY

BCE: before common era

HPHT: high-pressure high-temperature

DAC: diamond anvil cell

CVD: chemical vapor deposition

COQ10: Coenzyme Q₁₀

GO: graphene oxide

RF: resorcinol formaldehyde

AN: acetonitrile

BET: BrunauerEmmettTeller

BJH: BarrettJoynerHalenda

SEM: scanning electron microscopy

TEM: transmission electron microscopy

XRD: x-ray diffraction

RFA: resorcinol formaldehyde aerogel

GOA: graphene oxide aerogel

HMT: hexamethylenetetramine

EDS: energy-dispersive X-ray spectroscopy

DND: detonation nanodiamonds

NE8: nickel exhibiton 8

NI_C: substitutional nickel

N_C: substitutional nitrogen

MAP: multi anvil press

NV: nitrogen vacancy, NV⁻

SIV: silicon divacany, SiV⁻

GEV: germanium divacancy, GeV⁻

SNV: tin divacancy, SnV⁻

TCSPSC: time correlated single photon counting

SAED: selected area electron diffraction

EELS: electron energy loss spectroscopy

PL: photoluminescence

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It takes a village to raise a scientist. This is mine.

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DEDICATION

to that little kid who dared to dream of being a scientist so long ago, these are the fruits of
your labor and sacrifices

this thesis is only the beginning for you

"Many people seem to think it foolish, even superstitious, to believe that the world could still change for the better. And it is true that in winter it is sometimes so biting cold that one is tempted to say, What do I care if there is a summer; its warmth is no help to me now. Yes, evil often seems to surpass good. But then, in spite of us, and without our permission, there comes at last an end to the bitter frosts. One morning the wind turns, and there is a thaw. And so I must still have hope." –Vincent Van Gogh

Out of the night that covers me,/ Black as the pit from pole to pole,/ I thank whatever gods may be/ For my unconquerable soul./ In the fell clutch of circumstance/ I have not winced nor cried aloud./ Under the bludgeonings of chance/ My head is bloody, but unbowed./ Beyond this place of wrath and tears/ Looms but the Horror of the shade,/ And yet the menace of the years/ Finds and shall find me unafraid./ It matters not how strait the gate,/ How charged with punishments the scroll,/ I am the master of my fate,/ I am the captain of my soul.–William Ernest Henley

"You may write me down in history/ With your bitter, twisted lies,/ You may trod me in the very dirt/ But still, like dust, I'll rise./ Just like moons and suns,/ with certainty of tides,/ Just like hopes springing high,/ Still I'll rise./ Did you want to see me broken?/ Bowed head and lowered eyes?/ Shoulders falling like teardrops,/ Weakened by my soulful cries?/Leaving behind nights of terror and fear/ I rise./ Into a daybreak that's wondrously clear/ I rise./ I rise/ I rise/ I rise." –Maya Angelou

Chapter 1

INTRODUCTION

Ever since the first description of diamond in 4th century BCE India, diamond has enjoyed a longstanding reverence as an illustrious gemstone prized for its clarity and brilliance symbolically representing opulence, love, commitment, and wealth. To add to the lore of diamonds, after the seminal papers of Antoine Lavoisier and Smithson Tennet², in the late 18th century, which quantitatively determined the composition of diamond to be exclusively carbon, the pursuit of fabricating artificial diamonds became a scientific and engineering quandary that even inspired H.G. Wells to write a short story about the process in 1894³. Many scientists, engineers, and scam artists had claimed to produce diamond through synthetic means, but none of those techniques were reproducible. By the middle of the 20th century, H. Tracy Hall became the first scientist to synthesize diamond microcrystals through a HPHT avenue with his patented belt press⁴, for which, this author's opinion is, he did not receive near enough credit. From that point up until present day, many advancements in technologies have produced diamonds of ranging purity of up to 12 carats (1 carat = 200 mg).

During the quest for a synthetic avenue for pure diamond, research has focused on utilizing diamond as an engineering material; and, with diamond's remarkable physical⁵ and electronic⁶ properties, it can be utilized as a superior engineering material. Moreover, the optically active defects, or color centers, of diamond have shown promise for applications in quantum information science⁷, temperature metrology⁸, and bio-fluorescent imaging⁹, to name a few. Additionally, many studies have characterized the defects found in nanodiamond

grains from meteorites to elucidate the environment in which these defects, and by extension the diamond and meteorite, were made, lending insight into the elemental composition and thermodynamic surroundings of these celestial bodies from whence the meteorites came.

So, because of the advantageous properties of not only the color centers but also the diamond host material, it is prudent to devote time to engineer a synthetic avenue to rationally and deterministically incorporate these color centers within a diamond substrate. Current industrial syntheses employ both a bottom-up or top-down approach to intentionally creating a desired defect in diamond with moderate success for homoatomic color centers; however, current techniques fall short when incorporating more complex or heteroatomic color centers into diamond. Further discussion on these color centers and current techniques to fabricate them is found in Chapter 3.

1.1 Dissertation's Aims and Objectives

The crux of my Ph.D. work focuses on investigating a bottom-up molecular doping fabrication scheme to deterministically dope complex color centers in HPHT synthesized nanodiamond crystals. By designing small molecules, that match the stoichiometry and stereochemistry of a desired point defect in diamond, as designer dopants into a carbonaceous precursor material, and then placing this precursor into a photothermally heated DAC, the desired point defect can be fabricated. The amorphous carbonaceous precursor is a carbon aerogel, comprising of an interconnected network of amorphous sp^3 carbon sols, which has previously shown to incorporate dopants, enhancing the already impressive physical and electronic characteristics of the material. Further discussion of the carbon aerogel doping process and some potential applications for these doped carbon aerogels are discussed in Chapters 2 and 3. Chapter 3 discusses the HPHT synthesis of these molecularly doped carbon aerogels into nanodiamond.

Lastly, Chapter 4 discusses the unique phenomenon of optical refrigeration, or laser

cooling, at elevated pressures. Based on the crystal structure of the rare earth doped ceramic material at different pressures, the magnitude of cooling is observed to decrease.

Chapter 2

CRYSTALLINE LOADING OF LIPOPHILIC COENZYME Q₁₀ PHARMACEUTICALS WITHIN CONJUGATED CARBON AEROGEL DERIVATIVES

This work has been published in¹⁰ and has been a part of a former graduate student's, now Dr. Matthew Lim's, dissertation.

Pharmaceutical researchers are actively developing new methods to enhance the delivery of small-molecule, lipophilic drugs with low water solubility. For such substances, ultra-fine particles are often sought because of their improved transit through blood capillaries, leading to increased circulation, enhanced in vivo residence times, and larger bioavailability¹¹. Proposed systems for lipophilic drug delivery range from emulsification^{12,13} to solid dispersion with inert hydrophilic compounds¹⁴⁻¹⁶ to loading drugs onto electrospun fibers^{17,18}. While these techniques are viable, they have not been shown to enable control over the amorphous versus crystalline state of the pharmaceuticals. Crystalline pharmaceuticals offer several advantages over their amorphous counterparts, including greater chemical stability and longer release times for oral or dermal delivery¹⁹.

Aerogels are an alternative drug-loading platform that can provide controlled delivery through mechanisms such as biodegradation²⁰, swelling of the aerogel matrix²¹, thermal activation²², and changes of the local pH²³. Moreover, aerogels have porous, high-surface-area structures that can load large concentrations of nanoparticulate lipophilic drugs, suppress their aggregation²⁴, and prolong shelf life by hindering oxygen diffusion²⁵. Also, aerogels can be made from a variety of materials including silica (SiO₂)²⁶, amorphous carbon²⁷,

semiconducting chalcogenides²⁸, and graphene^{29,30}.

Typically, aerogels are produced by supercritical CO₂ drying of a wet gel. Molecular compounds can thus be loaded into the pores of the aerogel by mixing them with the gel precursors during synthesis, diffusion from solvents before or after supercritical drying, or diffusion from supercritical CO₂ during the drying process. Supercritical loading, in particular, can yield both amorphous and crystalline phases^{25,31}, but it is expensive to scale up and limited by low drug solubility in supercritical CO₂.

In this work, Coenzyme Q₁₀ (CoQ₁₀) was used as a model drug to demonstrate that carbon aerogels based on resorcinolformaldehyde (RF) polymeric gels can be loaded with lipophilic molecular nanocrystals using a mild, low-cost, diffusion-based procedure, as seen in Figure 2.1. We analyze the loading of CoQ₁₀ on amorphous carbon aerogels obtained from supercritical drying and pyrolysis of additive-free RF, as well as on sp²-rich cross-linked graphene aerogels obtained from addition of graphene oxide (GO) to the RF precursors. CoQ₁₀ was chosen based on its polyunsaturated chemical bonding, as seen Fig. 2.2, ubiquity and importance for human health. It is synthesized in human tissue and mediates the production of cellular energy in the form of adenosine triphosphate (ATP)³², acts as a stabilizing agent in cellular membranes³³ and is a potent antioxidant^{34,35}. In addition, because the production of CoQ₁₀ decreases with age due to impaired mitochondria functioning and oxidative stress³⁶, it is widely consumed as a dietary supplement. Furthermore, carbons derived from pyrolysis of RF polymers and graphene derived from pyrolysis of GO both show good biocompatibility from in vitro studies with human cells, making our aerogels good candidates for drug-loading hosts^{37,38}.

2.1 Materials and Methods

2.1.1 Carbon aerogel/GO-doped carbon aerogel synthesis

RF gels were made through a rapid acid-catalyzed technique in acetonitrile that yields gels on the order of 2 hours, compared to several-day timescales required for conventional aqueous base-catalyzed reactions^{39,40}. The procedure was adapted from one of our earlier reports⁴¹ but using slightly different precursor ratios. For aerogels incorporating GO, commercially obtained few-layer GO (CheapTubes, 24 layers) was first dispersed in acetonitrile (AN, OmniSolv) at 2.6 mg/mL in a polypropylene tube by bath sonication for at least 30 minutes (Branson 1510R-DTH). For aerogels based on RF alone, this step was omitted. Then resorcinol (R, Sigma-Aldrich) was added to the solution, such that the molar ratio of R:AN was 1:200, which corresponds to a 4:1 weight ratio of R:GO for a 2.6 mg/mL starting dispersion of GO. After complete dissolution of resorcinol, formaldehyde (F, 37% w/w aqueous solution with methanol as stabilizer, Sigma-Aldrich) was added to achieve a R:F molar ratio of 1:2. Lastly, hydrochloric acid (HCl, Macron, 37% w/w) was added to catalyze the gelation process, in sufficient quantity to achieve a R:HCl molar ratio of 8:1. The mixture was put back under continuous sonication, and within 2 hours, a solid gel was formed. The gel was then removed from the tube, washed with anhydrous ethanol (Koptec) four times over 48 hours to remove all acetonitrile (AN), and dried in supercritical CO₂ in an autoclave (Quorum Technologies E3100) to preserve the pore structure. The resulting aerogel was then pyrolyzed in a tube furnace (Lindberg/Blue M) at 1000°C for 4 hours (8.2°C/min ramp up, total 2 hours) under flowing nitrogen gas (0.4 L min⁻¹). The high pyrolysis temperature was employed to maximize the reduction of GO and formation of sp² carbon, as shown in previous literature^{42,43}. The pyrolyzed carbon aerogels obtained from gels with and without GO were called GOA and RFA respectively.

2.1.2 Porosimetry

Nitrogen sorption isotherms were collected at 77 K using a Quantachrome Nova 2200e analyzer. To remove pre-adsorbed species, the aerogel samples were heated in vacuum at 200°C for at least 12 hours prior to measurements, and immediately loaded in the analyzer thereafter. Specific surface area and pore size distributions were obtained by the BrunauerEmmettTeller (BET)⁴⁴ and BarrettJoynerHalenda (BJH)⁴⁵ methods respectively, using Quantachrome NovaWin software. A moving point average size of 3 was used for the BJH pore distributions.

2.1.3 Electron Microscopy

Scanning electron microscopy (SEM) was performed using a FEI Sirion XL30 with 5 kV accelerating voltage. Samples were prepared by dispersing on a conductive silicon wafer and sputter-coating with approximately 10 nm of gold for better imaging. Transmission electron microscopy (TEM) was performed using a FEI Tecnai G2 F20 with 200 kV accelerating voltage. Samples were prepared by dispersing on a copper grid with lacey carbon support film.

2.1.4 X-Ray Diffraction (XRD)

XRD was performed using a Bruker D8 Discover X-ray diffractometer equipped with a General Area Detector Diffraction System (GADDS) using a $\text{Cu}_{K\alpha}$ source at 1.54 Å. Samples were aligned in the system using the laser guidance system provided in the instrument.

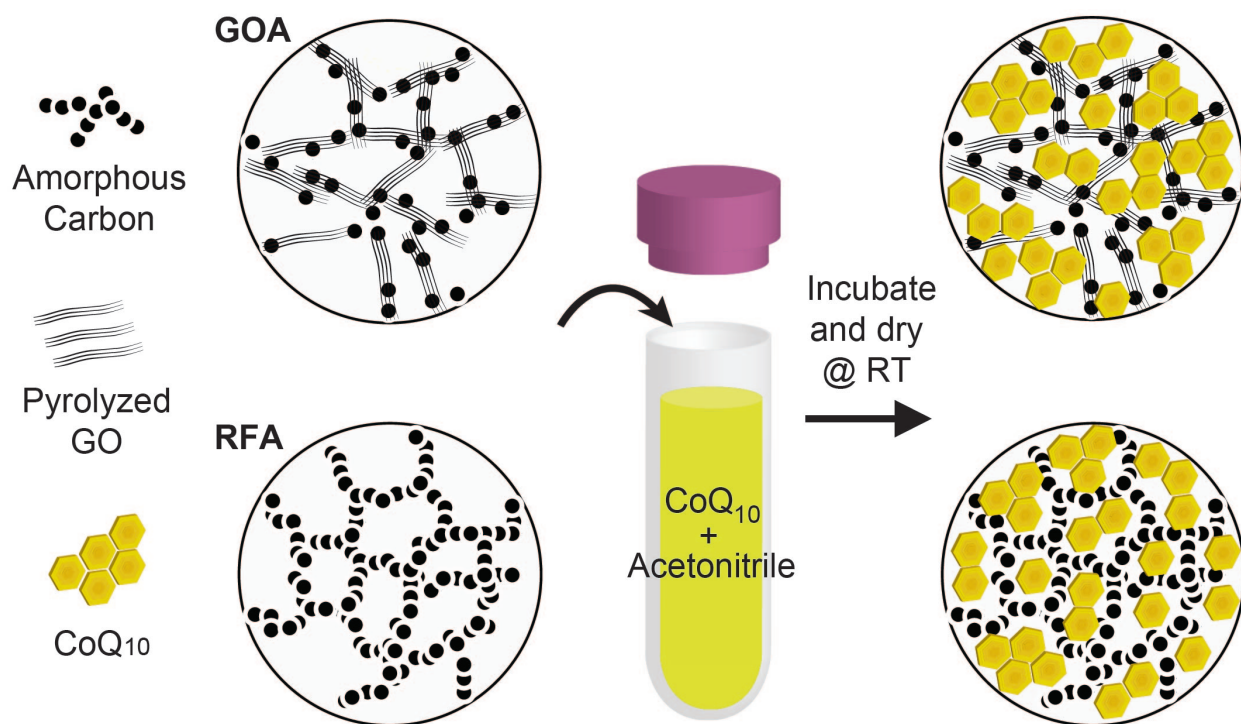


Figure 2.1: Schematic of crystalline drug (CoQ₁₀) loading on carbon aerogel derivatives.

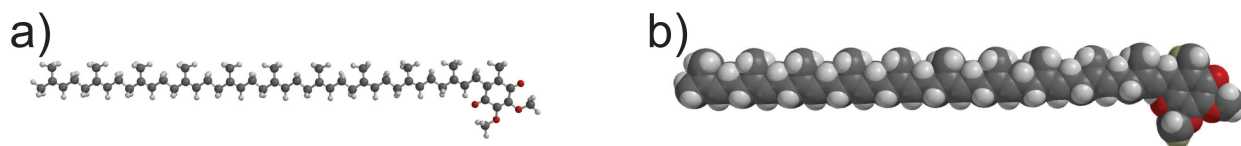


Figure 2.2: a) CoQ₁₀ linear structure (ball & stick), b) CoQ₁₀ linear structure (space filling)

2.1.5 *CoQ10 Loading*

CoQ10 loading on RFA and GOA was performed using a 1 mg/mL CoQ10 solution in acetonitrile, as CoQ10 had appreciable solubility in acetonitrile compared to other volatile solvents like methanol and hexane. Acetonitrile also leaves low residue after evaporation. A known mass of pyrolyzed aerogel was added to the CoQ10 solution in a polypropylene tube and incubated at room temperature for 12 hours. As diagrammed in Fig. 2.1, the solution infiltrated the aerogel pores and CoQ10 adsorbed onto the aerogel surface. This was evident from visual inspection, as the yellow solution became noticeably lighter (Fig. 2.3). The aerogel was then removed from the solution and air-dried at room temperature for at least 12 hours. Drying at elevated temperature was avoided due to the low melting point of CoQ10 (49°C)⁴⁶ and possible degradation of CoQ10 crystals. The mass gain of the dried aerogel relative to the pre-incubated aerogel effectively represents the mass of CoQ10 loaded into the aerogel, since control immersion/drying experiments of RFA in pure acetonitrile (without CoQ10) gave less than 0.64% mass gain (Fig. 2.4).

2.1.6 *UV-Vis Adsorption Measurements*

UV-Vis spectroscopy experiments were performed using a Thermo Scientific Evolution 300 spectrophotometer with a xenon lamp light source and Nova Biotech matched 10 mm, 3.5 mL quartz cuvettes. Wavelength range from 190 nm to 1100 nm was recorded with a scan speed of 240 nm/min. Measurements were collected in 15-minute intervals for 12 hours per experiment. CoQ10 solution was prepared using concentration of 0.1 mg CoQ10 per 1 mL acetonitrile per experiment. Approximately 5 mg aerogel was added to 3 mL of CoQ10-acetonitrile solution. Before each measurement, the base line of the spectrophotometer was calibrated against solvent. The standard curve, from which concentrations and kinetic parameters were derived, was obtained by plotting absorbance at 273 nm for solutions having various known concentrations of CoQ10 (Fig. 2.5).

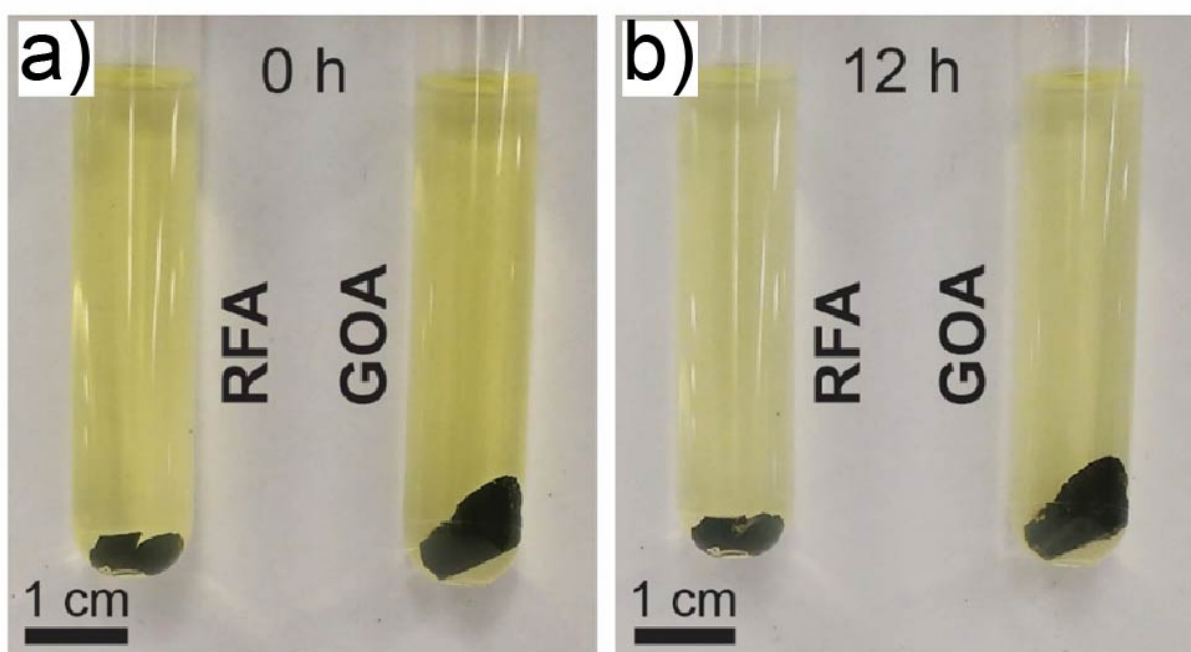


Figure 2.3: Carbon aerogel samples immersed in 1 mg/mL CoQ10/acetonitrile solution (5 mg of aerogel in 3 mL of solution) a) immediately after inserting aerogels; b) 12 h after inserting aerogels showing lightening of bulk solution.

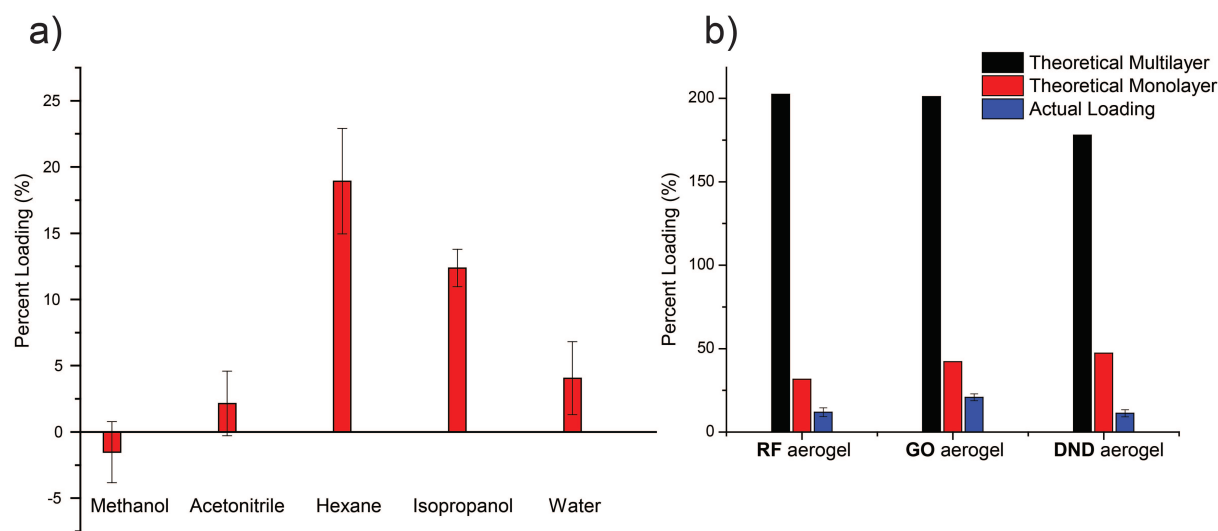


Figure 2.4: a) Mass loading for RFA incubated in various pure solvents for 12 h. b) Theoretical versus experimental mass loading on aerogels from CoQ10 in acetonitrile.

2.1.7 Theoretical Mass Loading Calculations

The theoretical multilayer mass loading was calculated from the assumption that the pores in the aerogel are filled with CoQ10. Thus the pore volume of the aerogel from nitrogen sorption analysis was divided by the volume of one CoQ10 molecule ($1033.58 \text{ \AA}^3$, as obtained from the Spartan14 molecular modeling software with the CPK space-filling model) to get the number of CoQ10 molecules in the pores, which was then converted to an equivalent mass. The theoretical monolayer mass loading was calculated by taking the surface area of one CoQ10 molecule ($1078.05 \text{ \AA}^2$, similarly obtained from Spartan14), assuming that the area it occupies on the aerogel is approximately 25% of that ($269.5 \text{ \AA}^2$), and then assuming that the entire surface of the aerogel is covered with CoQ10 molecules. Thus, the total surface area of the aerogel from nitrogen sorption analysis was divided by $269.5 \text{ \AA}^2$ to get the number of CoQ10 molecules in the monolayer, which was then converted to an equivalent mass.

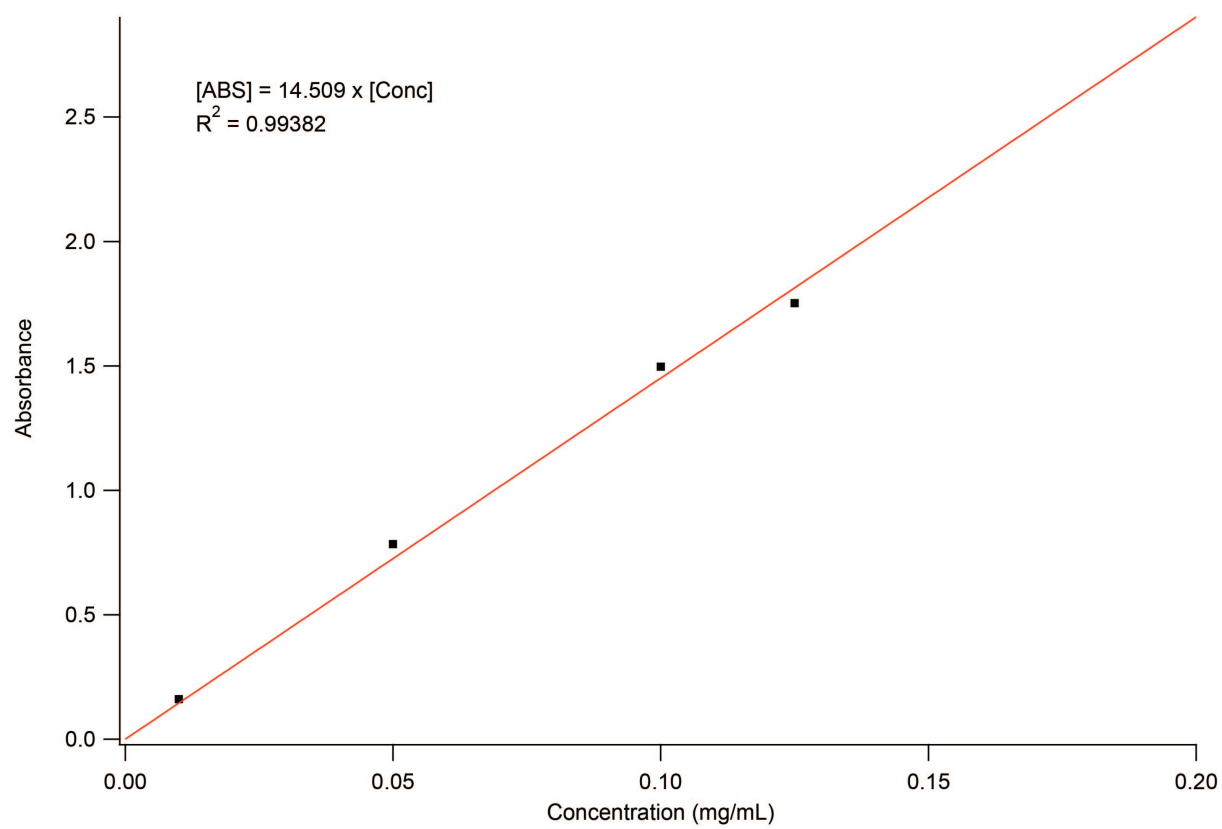


Figure 2.5: Calibration curve of CoQ10 absorbance for UV-vis.

2.1.8 Protein Loading

Previously, Coyle et al. isolated the dodecapeptide Car15 (RTYLPLPWMAAL) for its ability to bind preferentially to sp²-hybridized carbon versus sp³-hybridized carbon⁴⁷. Pyrolyzed aerogel samples were added to microcentrifuge tubes containing 0.5 mL of a 10 M solution of sfGFP-Car15, a variant of superfolder green fluorescent protein (sfGFP) with a genetically fused Car15 sequence at its C-terminus, in 20 mM Tris-HCl buffer (pH 7.5). The amount of aerogel added were chosen so that they had an approximately equivalent surface area (2.5 m²). The aerogels were incubated in the sfGFP-Car15 solution at room temperature for 12 hours. It should be noted that, to obtain a noticeable visual effect, the tested specimens had resorcinol to acetonitrile molar ratio of 1:75, and, in the case of GOA, resorcinol to GO mass ratio of 2:1 (instead of 1:200 and 4:1 respectively as used for CoQ10 loading).

2.1.9 X-ray Photoelectron Spectroscopy (XPS)

XPS was performed on a Surface Science Instruments S-Probe spectrometer (Service Physics, Bend OR) with a monochromatized Al K X-ray source. Aerogel samples were ground and taped to a silicon wafer. A low-energy electron flood gun was used for all acquisitions, and X-ray spot size was 800 x 800 μ m. Pass energy for survey spectra (to determine composition) was 150 eV. Data analysis was carried out using the Service Physics Hawk Data Analysis 7 program (Service Physics, Bend OR).

2.1.10 Raman Spectroscopy

Raman spectroscopy was performed using Coherent 532 nm (2.33 eV) laser excitation on a home built optical setup. GOA and RFA samples were adhered to a Si wafer chip with double sided adhesive tape. After laser light was directed through a 50x Mitutoyo objective and

focused on the samples, the forward scattered signal was passed through a 532 nm Thorlabs notch filter. The signal was collected with a SpectraPro HRS-500 spectrometer. Raman signal was deconvoluted into four sub-peaks typical of disordered carbon materials. The G band at 1610 cm^{-1} corresponds to the E_{2g} vibration mode in the ideal graphitic lattice, while the D band at 1360 cm^{-1} corresponds to the A_{1g} mode in a disordered graphitic lattice. In addition to those major bands, there is a D band at 1510 cm^{-1} associated with amorphous carbon, and an I band at 1240 cm^{-1} associated with ionic impurities or CC stretching in polyene-like structures⁴⁸. Following the method of Vallerot et al.⁴⁹, the D and G bands were fitted to Lorentzian profiles, and the I and D bands were fitted to Gaussian profiles. Curve fitting was performed in MagicPlot Pro software.

2.2 Results and Discussion

From SEM, both aerogels exhibit a highly porous morphology as expected, although GOA has somewhat larger pores than RFA (Figure 2.6 a,b). Multilayer graphene or graphite is embedded within GOA, as evidenced by the micron-scale, sheet-like particles that are much larger than the pores and filaments of the carbonized RF network. Bright-field TEM images reveal the irregular shape and wrinkled texture of these sheets (Figure 2.7). In contrast, RFA is more homogeneous, being comprised solely of the spherical carbon grains ($\sim 20\text{ nm}$ in diameter) that make up the matrix of GOA. SEM images of the dried aerogels after incubation with CoQ10 reveal a smoother texture and enlarged features compared to their unloaded counterparts, suggestive of species adsorption (Figure 2.6 c,d).

Nitrogen sorption analysis of the bare aerogels agrees with the electron microscopy observations (Figure 2.8). The sorption isotherm of RFA, Fig. 2.8a, shows type H1 hysteresis (IUPAC classification), characteristic of porous materials with approximately uniform spherical particles⁵⁰. GOA, Fig. 2.8b, shows type H3 hysteresis, characteristic of aggregates of plate-like particles like GO or graphene. The surface areas of RFA and GOA were 597

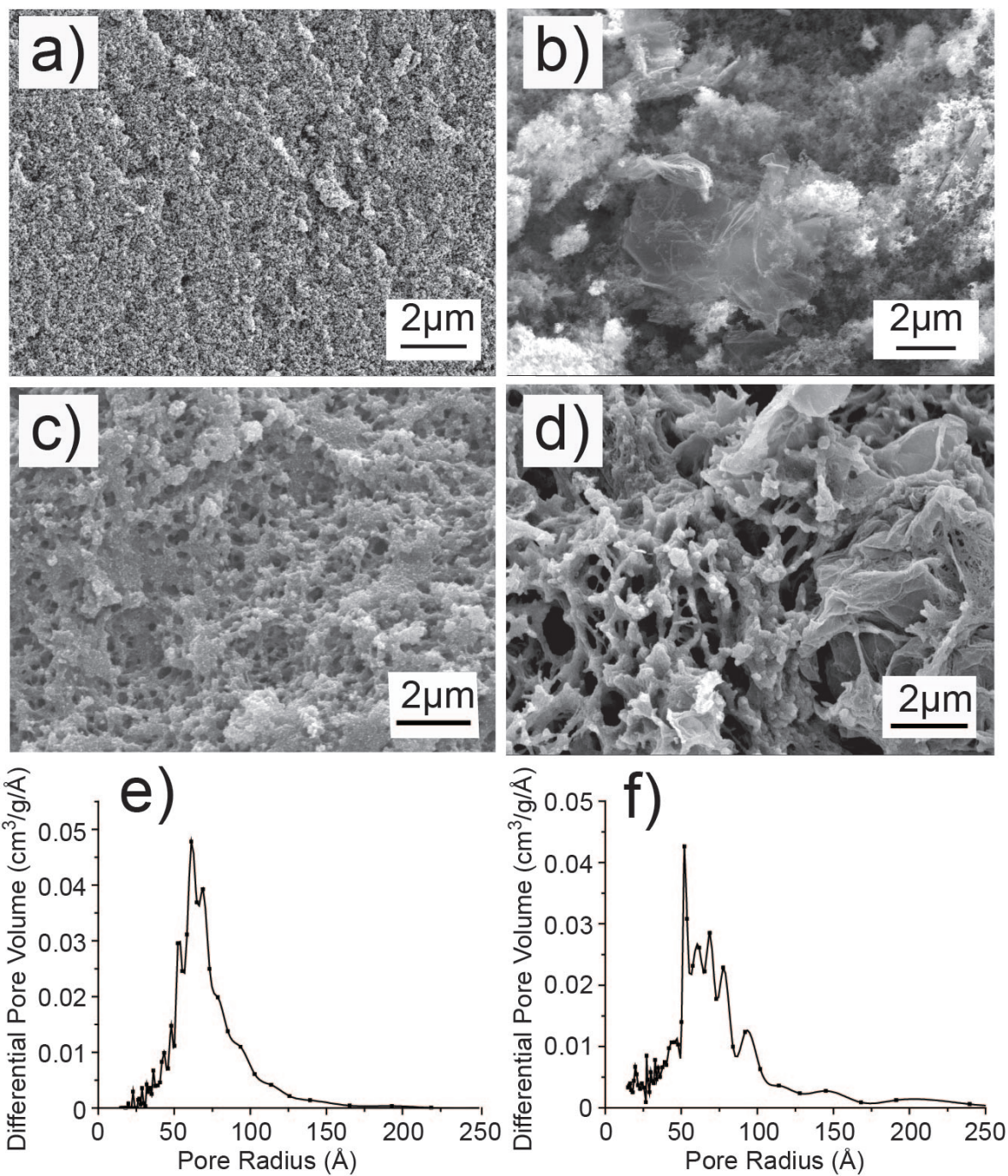


Figure 2.6: Physical characterization of aerogels. SEM images of a) RFA, b) GOA, c) CoQ10-loaded RFA, d) CoQ10-loaded GOA.

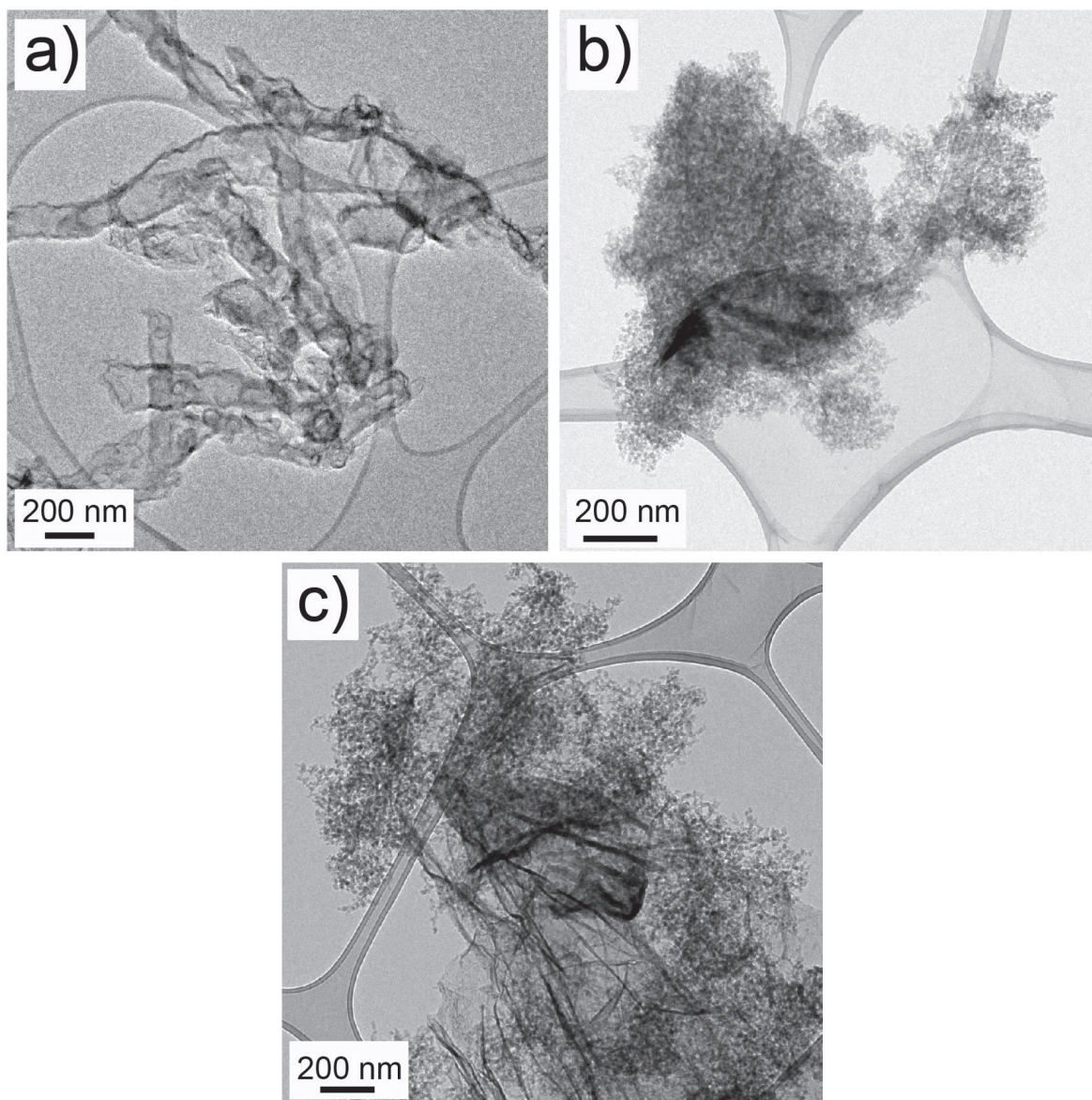


Figure 2.7: Bright-field TEM images of a) bulk CoQ10 crystals, b) CoQ10-loaded RFA, c) CoQ10-loaded GOA.

m^2/g and $792 \text{ m}^2/\text{g}$ respectively, whereas the pore volumes were similar, at $1.46 \text{ cm}^3/\text{g}$ and $1.45 \text{ cm}^3/\text{g}$ respectively. The higher surface area of GOA may be due to reinforcement of the carbonized RF matrix provided by GO, which has good mechanical strength and dispersibility, mitigating pore collapse⁵¹. Consistent with this idea, the GO-loaded aerogels exhibited less shrinkage after supercritical drying than the pure RF aerogels. Looking at the pore size distributions (Figure 2.8c, 3.8d), GOA has a slightly smaller peak pore diameter than RFA (108 and 130 Å respectively). However, GOA still has a greater fraction of large pores, with 25% of its pore volume coming from pores above 200 Å in diameter, compared to 9.4% for RFA.

XRD confirmed the presence of graphitic material in GOA and the amorphous nature of RFA (Figure 2.8e). The GO powder has its primary peak at $2\theta = 11.6^\circ$ (Figure 2.9), representing the (002) basal plane with an interlayer spacing of 7.6 Å, more than twice that of pure graphite (3.35 Å) due to the introduction of oxygen moieties that expand the lattice. Although a graphitic peak ($2\theta = 26.5^\circ$) is also present in the GO powder, it is broad and weak. On the other hand, in GOA, the lower-angle peak has disappeared while the graphitic (002) peak remains, suggesting decomposition of the oxygen functionalities and conversion of GO to graphite that is expected during pyrolysis^{41,52,42}. In contrast to GOA, RFA shows no sharp crystalline peaks, only the two broad humps centered at $2\theta = 23^\circ$ and 44° that are also visible in GOA and are typical of porous amorphous carbons^{53,54}.

The size of the graphitic crystallites in GOA was estimated using the Scherrer equation after subtracting the background and correcting for instrumental broadening. We quantified the size of the graphitic crystallites within GOA using the Scherrer equation^{55,56}:

$$L_{c,a} = \frac{k_{c,a} \lambda_{\alpha,\kappa}}{\beta \cos \theta} \quad (2.1)$$

where $L_{c,a}$ is the apparent crystallite size parallel and perpendicular to the c-axis

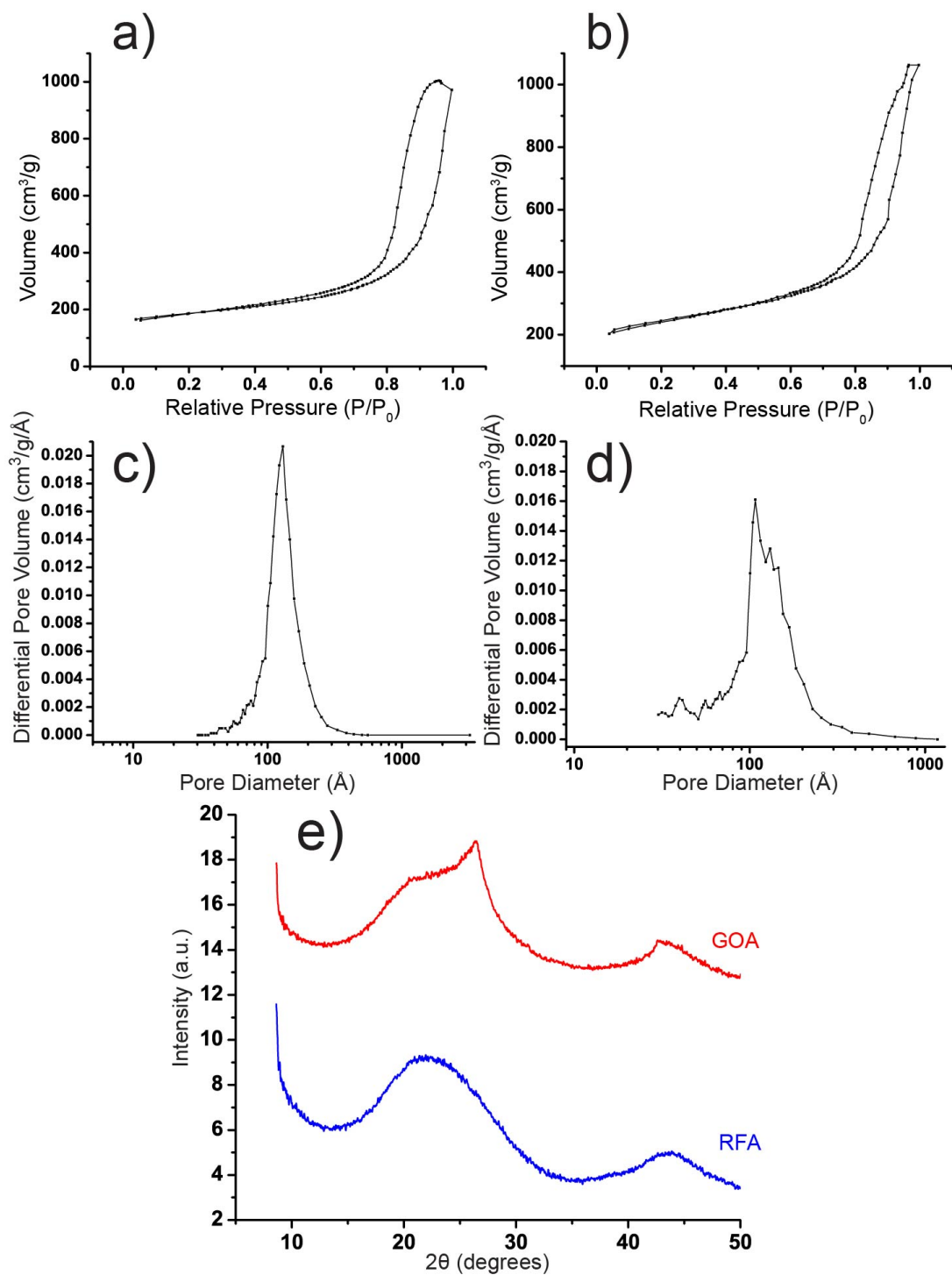


Figure 2.8: Nitrogen sorption isotherms of a) RFA, b) GOA. Pressure is relative to 1 atm. BJH pore size distributions of c) RFA, d) GOA. e) XRD of as-synthesized RFA and GOA.

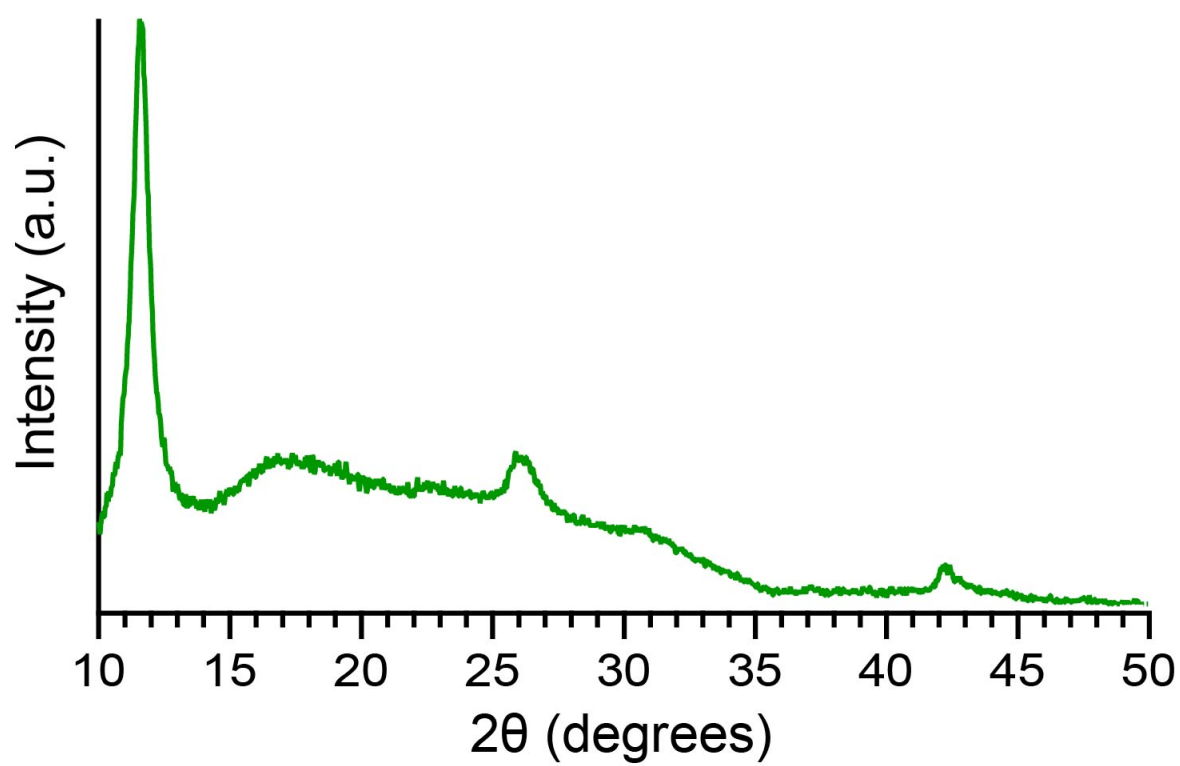


Figure 2.9: XRD pattern of as-received GO.

(i.e., out-of-plane and in-plane) respectively, $k_{c,a}$ is a particle shape- and direction-dependent factor, $\lambda_{K\alpha}$ is the X-ray wavelength (0.154 nm for $\text{Cu}_{K\alpha}$ radiation), θ is the position of the appropriate diffraction peak, and β is the full width at half-maximum (FWHM) of that peak in 2θ (radians) units. To calculate L_c , the (002) diffraction peak of graphite is used ($2\theta = 26.5^\circ$), and $k_c = 0.91$. To calculate L_a , the (100) diffraction peak is used ($2\theta = 42.8^\circ$), and $k_a = 1.84$. β was corrected for instrumental broadening using the expression:

$$\beta = \sqrt{\beta_m^2 - \beta_{ref}^2} \quad (2.2)$$

where β_m is the measured FWHM of the GOA (002) or (100) peak, and β_{ref} is the measured FWHM of the (012) or (113) peak (respectively) of a sintered corundum disc with large crystal size (NIST SRM 1976b). These corundum peaks were chosen because they occur at angles ($2\theta = 25.6^\circ$ for (012) and $2\theta = 43.4^\circ$ for (113)) close to the graphitic (002) and (100) peaks respectively. The FWHM of the corundum peaks were determined by applying a flat baseline to the diffraction pattern and fitting each peak to a Gaussian profile. This gave FWHM of 0.195° and 0.189° for the corundum (012) and (113) peaks respectively.

Determining the FWHM of the GOA (002) peak to obtain L_c required a more complex process due to the broadness and large background of the peak from the amorphous carbon. First, the diffraction pattern of RFA (taken under the same measurement conditions as GOA and having a similar amorphous carbon matrix) was subtracted from that of GOA. This eliminated much of the background but still left a sloping baseline to the left of the (002) peak, and a flat baseline to its right. We therefore applied either a linearly sloping baseline correction or a flat baseline correction, fit the peak to a Gaussian curve, and reported the crystallite sizes as a range, based on the values calculated by applying each baseline correction. The subtracted signal with the two possible baseline corrections and peak fits for (002) is illustrated in Figure 2.10 below. This analysis gives $L_c = 4.15.2$ nm which corresponds to 1215 graphitic layers. The flat baseline alone was used to fit the GOA (100)

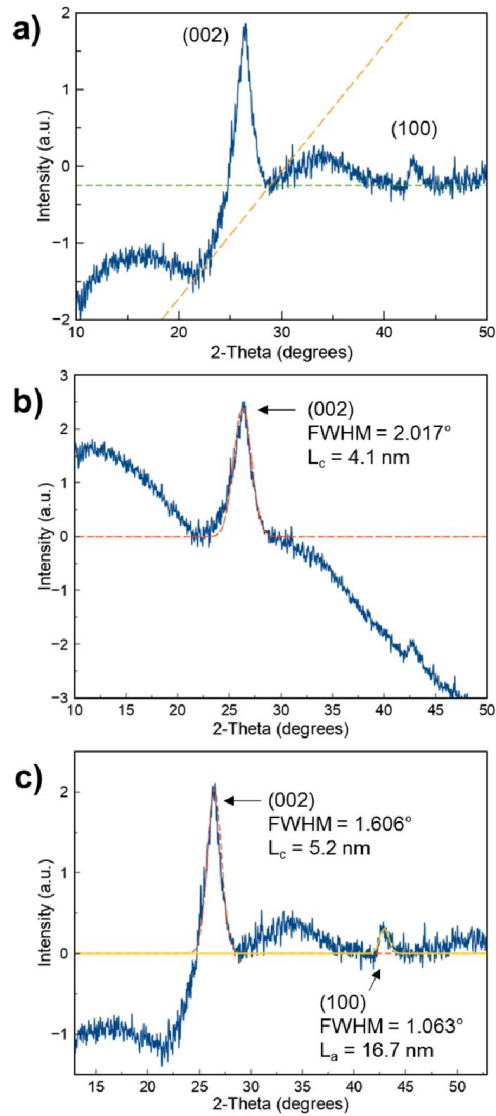


Figure 2.10: Scherrer analysis for GOA. a) XRD pattern of GOA obtained by subtracting pattern of RFA as background signal, showing prominent (002) peak at $2\theta = 26.5^\circ$ and smaller (100) peak at $2\theta = 42.8^\circ$. Sloping baseline for (002) peak (dashed orange line) and flat baseline for both (002) and (100) peaks (dashed green line) are shown. b) XRD pattern of GOA with sloping baseline subtracted from signal and (002) peak fitted to Gaussian profile for determination of L_c . c) XRD pattern of GOA with flat baseline subtracted from signal, and (002) and (100) peaks fitted to Gaussian profiles for determination of L_c and L_a respectively.

peak to a Gaussian profile (Figure 2.10(c)), from which the FWHM and L_a were obtained. This analysis gives $L_a = 16.7$ nm.

Based on this analysis, the dimension of the crystallites along the c-axis (out-of-plane) is 4.15.2 nm, corresponding to 1215 graphitic layers, whereas the in-plane dimension is 16.7 nm. We note that although flakes of micron-scale lateral size were observed in SEM (Figure 2.6b), they may have significantly smaller graphitic domain size due to defects in the lattice and residual oxygen, which are characteristic of thermally reduced GO⁵⁷. For example, phenol groups develop from the reaction of basal plane epoxides with adjacent hydroxyl groups at 400°C and can survive even at our aerogel pyrolysis temperature of 1000°C⁵⁸. XPS analysis confirmed the minor presence of oxygen in both GOA and RFA, which had average C:O atomic ratios of 15.3 and 24.3 respectively (Figure 2.11).

After loading with CoQ10, GOA gained significantly more mass than RFA (20.82.1% versus 11.92.7%, Figure 2.4b). Comparing to other adsorptive studies of CoQ10 in the literature, our loading of CoQ10 on GOA is higher than the maximum loading achieved with supercritical CO₂ solubilization and precipitation of CoQ10 onto -glucan and gum arabic powder recently reported by Couto et al. (17.50.2% and 3.61.7% respectively), but less than the maximum loading reported with a similar supercritical technique on sodium alginate (46.9%)^{59–61}. While this method can load the CoQ10 in crystalline form, it requires complex processing equipment with pressures of 200 bar, in contrast to our ambient-condition impregnation procedure. In addition, while CoQ10 loading up to 55% was recently reported on hierarchical aluminosilicate zeolites (ZSM-5) at room temperature and pressure, the adsorbed CoQ10 was amorphous, unlike our aerogels where CoQ10 remains crystalline, as described later in this section⁶². The larger uptake of CoQ10 by GOA is likely attributed to the abundance of -conjugated graphene surfaces in GOA, with which CoQ10 molecules can interact via $\pi\pi$ stacking⁶³.

Raman analysis of GOA and RFA further substantiates this hypothesis (Figure

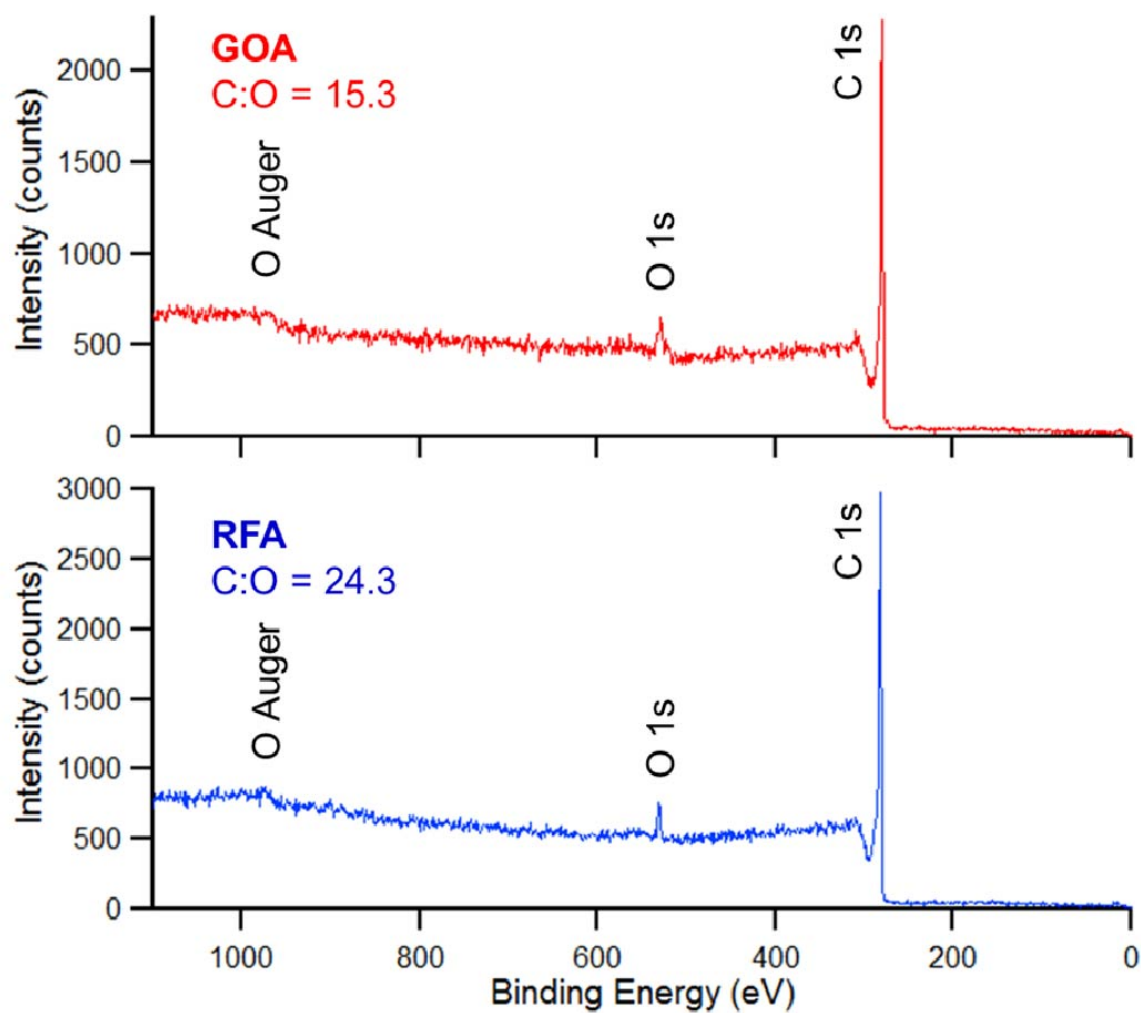


Figure 2.11: Representative XPS survey spectra of GOA and RFA with average C:O atomic ratios (calculated from 3 survey spectra performed on each sample).

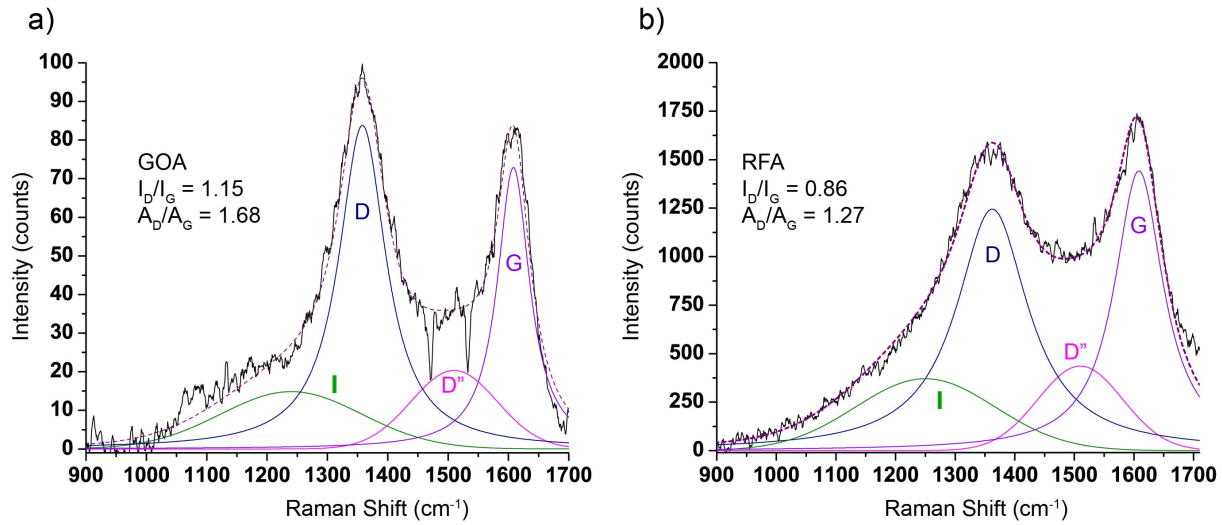


Figure 2.12: Raman analysis of a) GOA and b) RFA including the deconvoluted peaks corresponding to the D, G, D', and I bands. The average intensity ratio and area ratio are reported for each sample.

2.12). Fitting the characteristic D and G bands to the Raman spectrum and determining their intensity (I_D/I_G) and area (A_D/A_G) ratios can lend insight into the amount of disordered carbon contained in the two samples. The position of the G peak at 1610 cm^{-1} (compared to 1580 cm^{-1} for bulk graphite), along with the prominent D band (characteristic of A_{1g} vibrations in disordered graphite) in GOA, are consistent with the presence of nanocrystalline graphite as observed in XRD⁶⁴. In addition, RFA had a lower I_D/I_G (RFA: 0.86; GOA: 1.15), lower A_D/A_G (RFA: 1.27; GOA: 1.68), and broader G band (FWHM for RFA: 99.5 cm^{-1} ; GOA: 65.3 cm^{-1}) than GOA. These differences are consistent with changes in phonon modes as defects are introduced into the graphitic lattice and the proportion of sp^3 bonds increases (up to 20%)⁶⁴. Finally, while these ratios cannot quantify the sp^2 and sp^3 content unless there is some relationship between the sp^2 and sp^3 phases in the material⁶⁵, the A_D/A_G ratio is inversely proportional to the in-plane size of the graphitic crystallites in the

material L_a , which can be approximated by⁶⁶:

$$L_a(nm) = \frac{560}{E_l^4} \left(\frac{A_D}{A_G} \right)^{-1} \quad (2.3)$$

where E_l is the excitation laser energy in eV, which in this case is 2.33 eV (wavelength = 532 nm). This analysis gives an in-plane crystallite size of 11.3 nm for GOA, similar to the value obtained from XRD analysis (16.7 nm).

To further corroborate this reasoning beyond direct characterization of GOA, similar aerogel incubation experiments were performed in buffered aqueous solutions of superfolder green fluorescent protein (sfGFP) fused to Car15, a peptide of amino acid sequence RTYLPLPWMAAL that binds specifically to sp^2 carbon⁴⁷. After 12 h, the original light green coloration had disappeared for the protein solution containing GOA, whereas the color persisted in the solution supplemented with RFA (Figure S10), showing enrichment of sp^2 carbon in GOA. Besides π stacking, the favorability of GOA for CoQ10 may come from hydrogen bonding between the carbonyl groups of CoQ10 and residual phenol groups on the pyrolyzed GO. Finally, the presence of larger pores and more surface area per unit mass in GOA would also facilitate uptake of CoQ10 from solution.

The mass loading of CoQ10 within the aerogels can determine whether adsorption is greater than one molecular monolayer, if the surface areas of the aerogel and CoQ10 molecules are known. We used the Spartan14 molecular modeling software with the CPK space-filling model to calculate the surface area and volume of one CoQ10 molecule (depicted in Figure 2.2), which are 1078.05 Å² and 1033.58 Å³ respectively. The longest distance of the molecule is 55.38 Å and the width of the side chain is 3.8 Å, whereas the width of the quinone is 7.57 Å. With this information, along with the nitrogen sorption measurements of the aerogels surface area and pore volume, the maximum possible theoretical mass loading for both monolayers and multilayers of CoQ10 molecules on aerogels were then calculated. The theoretical values

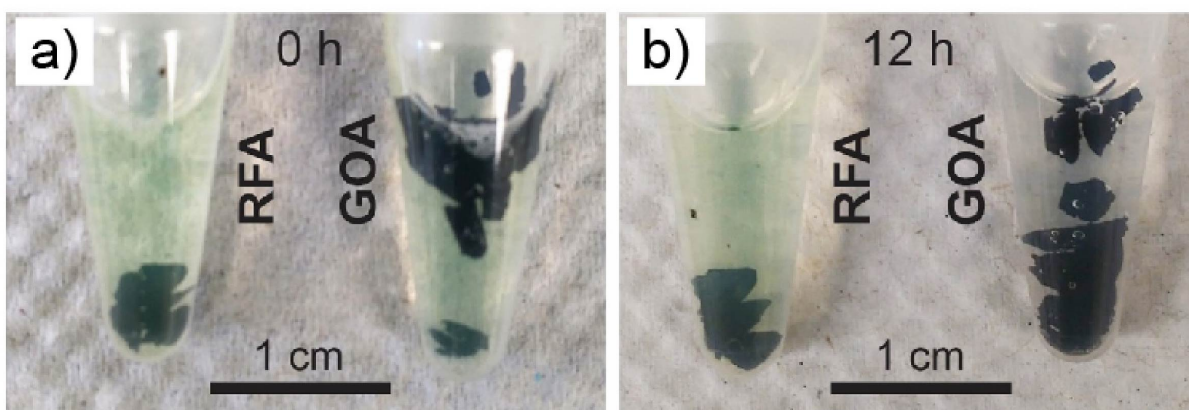


Figure 2.13: Carbon aerogel samples immersed in sfGFP-Car15 solution a) immediately after inserting aerogels; b) 12 h after inserting aerogels showing loss of green color for solution containing GOA, but not for solution containing RFA.

for monolayer or multilayer CoQ10 were much higher than the experimental CoQ10 mass loading (Figure 2.3), as drug loading of the aerogel from a liquid phase will be hindered by diffusion through the porous structure.

The loss of CoQ10 from bulk solution was quantified via UV-vis spectroscopy. The UV-vis spectrum of CoQ10 has two main absorption peaks at 210 nm and 273 nm^{67,68}. The intensity of the 273 nm absorption band is observed to decrease following addition of the aerogel (Figure 2.14), suggesting adsorption of CoQ10 within the aerogels pores. The time dependence of this decrease in absorption was monitored over 12 hours to analyze loading kinetics. The UV-vis measurements were analyzed by both pseudo first-order and pseudo second-order models (Figure S11). The pseudo first-order rate expression of Lagergren is⁶⁹:

$$\ln(q_e - q_t) = \ln(q_e) - k_t t \quad (2.4)$$

where k_t is the rate constant (per min) and q_e and q_t are the amounts of CoQ10

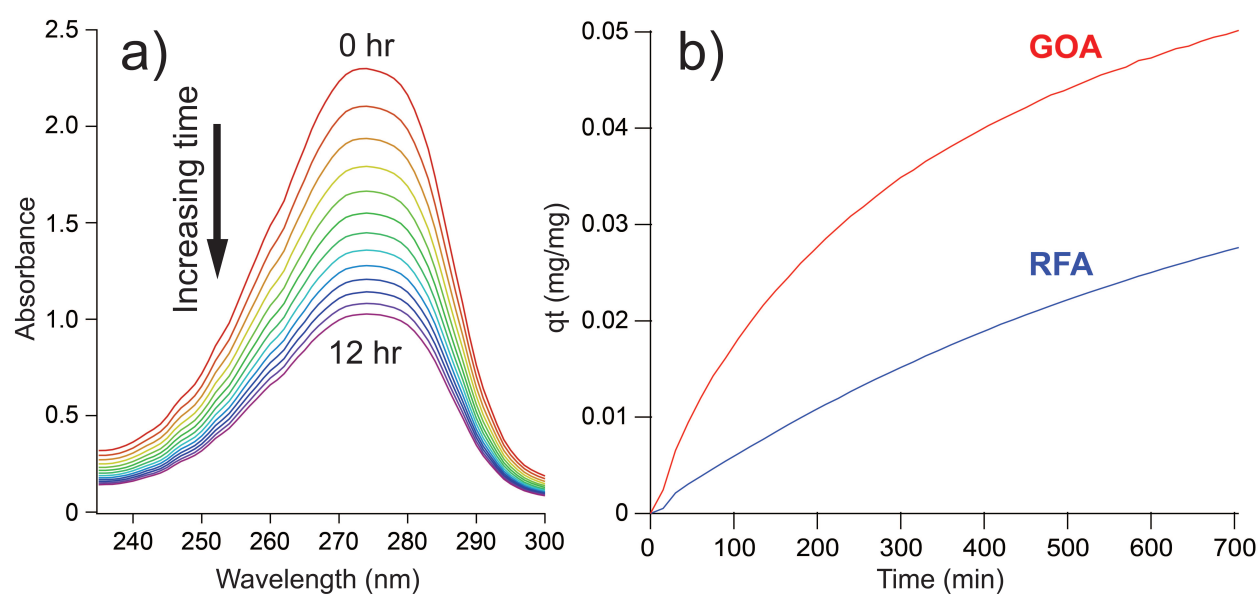


Figure 2.14: Kinetic analysis of CoQ10 loading on aerogels. a) UV-vis spectrum of GOA over 12 h in CoQ10 solution showing decrease in intensity of absorption band centered at 273 nm. b) Plot of adsorbed concentration of CoQ10 in aerogels over time as derived from UV-vis measurements.

adsorbed onto the aerogel at equilibrium and at time t respectively (mg/mg). A straight line plot of $\ln(q_e - q_t)$ versus t fits experimental data to this model, which is generally valid for conditions far from saturation⁷⁰. It should be noted that the equilibrium adsorption capacity (q_e) is required to fit the data; however, q_t often remains unknown due to slow adsorption processes⁷¹. For this study, q_t was determined by the equation:

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (2.5)$$

where V is the volume of solution (mL), m is the mass of aerogel (mg), and C_0 and C_t are the initial CoQ10 concentration and concentration at time t respectively (mg/mL). q_e was thus approximated by the concentration at the end of the experiment ($t \approx 12$ h) and is redefined as q_{12} . Concentrations were derived from absorbance measurements based on a calibration curve of CoQ10 solutions with various known concentrations (Figure 2.5). As seen in the plot of q_t versus time (Figure 2.14b), GOA takes up CoQ10 much more rapidly than RFA, and q_e of GOA is almost double that of RFA (Table 2.1), consistent with the mass gain experiments and lipophilic nature of the pyrolyzed GO. The pseudo second-order kinetic model is expressed in linearized form as⁷¹:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{12}^2} + \frac{1}{q_{12}} t \quad (2.6)$$

where k_2 is the rate constant (mg aerogel/mg CoQ10 per min). The plot of t/q_t versus t shows a linear relationship for second order kinetic phenomena. Unlike the pseudo first-order model, it predicts behavior over the whole range of adsorption and does not require q_{12} to be known for fitting⁷².

The pseudo first-order and second-order rate constants, along with a calculated equilibrium adsorption capacity ($q_{12}(\text{calc})$) for both models were obtained from the coeffi-

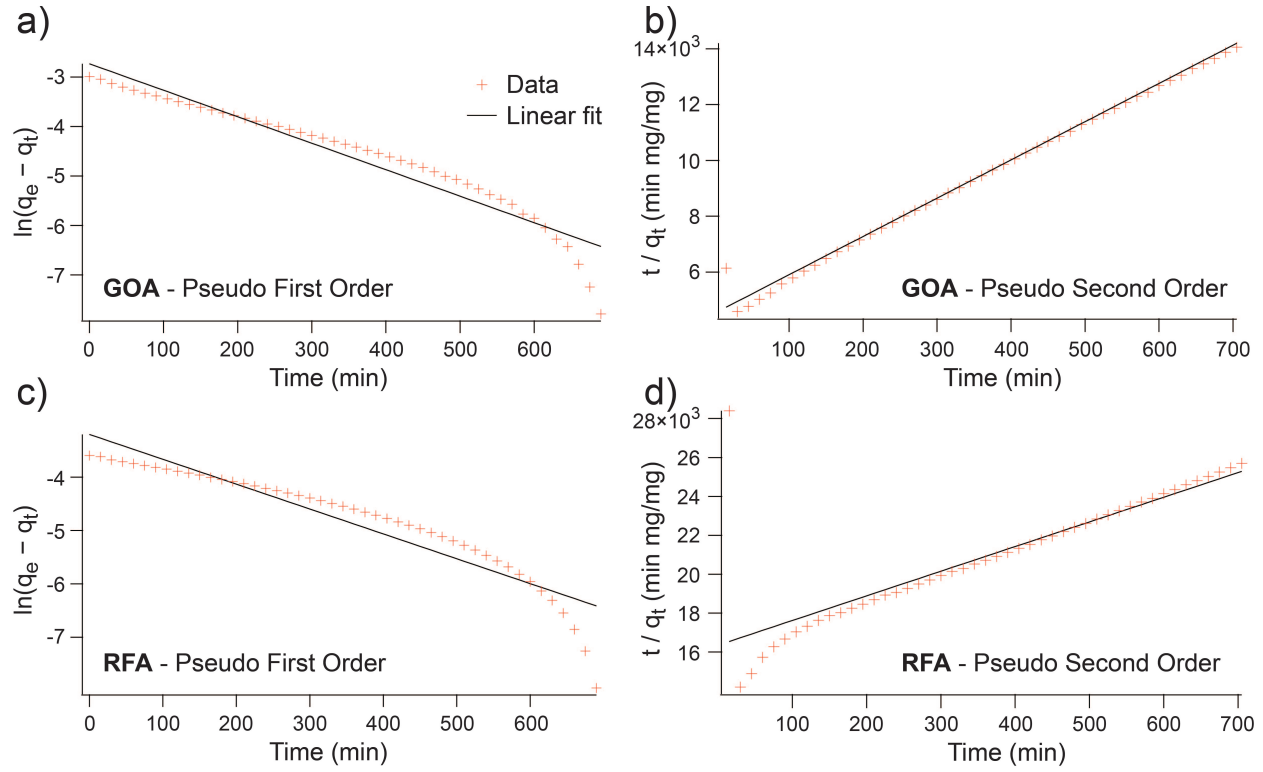


Figure 2.15: Pseudo first-order and pseudo second-order kinetic fits for CoQ10 adsorption on (a, b) GOA and (c, d) RFA.

Table 2.1: Kinetic parameters for CoQ10 adsorption on aerogels

Sample	Experimental q_{12} (mg/mg)	Pseudo First Order Model			Pseudo Second Order Model		
		k_1 (min^{-1})	$q_{12\text{calc}}$ (mg/mg)	R^2	k_1 (min^{-1})	$q_{12\text{calc}}$ (mg/mg)	R^2
RFA	0.0274	0.0107	0.0408	0.876	0.0789	0.0790	0.664
GOA	0.0498	0.0123	0.0651	0.921	0.0415	0.0729	0.993

cients of the linear fits described above. The results with correlation coefficients (R^2) are presented in Table 2.1. For GOA, the pseudo second-order model is more appropriate as its corresponding R^2 is over 0.99, compared to 0.921 for the pseudo first-order model. However, neither model is a good fit for the overall RFA dataset. Rather, it appears that RFA follows first-order kinetics at short times ($t \leq 120$ min), but second-order kinetics at longer times. The initial first-order kinetics in RFA suggest that the rate-limiting step is film diffusion⁷³. This is consistent with the smaller average pore size of RFA, which would slow penetration of CoQ10 into the aerogel matrix relative to GOA. On the other hand, the pseudo second-order behavior in both aerogels at longer times suggests that the rate-limiting step is associated with chemisorption, in which electrons are shared or exchanged between the CoQ10 molecules and aerogel⁷². Additionally, the calculated q_{12} for both models are high compared to experimental q_{12} values. This is likely due to the slowness of the adsorption process; as seen in Figure 2.14b, the concentration of CoQ10 on both aerogels continued to increase even at 12 h. XRD was also performed on the loaded carbon aerogels to check the crystallinity of the CoQ10 (Figure 2.16). The XRD pattern of our as-received CoQ10 powder is observed to be highly crystalline and matches previous reports^{15,74}. Interestingly, the loaded GOA and RFA show crystalline peaks at similar positions that are not present in the unloaded counterparts and obviously differ from the as-received CoQ10, which has many more peaks. It is worth noting that an earlier XRD study by Katsikas and Quinn⁷⁵, on a sample of CoQ10 prepared by slow cooling from its liquid phase, showed only eight reflections from $7.862.40 \text{ \AA}$ ($2\theta = 11.337.5^\circ$), indicating that CoQ10 can adopt simpler crystal structures. In addition, the peaks are slightly more intense for the loaded GOA than the loaded RFA, consistent with the higher CoQ10 mass loading of the former. Although the diffraction patterns of the loaded aerogels do not completely match any previously reported phase of CoQ10, four of the peaks at $2\theta = 22.0^\circ$, 26.2° , 29.6° , and 32.1° match reflections observed by Katsikas and Quinn, whereas the three reflections that they observed at lower angles are not visible in the aerogels. We hypothesize that the narrow pores of the aerogel have a confining effect on the CoQ10 molecules that prevents them from adopting long-range order when crystalliz-

ing, thus explaining the absence of the low-angle (large d-spacing) peaks. This makes sense considering that the longest dimension of the free CoQ10 molecule (55.38 Å) is on the same order as the peak pore radii of the aerogels.

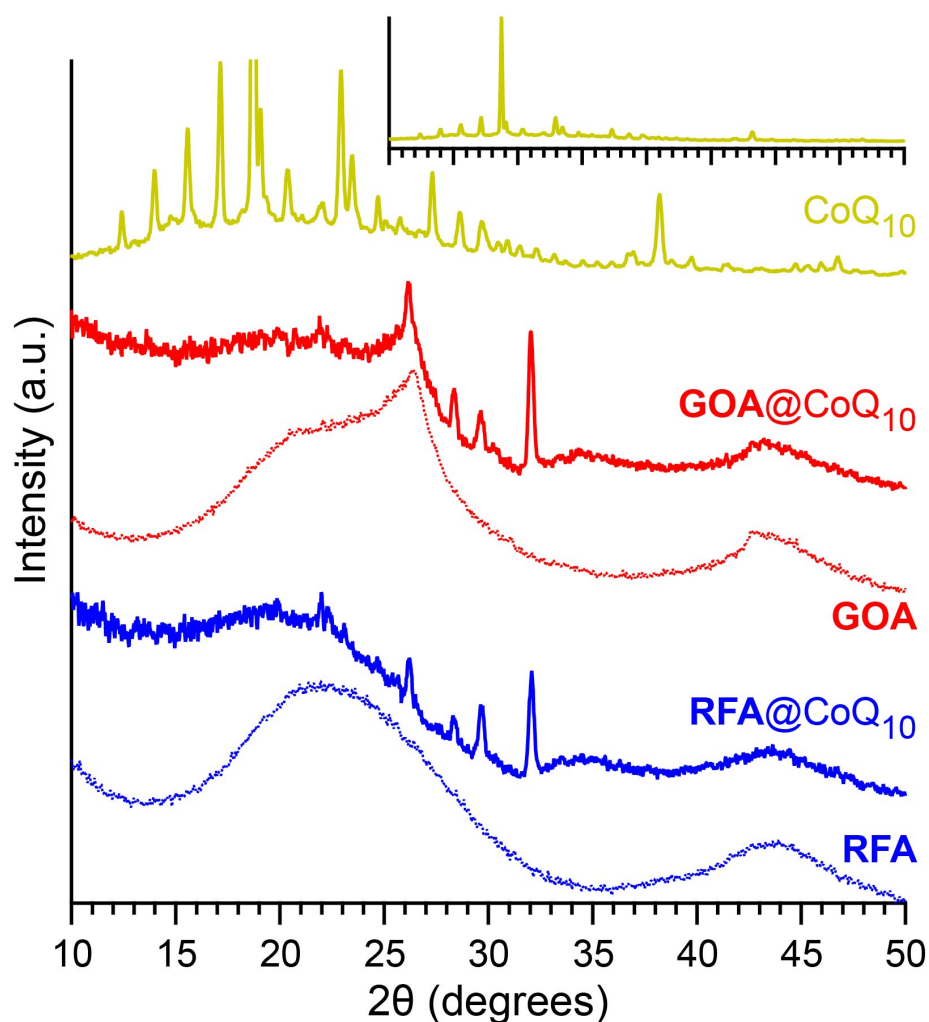


Figure 2.16: XRD patterns of as-received CoQ10 powder and carbon aerogels. Inset shows full scale of CoQ10 diffraction pattern for same range of 2θ . For aerogels, solid lines denote aerogels loaded with CoQ10 and dotted lines denote their unloaded counterparts.

2.3 Conclusions

In summary, we have demonstrated the loading of a key lipophilic pharmaceutical, CoQ10, on carbon aerogel hosts using a simple, solution-phase impregnation technique. The carbon aerogels are biocompatible and can be synthesized by a rapid, scalable technique. Mass gain and spectroscopic studies confirm that graphene oxide, when added to and pyrolyzed with the carbon aerogel precursors, greatly enhances the aerogels loading capacity and rate of uptake for CoQ10. We attribute this improvement to the highly lipophilic nature of the sp^2 -hybridized, π -conjugated graphene surfaces provided by the pyrolyzed GO. Furthermore, the loaded CoQ10 forms a unique crystalline phase on both pure amorphous carbon aerogels and aerogels containing pyrolyzed GO, providing several potential advantages for drug delivery applications, such as slower, sustained release, as well as the possibility to control the microstructure of CoQ10. More broadly, our platform can easily be tailored to other important pharmaceuticals, simply by incorporating additives into the carbon aerogel during synthesis that can favorably interact with the drug of interest.

Chapter 3

MOLECULAR DOPING OF HPHT SYNTHESIZED NANODIAMOND

As of the date of this dissertation’s publication, this work is currently in preparation for submission.

We developed a molecular doping approach based on hexamethylenetetramine (HMT) to demonstrate the creation of nanodiamonds containing a large concentration (0.5 atomic %) of nitrogen point defects following extreme high-pressure, high-temperature (HPHT) synthesis within a laser-heated diamond anvil cell. Energy-dispersive X-ray spectroscopy (EDS) measurements confirm the nitrogen content within the recovered nanodiamonds is ~ 5 times higher than a nanodiamonds synthesized in control experiments without HMT molecular dopants. Photoluminescence from the negatively charged nitrogen vacancy (NV^-) center is observed to increase by a factor of 5 from doped materials at room temperature. The zero phonon line (ZPL) of NV^- centers was observed to be broader (FWHM= 0.03 eV) and the lifetime shorter (~ 8 ns) in comparison with what has been reported bulk single crystals with low doping concentrations. EDS measurements also observed dopant atoms of the noble gas argon within the recovered nanodiamonds. Theoretical *ab initio* quantum cluster calculations are used to predict the absence of an optical dipole transition of the argon-split-vacancy in diamond which is consistent with experimental results. Calculations are also reported for the B-center in nanodiamond which may form under these HPHT conditions but remains to be observed experimentally.

Diamond is a wide-bandgap semiconductor with remarkable chemical⁵, electronic⁶,

and optical properties⁷⁶. In particular, a large number (>100) of heteroatomic color centers⁷⁷ have been discovered in natural diamonds and several of these have shown promise for applications in quantum information science including single photon emission⁷⁸, quantum information processing^{7,79–82}, magnetic-^{83,84}, temperature-^{8,85}, and pressure-^{1,86} metrology, and also bio-fluorescent imaging^{9,87–89}. However, the deterministic doping of diamond with well-defined color centers remains an outstanding synthetic challenge.

In contrast with silicon, diamond is a metastable phase with an extremely compact crystal lattice consisting of covalent sp^3 bonds. Consequently, the diffusion of many dopants in diamond⁹⁰ does not occur until above 1000 K⁹¹, a temperature at which diamond will graphitize under ambient pressures. This resistance to impurity migration required the development of several synthetic approaches for the creation of color centers in diamond that are now utilized as industry standards for commercial scientific use.

Although molecular high explosives have also been reported to dope detonation nanodiamonds (DND) with heteroatomic point defects, along with a number of other metallic species⁹² originating from the explosion metallic chamber, DND materials normally must be treated following synthesis to remove surface impurities⁹³. Although large quantities of DNDs can be produced, the non-equilibrium conditions of detonation processing makes it challenging to deterministically form more complex, polyatomic point defects.

DND materials are also used frequently to seed the growth of diamond through chemical vapor deposition (CVD). The combination of CVD, which is the industry standard to produce pristine diamond substrate, followed by ion implantation of a desired dopant, and thermal annealing has been highly successful in producing single atom vacancy color centers in diamond⁹⁴. However, the high energies of the technique necessary to bombard the small crystal lattice, cause subsequent lattice damage that is difficult to remove completely through annealing⁹⁵. Given the statistical distribution of final ion locations following implantation⁹⁶, it is difficult to create complex, polyatomic defects in CVD diamond, like the NE8 center.

The NE8 center consists of a substitutional nickel atom (Ni_C) bound to four substitutional nitrogen (N_C) atoms in a tetrahedral configuration. This defect has been characterized in natural diamonds, but has not been synthesized directly⁹⁷. Additionally, hydrogen atoms are known to deactivate color centers within CVD diamond materials⁹⁸. Removing hydrogen from CVD diamond is difficult due to the large amount of hydrogen in H_2 and CH_4 processing gases.

More recently, high-pressure, high-temperature (HPHT) processing has been reported to produce diamonds with a wide range of color centers^{86,99,100} at temperatures and pressures similar to those that exist in Earth’s mantle^{101,102}. The HPHT conditions involved in the synthesis of natural diamonds can be reproduced experimentally using approaches based on either a multi-anvil press (MAP)^{103,104} or a diamond anvil cell (DAC)^{105,106}. Of the over 100 optically active point defects discovered so far⁷⁷, a majority were found in HPHT grown diamond, including those with more complex poly-heteroatomic compositions. Nanodiamonds are also produced from HPHT diamonds that are grown in bulk within a multi-anvil press or CVD processing after subsequent ball-milling to nanoscale sizes. Ball milling has been observed to increase intrinsic strain within the recovered nanodiamonds, which adversely affects their optical properties, and are limited to bulk diamond doping strategies. Nanodiamonds have also been grown directly within a DAC with the potential advantage that strain can be relaxed under quasi-hydrostatic HPHT growth conditions⁹⁹.

Molecular doping at HPHT conditions is an emerging approach for the formation of point defects in nanodiamond which has been used recently in the synthesis of silicon- (SiV), nitrogen- (NV), germanium- (GeV), and tin- (SnV) vacancy centers based on tetraethylorthoxysilane⁸⁶, additional silane molecular dopants¹⁰⁷, adamantane¹⁰⁸, germanium molecular dopants¹⁰⁹, tin molecular dopants¹¹⁰. In this prior work the dopant molecules contain one heteroatom; however, to date the use of molecules with more than one heteroatom per molecule remains unexplored. Here we investigate the molecular dopant hexamethylene tetramine (HMT, $\text{C}_6\text{N}_4\text{H}_{12}$) which serves as a polyatomic source of N_C dopants during the

extreme synthesis of nanodiamonds within a laser-heated diamond anvil cell. The HMT molecule has an adamantane structure with a tetrahedral distribution of nitrogen atoms with a stoichiometric nitrogen to carbon ratio is 2:3, which has the potential to create a large number of heteroatomic nitrogen point defects within the resulting nanodiamonds. Argon serves as the quasi-hydrostatic pressure transmitting medium inside the DAC. Following the synthesis, the nanodiamonds are characterized using pressure-dependent photoluminescence spectroscopy, pressure-dependent time-correlated single photon counting (TCSPC) lifetime spectroscopy, selected area electron diffraction (SAED), energy-dispersive x-ray spectroscopy (EDS), and electron energy loss spectroscopy (EELS) TEM. X-ray fluorescence spectroscopy is used to demonstrate that the concentration of nitrogen increases by approximately 5 times above background levels as compared to undoped samples synthesized through similar pressure and temperature conditions. Further analysis of the photoluminescence spectroscopy is used to correlate the increase in atomic nitrogen dopants with a 5-fold increase in optical luminescence from nitrogen vacancy centers as compared to an undoped sample.

3.1 Experimental

3.1.1 Synthesis of HMT Doped Carbon Aerogels

Resorcinol-formaldehyde (RF) aerogels were synthesized to a similar scheme established previously as seen in Figure 1a. Approximately 0.3638g (0.03304 mol) of resorcinol (R), 0.4920 mL (0.006608 mol) of formaldehyde (F), and 0.393 mL 1 M HCl were added to a falcon tube containing 13.11 mL of acetonitrile (AN) yielding ratios of: R:F 1:2, R:HCl 2:1, and R:AN 1:76. Approximately 0.140 mL of a 0.1 M solution of hexamethylenetetramine (HMT) was added to the precursor reaction mixture and the whole tube was vortexed to mix. After three hours of sonication, the characteristic hot-pink gel began to form. The round end of the tube was cut off with a razor blade and the gel inside was gently pushed into a 50-mL falcon tube holding 30 mL of ethanol. Over the next three days, the ethanol is changed out

three times to replace acetonitrile in the pores with ethanol. On the third day, the gels were washed and kept in DI water for three days before going through the freeze dry process. A quartz tube containing the HMT doped RF aerogel was placed into the furnace where flanges were tightened on the ends of the tube and nitrogen flowed through at a rate of 0.4 L min^{-1} . Samples were then pyrolyzed at 1000°C for approximately 4 hours to form the HMT doped carbon aerogel.

3.1.2 ICP-MS elemental quantification

Trace elemental analysis was performed with a Thermo Jarell Ash ICP-Emission Spectrometer according to the EPA 200.7 methodology¹¹¹.

3.1.3 Combustion analysis to quantify carbon and nitrogen

Combustion analysis was performed with a Perkin Elmer Co. 2400 series CHNS Organic Element Analyzer according to the 29-2.2 methodology¹¹¹.

3.1.4 Analytical Mie

Solution of the Laplace equation in spherical coordinates for an electron probe source positioned both inside and outside of a sphere with the measured frequency dependent nano-diamond dielectric function produces a potential that is the sum of both direct Coulombic and induced plasmonic contributions. The action of the induced potential, which encodes both surface and bulk responses, back on electron probe does work on the electron itself resulting in a closed form analytic expression for the electron energy loss probability per unit frequency. Figure 3.8 shows the resulting electron energy loss probability for varying sphere radius. The fact that the theory is classical precludes the excitation of multi-quanta

surface and bulk plasmon responses, thereby limiting the electron energy loss probability to one quantum excitations only.

3.1.5 Characterization of HMT Doped Carbon Aerogels

The carbon aerogels were characterized through a variety of techniques including proton NMR (HNMR), FTIR, and TEM. To perform the HNMR experiment, a small sample of the precursor RF-aerogel reaction mixture was placed into an NMR tube with D₂O. To perform the FTIR experiment, an ATR attachment was utilized, and a small quantity of RF aerogel was placed into a Vertex 70 FTIR while the sample chamber was purged with nitrogen for about 30 minutes.

3.1.6 DAC Preparation

A Boehler-Almax DAC was utilized for the HPHT synthesis and the spectroscopic characterization of the nitrogen doped nanodiamonds. The anvils, which were type Ia diamonds, have a height of approximately 1.40 mm, and a culet diameter of 0.300 mm (Figure 3.2a). Epoxy resin was utilized to glue a 0.250 mm thick rhenium gasket to the gasket support table, which holds the gasket in place between the top and bottom diamond anvils. The gasket was indented to a thickness of 0.035 mm by advancing the anvils together when a blank gasket was placed in between them. An electric discharge machine and a tungsten wire 0.080 mm in diameter was utilized to drill a hole in the center of the dimpled gasket.

3.1.7 Nanodiamond Synthesis and Characterization

After pyrolysis, the carbon aerogels were gently ground into a powder with aluminum foil. Using a Marzhauser Wetzlar, type MCL-3 nanomanipulator with a tungsten tip, aerogel

samples and ruby chips were moved into the makeshift chamber created from the above protocol. The top anvil was slowly advanced towards the chamber until it reached a distance of 0.060 mm above the bottom anvils culet. Argon was then condensed with liquid nitrogen in a makeshift chamber. The chamber was checked if it was sealed through the photoluminescence R2 line of ruby with a 532nm Coherent laser and a liquid nitrogen cooled Princeton spectrophotometer (as seen in Figure 3.4a). After laser light was directed through a 50x Mitutoyo objective (NA: 0.55, WD: 13.0 mm, half-angular aperture: 33) and focused on the samples, the forward scattered signal was passed through a 532 nm Thorlabs notch filter. After all spectra were collected, wavelength and intensity calibration spectra were collected through the same acquisition parameters and optical setup as when the measurements were taken. The wavelength calibration was performed with a HG-1 Mercury Argon Calibration Light Source and the intensity calibration was performed with a e HL-2000-CAL Calibrated Tungsten Halogen Light Source. Once sealed, the chamber was taken to a pressure of 27 GPa and verified again through the signature ruby spectrum. The DAC chamber was aligned to a 1070nm iPG laser capable of up to 100 W of CW power. Multiple rounds of photothermal heating were performed to convert as much of the amorphous carbon to nanodiamond. During conversion, the chamber began to glow bright with white light and Planck emission data was collected with an Ocean Optics UV/Vis spectrophotometer and analyzed for temperatures reached during nanodiamond synthesis. Based on fitting the spectral energy density of the collected spectra during photothermal heating, after calibrating the intensity, to the planck's blackbody radiation function, the temperature is found by utilizing Wein's displacement law. Once the nanodiamond had been made, photoluminescence spectra of NV^- centers was taken with the same 532nm laser and spectrometer as mentioned above. Lifetime measurements of NV^- centers were pumped with a 470 nm pulsed diode laser (PDL-800 LDH-P-C-470B, 300 ps pulse width) with a repetition rate of 10 MHz. The emission was filtered through a 50/50 dichroic beamsplitter and a 500-600 nm bandpass filter (500 LP and 600 SP). Photoluminescence from the sample was directed to a Micro Photon Devices (MPD) PDM Series single photon avalanche photodiode with a 50 μm active area for Time-resolved

photoluminescence measurements.

3.1.8 TEM Characterization

After the DAC was brought to ambient pressure and released, the liquid argon returned to its gaseous state and diffused out of the chamber, leaving behind the laser heated material. Using electrostatic forces exerted from a Marzhauser Wetzlar nanomanipulator, the samples were transferred to the copper TEM grid. Bright field images and selected area diffraction patterns were acquired with a JEOL 2200FS TEM equipped with a Gatan Oneview camera, operated at 200 kV. The image magnification was calibrated with a MagICal silicon standard, and the diffraction camera lengths were calibrated with a polycrystalline aluminum standard. The EDS maps were acquired at an operating voltage of 60 kV with a Nion UltraSTEM 200X equipped with a Bruker Xflash 100 energy dispersive x-ray (EDS) detector. Net count maps for the K edges of C, N and Ar are calculated with Bruker Esprit 2.0 software.

3.1.9 Ab Initio Calculations

Nanodiamonds were constructed to be nearly spherical with a bulk fcc lattice parameter of $a = 0.357 \text{ nm}$ ¹¹² according to the procedure presented in Ref. 113. Hydrogen atoms were used to passivate the surface carbon atoms and to saturate surface dangling bonds. Although other moieties are generally present on the surface, chemical treatments of the surface can provide a more uniform passivation.¹¹⁴ A $\text{C}_{121}\text{H}_{104}$ (diameter $\sim 1.2 \text{ nm}$) cluster was used as a starting model for the doped diamond systems. This nanodiamond size is similar, though smaller, than those available through either detonation or laser-heated diamond anvil cell synthesis methods.^{99,114,115} Given that the Bohr exciton radius for diamond is $\sim 1.6 \text{ nm}$ ¹¹⁶, the electronic and vibrational properties for these diamond systems are expected to exhibit quantum confinement effects.^{113,117} The B-aggregate (N_4V) was created by replacing five

carbon atoms near the center of the nanodiamond along the $\langle 111 \rangle$ axis of the model with four nitrogen atoms and positioning the vacancy at the center resulting in a center with a local T_d symmetry within the C_{3v} host lattice. The argon-vacancy (ArV) system was constructed in a similar way to that of the xenon split-vacancy,^{118?} where two carbon atoms were removed from the center of the diamond model, and an Ar atom placed into the center space between them forming a local D_{3d} environment before optimization. The systems were fully optimized, and vibrational analysis was performed to verify the obtained geometries were true minima. Geometries were considered optimized with both the forces [maximum and root-mean-square (rms) of the force 0.000450 and 0.000300 Hartree/Bohr, respectively] and displacement [maximum and rms displacement 0.00018 and 0.0012 Bohr, respectively] values were below the threshold criteria. Calculations were performed using the Gaussian¹¹⁹ electronic structure software package. The ground-state electronic structures were obtained by solving the Kohn-Sham equation using the hybrid Becke, 3-parameter, Lee-Yang-Parr (B3LYP) functional^{120–122} with a 6-31G(d) basis. The theory level employed has been previously validated for the description of the electronic structure, optical properties, and vibrational structures of both pure diamond and those doped with nitrogen and silicon vacancies of similar dimensions.^{86,113,117}

3.2 Results and Discussions

Amorphous carbon has been shown to help lower the kinetic barrier of diamond phase conversion as compared to other carbonaceous materials like graphite^{123,124}. The synthetic scheme of fabricating the doped amorphous carbon aerogel precursor is shown in Figure 3.2a. Based on the synthesis of Pekala *et al.*⁴⁰, the resorcinol (R) and formaldehyde (F) polymerize via a ortho- and para-directed poly-electrophilic addition to the phenol ring, through a Lederer-Manasse mechanism^{125,126}, also known as hydroxymethylation. Then, the intermediates proceed through a condensation reaction to form either methyl- or methylether-bridges between adjoining resorcinol molecules. Although the original synthesis of the organic aerogel utilized

alkaline conditions, heat, and almost 7 full days to gel the product, it has been previously demonstrated that an ultra-fast synthetic scheme—including an acid catalyst (HCl) and the polar, organic solvent acetonitrile serves to dramatically speed up the polymerization reaction¹²⁷. The acid catalyst serves to accelerate the hydroxymethylation by increasing the positive charge on the electrophile, formaldehyde, which then performs nucleophilic attack on the π -conjugated system of resorcinol. Further protonation of the hydroxymethyl group leads to either unimolecular water cleaving to form an *o*-quinone methide-type intermediate, or a bimolecular reaction involving the direct attack of a carbocation at the CH_2OH_2^+ site by the π -system of another resorcinol molecule¹²⁷. During gelation, and even after solvent exchange and super-critical drying, a bright pink/deep brick red color persists in these organic aerogels, only changing color if different dopants are added to the polymerization reaction^{41,128}. This deep red color, also depicted in Figure 1a, has been postulated to originate from “locked in” *o*-quinone methide intermediates in the gel matrix. As the polymerization continues, the RF polymer begins to condense into microporous carbon sols of approximately 10-20 nm in diameter⁴⁰. These individual sols then form an interconnected network of larger mesopores¹²⁹ which contain the solvent, acetonitrile. Solvent exchange of acetonitrile with ethanol enables super-critical drying with CO_2 while maintaining the pore structure of the RF hydrogel. After super-critical drying, the doped RF-aerogel is pyrolyzed under argon at 1000 °C for approximately four hours, to drive off O and H in the form of H_2O , CO, or CO_2 .

Sol-gel processing has been employed previously to deliberately incorporate nanostructures and molecular dopants within the carbon aerogel matrix^{41,86,128}. The overall approach in this work is to incorporate a poly-heteroatomic molecular dopant into the carbonaceous precursor matrix with the goal of creating specific point defects in diamond such as the B-center, a carbon vacancy surrounded by a tetrahedral group of nitrogen atoms. Hexamethylene tetraamine (HMT, or hexamine) served as the desired molecular dopant since the stereochemistry and stoichiometry of the molecule closely matches that of the B center¹³⁰. A comparison of HMT and the B-center can be found in Figure 3.2. As seen in Fig. 3.1 and

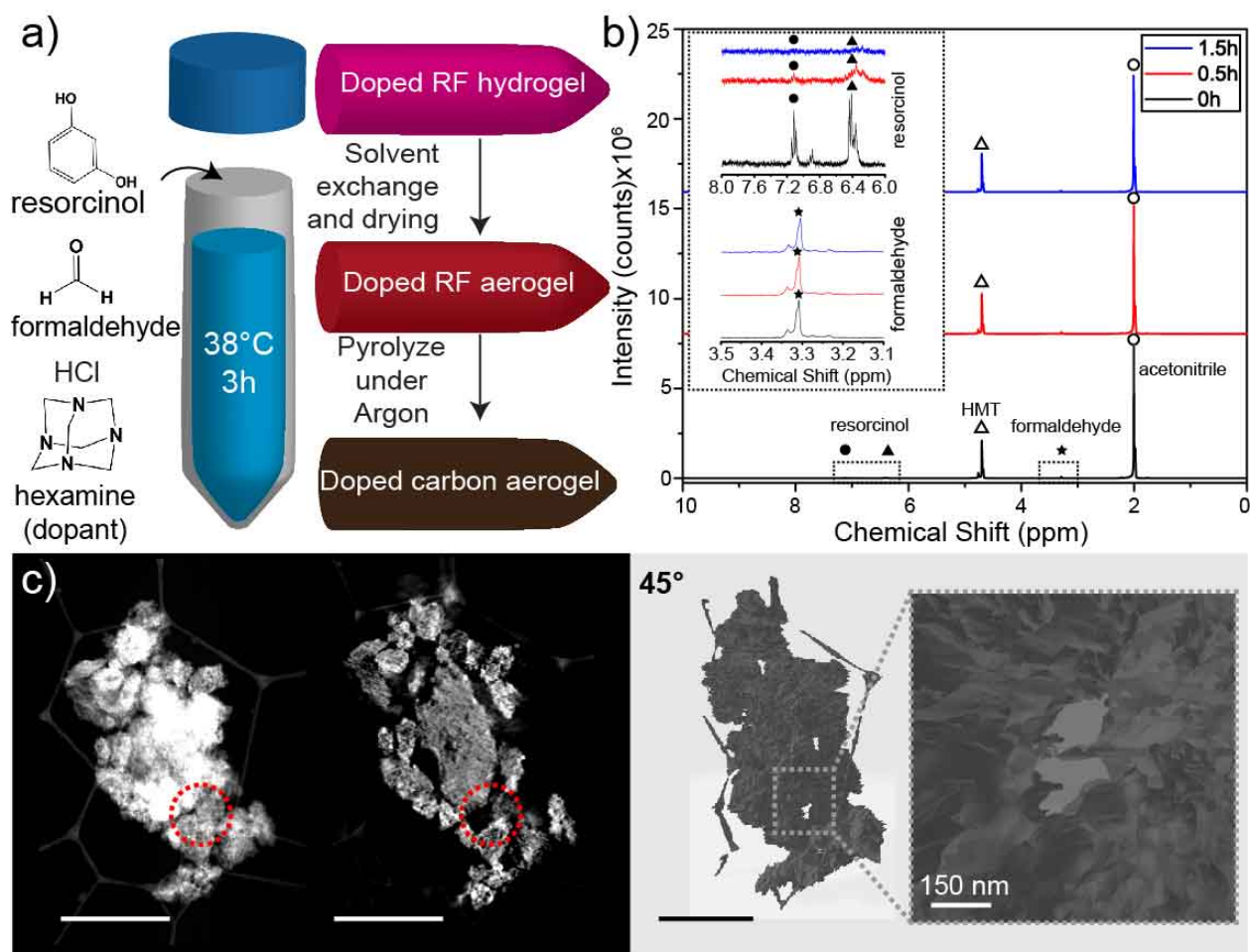


Figure 3.1: Formation of Carbonaceous Precursor (a) Synthetic scheme of fabricating the HMT-doped carbon aerogel (HMT-CA) from molecular precursors. During the acid catalyzed (HCl) polymerization of resorcinol (top) and formaldehyde (second from top), the molecular dopant, hexamethylenetetraamine (HMT, third from top) is introduced (b) Time varied ^1H NMR demonstrating no untimely decomposition of reagents during polymerization. Because polymerization of the RF-gel was essentially complete within 1.5 hours, ^1H NMR spectra were not collected after 1.5 hours. (c) Scanning transmission electron microscopy (STEM) tomographic analysis of the pyrolyzed HMT-CA on top of lacey carbon. Descriptions going from left to right panel. A representative image from STEM tomography. Next, a cross sectional tomogram slice depicting the porosity of the HMT-CA. Red circles indicate where hidden pores of the STEM tomography still become illuminated when analyzing the tomographic cross-sectional slices. Next, a 3D reconstruction of the HMT-CA sample tilted 45° to demonstrate rough surface morphology. The inset of 3D reconstruction further demonstrates the rough morphology of the amorphous surface of the as pyrolyzed HMT-CA. The scale bar in the bottom left corner of each image is 1 μm , unless otherwise noted.

3.2, hexamine ($\text{C}_6\text{H}_{12}\text{N}_4$) has an adamantane-like cage structure with 6 sp^3 carbon and 4 sp^3 nitrogen, however there is no void space within the “cage”. HMT is added at a concentration of 1 μM in the initial acetonitrile solvent, establishing a preliminary nitrogen-to-carbon molar ratio of 5620 ppm.

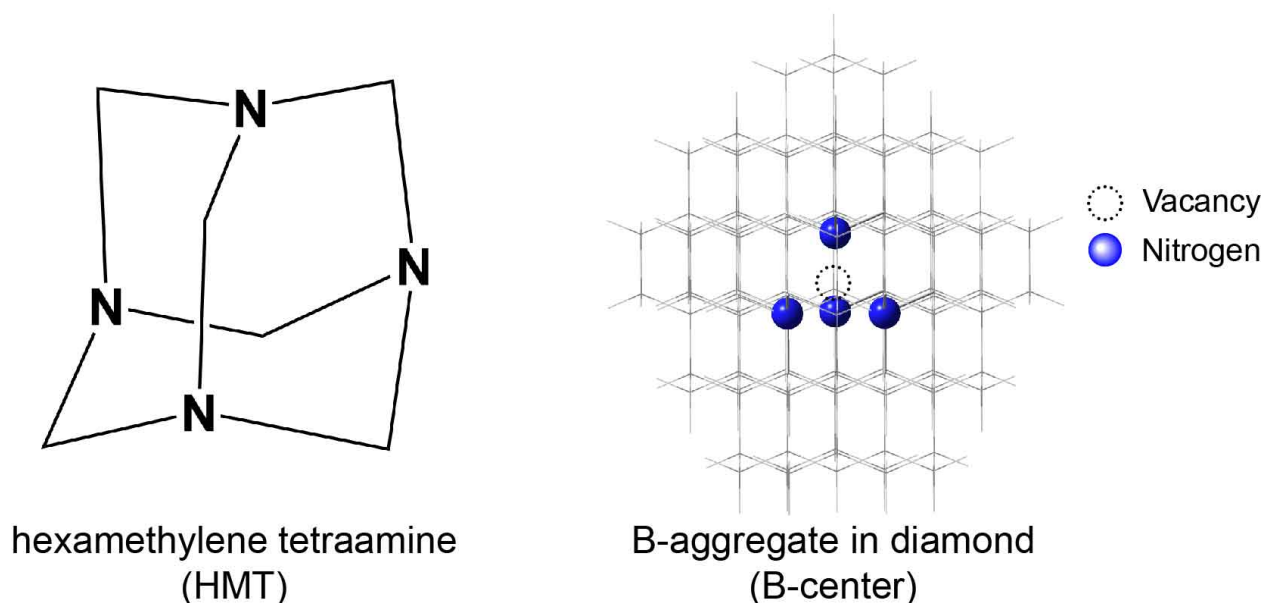


Figure 3.2: Model of the molecular dopant (HMT) used in this study compared to the desired point defect in diamond (B-center).

Historically, HMT has been shown to decompose under acidic conditions into ammonia and formaldehyde, and since the RF aerogel polymerizes under acidic conditions, it is important to monitor whether or not HMT decomposes over the course of the RF-gelation reaction. To observe whether HMT would decompose during the polymerization, time dependent ^1H -NMR was performed, as seen in Figure 3.1b. Over the course of the polymerization, the characteristic peaks for resorcinol (6.4 ppm, 7.1 ppm) decreases while the peak representing HMT (4.7ppm) remains constant as seen in Fig. 3.3. Although HMT normally

decomposes into both formaldehyde and ammonia under acidic conditions, there were no discernible peaks for either ammonia or formaldehyde at any point in the reaction. These observations indicate that HMT does not decompose during the RF hydrogel formation.

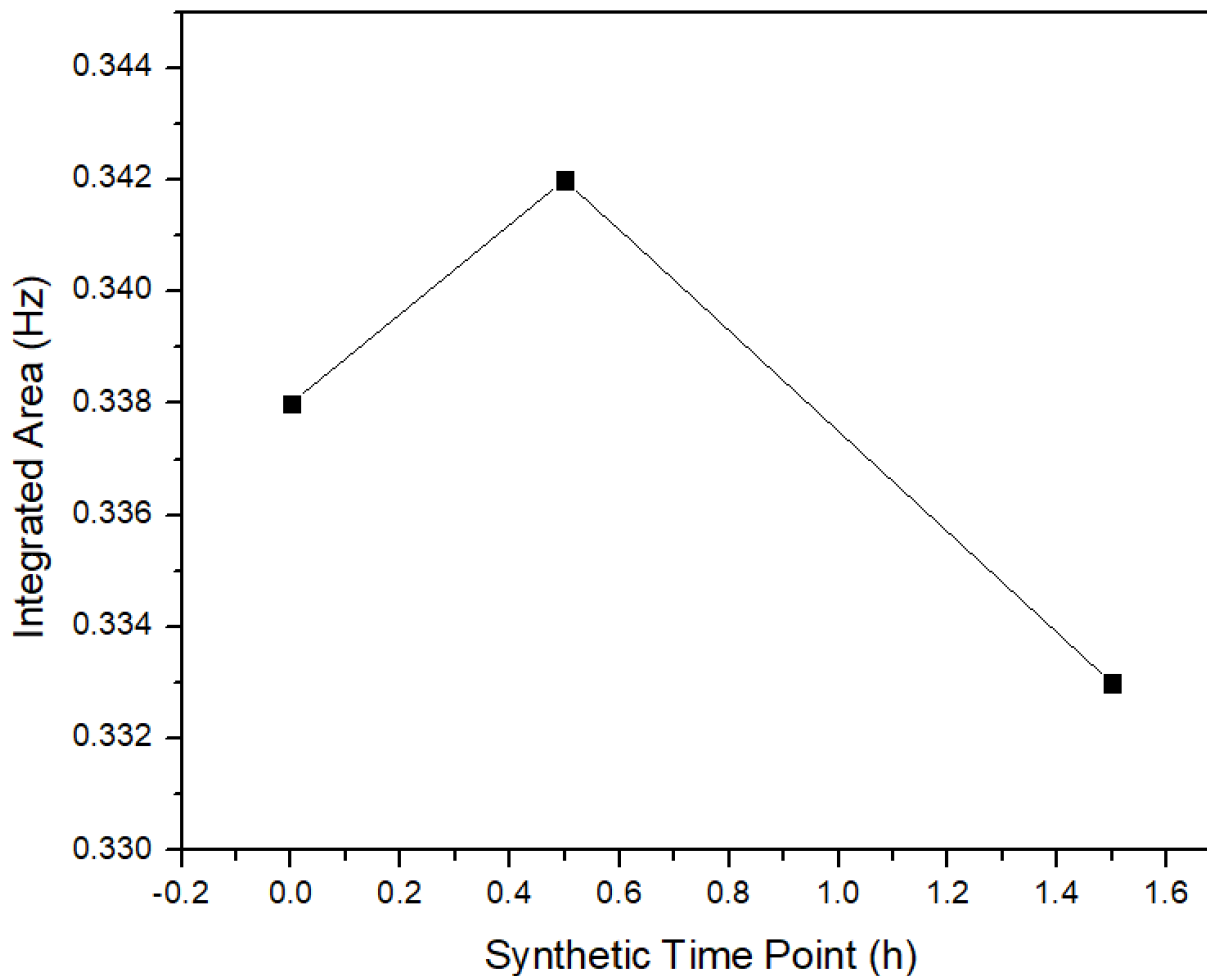


Figure 3.3: Integrated area of HMT 1HMNR signal at varying synthetic time points.

Hexamine is also known to decompose at temperatures of about 200 °C and above¹³¹. Given the organic aerogel is pyrolyzed at 1000 °C under argon for four hours, HMT molecules can be assumed to decompose during pyrolysis. Previous studies have characterized the identities, the rates, and the activation energies of the thermally decomposed products of HMT

mixed with phenolic-formaldehyde resins¹³¹ from 200-1100 °C. As the pyrolysis is performed at a temperature of 1000°, this study has provided invaluable insight into the question of how HMT decomposes within the carbon aerogel matrix. Two major conclusions came from this study, the first being that gaseous substances like CO₂, CO, H₂, O₂, NH₃, and NO₂ evolved during pyrolysis. Since pyrolysis is typically performed in vacuum or in an inert atmosphere, the oxygen containing gases must come from the reaction of the methyl-bridges and water dehydrated from the hydroxyl groups of resorcinol. The carbon from resorcinol and formaldehyde, however, were most likely not eliminated as gases and stayed behind to form coke¹³¹. The second major conclusion from these studies is that the carbon residue left behind after pyrolysis had acted as a catalyst for HMT decomposition and was rich in nitrogen due to the decomposition of HMT¹³¹. We hypothesize that HMT molecules will significantly increase the amount of nitrogen doping within the pyrolyzed amorphous carbon aerogel, and that these nitrogen atoms will produce substitutional nitrogen point defects within nanodiamonds following HPHT processing.

To further quantify the amount of trace elements and nitrogen in the HMT CA samples, ICP-ES and combustion analyses of both the doped and undoped CA samples were performed as seen in Tables 3.1 and 3.2. In comparing the overall nitrogen amount between doped and undoped samples, the HMT-doped CA has approximately seven times the amount of nitrogen as the undoped sample, and a post-pyrolysis N:C molar ratio of 7680 ppm.

Tomographically reconstructed imaging of inorganic and composite aerogel matrices have been performed with X-rays^{132,133} and TEM¹³⁴ since the early 2000's. From these early investigations, TEM tomography has become a powerful tool to model the morphology of amorphous, complex materials at nano- and atomic resolutions¹³⁵. Figure 3.1c shows a scanning transmission electron microscopy (STEM) image and a corresponding 3-dimensional (3D) tomographically reconstructed cross section of the resulting carbon aerogel to observe its microstructural porosity following pyrolysis. The red dotted circle illustrates the internal porous nature of the carbon aerogel revealed from the tomographic reconstruction that

Table 3.1: Summary of ICP-ES Elemental Quantification of as Pyrolyzed HMTCA and Undoped Carbon Aerogels

Element	HMTCA ($\mu\text{g/g}$)	Control ($\mu\text{g/g}$)
Al	27.1	490
B	TR	8.03
Ba	TR	TR
Ca	321.5	161.9
Fe	170	108
Mg	76.39	TR
Mn	5.23	2.94
Na	399	TR
Ni	ND	17.5
P	TR	45
Pb	TR	TR
S	TR	96.7
Si	72.43	80.51

Table 3.2: Summary of Combustion Analysis of Pyrolyzed HMTCA and Undoped Carbon Aerogels

Element	HMTCA (wt%)	Control (wt%)
C	50.24	41.7
N	0.768	0.19

would otherwise be hidden from typical STEM imaging. Based on the reconstructed images depicted in Fig. 3.1c, after pyrolysis, the sample maintains the amorphous scaffolding similarly seen in the unpyrolyzed sample. The final two panels of Fig. 3.1c, a 3D reconstruction and an inset of a selected area of the 3D reconstruction, show that the surface of the carbon aerogel has a rough texture.

After the HMT-doped carbon aerogel (HMT CA) was synthesized, small pieces were placed inside a DAC chamber, along with ruby chips for pressure sensing, as seen in Figure 3.4a. Liquid argon was condensed into the chamber to serve as a quasi-hydrostatic pressure transmitting medium. The hydrostaticity of the DAC chamber was confirmed by ruby fluorescence following the procedures found in Chai and Brown¹³⁶. As the pressure increased, the liquid argon, which infiltrated the pores of the HMT CA, transformed into solid (face-centered cubic) argon and helped maintain the carbon aerogel's pore structure during the subsequent laser heating. After a pressure of around 25 GPa was confirmed via ruby fluorescence, a high-power continuous wave (CW) 1070 nm laser was directed to the HMT CA pieces to convert the amorphous carbon to nanocrystalline diamond. A previous study¹³⁷ showed that, upon laser heating, the noble gas pressure medium melts, lowering the local thermal conductivity to form a thermally-insulating, super critical fluid surrounding the HMT CA sols which drives the phase conversion of the amorphous HMT CA to diamond. A high CW irradiance is produced by focusing the NIR laser to a near-diffraction limited spot on the carbon aerogel using a long working distance objective lens. Focusing the laser creates high temperatures that produce bright Plank emission that is analyzed using a UV/Vis spectrometer. The spectra were then fit using Wein's approximation to determine the estimated temperature (~ 2000 K), during the conversion of the amorphous HMT CA to diamond.

Figure 3.4b compares the photoluminescence (PL) spectra collected from a HMT CA sample after laser heating at high-pressure (red), and the same material recovered from that region and transferred to a TEM grid at ambient pressure (blue), and an undoped

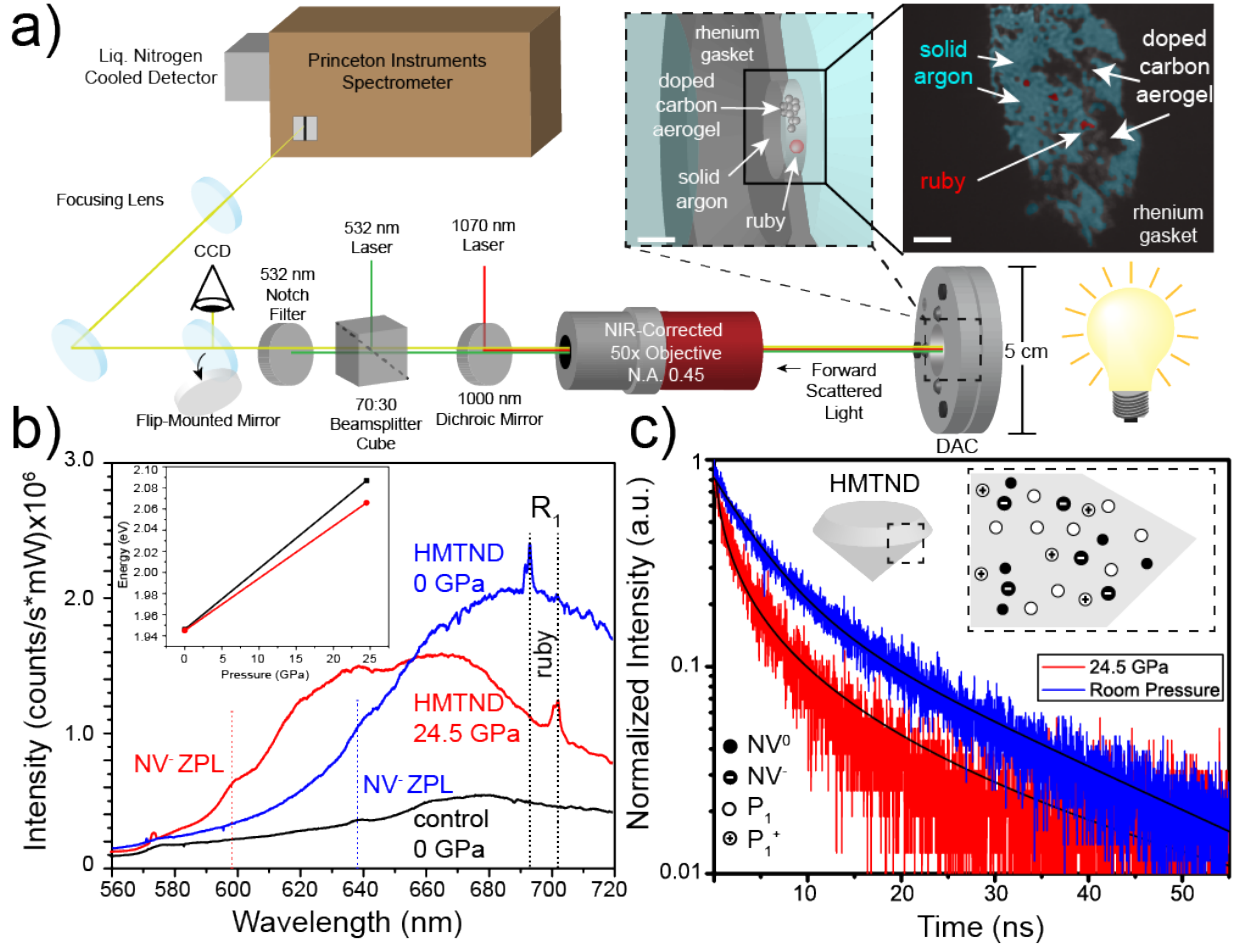


Figure 3.4: (a) Optical schematic of the photothermal HPHT conversion of amorphous HMT-CA inside a DAC chamber. Inset to the far right depicts a false colored optical micro-graph of the experimental DAC chamber, before any laser heating, at a pressure of 24.5 GPa. Further seen in the DAC inset to the left of the false colored image, a rhenium gasket contains the HMT-CA samples (~ 50 microns in size), ruby chips, and the pressure transmitting medium, solid argon. The scale bar in these insets are 50 microns. (b) Pressure dependent photoluminescence of NV- at 24.5 GPa (red) and ambient pressure (blue) of the same location of the HMT-CA after HPHT treatment is compared to a undoped sample (black) that was synthesized under similar conditions. The spectra have been denoted HMT-doped nanodiamonds (HMTND) with the corresponding pressure during acquisition of the spectrum. The R1 peak of ruby is indicated in the red and blue spectra with the black dotted lines. The zero phonon lines (ZPL) have also been labeled with the red and blue dashed lines. The inset compares the experimentally fitted NV- ZPL (red), as it shifts from the highest to the lowest experimental pressures, with the literature NV- values at those pressures as reported by Doherty et al.¹. (c) TCSPC lifetime signal of the same NV- locations as (b). The inset represents the different factors that could contribute to the difference in average lifetimes between the highest and lowest pressures.

control sample (black line, 20-25 GPa and ~ 1800 -3000K).

The PL spectra suggest the formation of the negatively charged nitrogen vacancy center (NV^-)¹. This defect is one of the most characterized color centers in diamond^{138,139}. This center comprises of a substitutional nitrogen atom (C_N), also known as a P1 center, next to a carbon vacancy (C_V) that has a C_{3v} rotational symmetry along the [111] diamond crystallographic axis. NV^- centers form from the neutral nitrogen vacancy center (NV^0) following electron tunneling from another local P1 center to the NV^0 center, leading to an overall negative charge. The electronic structure of the NV^- has been determined through electron spin resonance techniques: the visible emission originates from an optical dipole transition between the ^3E state to the ^3A ground state, which has an energy difference of 1.94 eV. The defect's Huang-Rhys parameter¹⁴⁰ is 3.7, indicating that the majority ($\sim 97\%$) of its emitted photons are red-shifted from the zero phonon line (ZPL) into phonon overtones at wavelengths between ~ 637 nm to ~ 800 nm at atmospheric pressure. Also seen in Fig. 2b is a small peak at 574 nm. Although the ZPL of the neutral nitrogen vacancy (575 nm) also appears in this region, the origin of this peak is from the diamond anvil Raman¹⁴¹. There is also a singlet-singlet transition in the near-infrared at approximately 1.18 eV due to a transition between ^1A to ^1E levels. Spin manipulation allows intersystem crossing to these singlet states, and forms the basis of spin initialization in quantum information science applications¹⁴².

The characteristic line shape of NV^- is shown in each plot, including its broadened zero phonon line (ZPL) and its broad distribution of phonon overtones. The intensity of all spectra were normalized by the experimental acquisition time and laser power. Comparing the blue and black spectra, which were collected with identical equipment and similar irradiances, a higher density of NV^- centers in the HMT-doped CA than the control sample. It has been previously shown that atmospheric nitrogen readily adsorbs in carbon aerogel micro- and mesopores¹²⁹. Adsorbed nitrogen would then become trapped by the solid argon during laser heated conversion to diamond, thus easily contributing to the appearance of

NV^- in the control sample seen in Figure 3.4a. Because HMT was deliberately doped during the polymerization reaction, even though it has already been discussed to decompose at the pyrolysis temperatures, the nitrogen from the HMT still contributes to the overall increase in nitrogen vacancy density from the HMT CA.

The red spectrum in Figure 3.4b illustrates blue shifted emission from nanodiamonds at 24.5 GPa in comparison with their spectra at room pressure. Reports from the literature indicate that the NV^- center is susceptible to pressure variation and the ZPL shifts linearly by a gradient of $5.75 \text{ meV GPa}^{-1}$ under hydrostatic conditions¹. As hydrostatic pressure is applied to the diamond lattice, the lattice contracts isotropically, thus compressing the equilibrium nuclear coordinates of the NV^- center. Responding to this compression, the unpaired electron spin density also contracts, which increases the electronic spin-spin interactions of the ground state, $^3\text{A}_2$, thus blue shifting the ZPL¹. Using this slope, the position of the ZPL at each of the pressures in this study were predicted and matched with the experimental ZPL Lorentzian fit to further verify that the emitting center was indeed the NV^- point defect. This comparison can be seen in the inset of Fig. 3.4b. The black line indicates the predicted ZPL location at 24.5 GPa and ambient pressure calculated from the gradient reported in Doherty *et al.*¹. The red line depicts the ZPL location at the same pressures, and has a gradient of $4.94 \text{ meV GPa}^{-1}$. Precise fitting parameters for the highest and lowest pressure NV^- PL spectra can be found in Fig. 3.5.

There is significant broadening of the NV^- center's ZPL for both the high (red) and low (blue) pressure spectra in comparison with literature data for bulk, low-strain diamonds¹³⁸. Manson *et al.*¹⁴³ have reported the impact of Stark shifting on the ZPL's FWHM and also the lifetime of the NV^- center. Doping with HMT leads to a significant increase in the amount of nitrogen doping. The broadness observed in the HMT-doped nanodiamonds most likely is related to Stark shifting due to positively-charged P1 centers in close proximity to the NV^- .

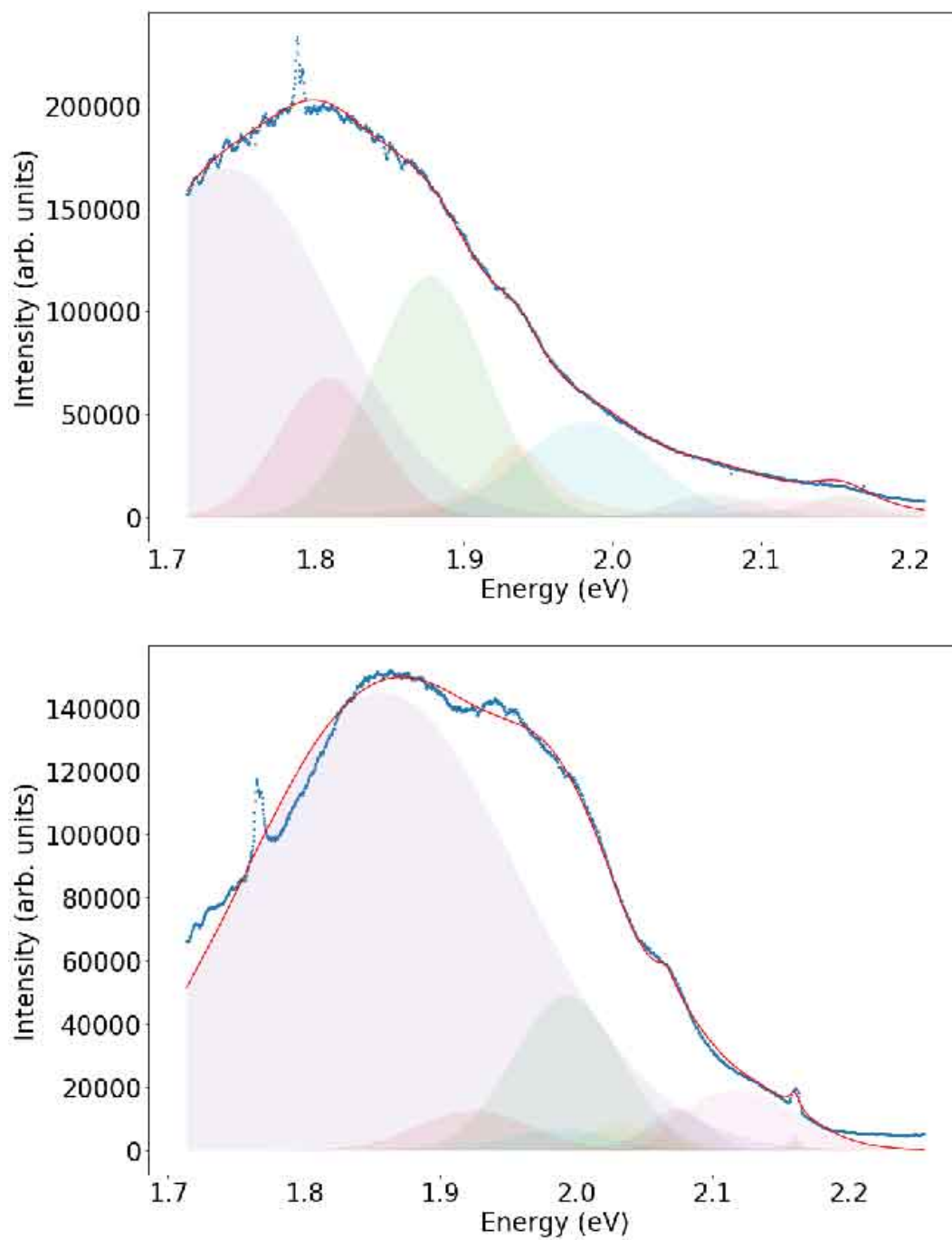


Figure 3.5: Lorentzian and Gaussian fittings of the highest and lowest experimental NV-photoluminescence spectra.

Table 3.3: Average Lifetime fittings from a stretched exponential fitting

Pressure (GPa)	τ_{avg} (ns)
24.5	2.52
24	2.78
23.3	3.58
21.8	3.28
20.1	2.97
19.7	3.2
21.3	3.35
20.5	2.78
17.2	4.51
7.96	4.66
4.22	5.04
room	7.98

PL lifetime measurements for ensembles of HMT-doped nanodiamonds are presented in Fig 3.4c at both atmospheric and high-pressure conditions using time-correlated single-photon counting (TCSPC). As the pressure is decreased, the averaged lifetime (τ_{avg}) increases from 2.5 ± 0.6 ns at 24.5 GPa, to 8.0 ± 0.8 ns at ambient pressure when the material was recovered from the DAC chamber, as seen in Table 3. Fitting was performed with a stretched exponential curve under the assumption that the sample contains a distribution of NV⁻ centers with varying lifetimes. Data used to calculate the average lifetime pressure can be found in SI Table S3. These PL lifetimes are faster than literature reports for NV⁻ centers in bulk diamond which has values in the range of 10-13 ns¹⁴⁴ and much faster than literature reports for the NV center in nanodiamonds, which are reported to be ≈ 25 ns.

The time resolved PL decays for the nano-diamonds is fit to a stretched exponential decay function as shown in Eq 3.1. In Eq 3.1, I_0 is the initial PL intensity, t is the time, c is the characteristic decay lifetime defined as the time taken to reach 1/e value of the initial PL intensity and is the distribution coefficient that captures the distribution of the local rates.

$$I = I_0 e^{\left(\frac{-t}{\tau_c}\right)^\beta} \quad (3.1)$$

Stretched exponential decay laws are encountered in systems where there is a distribution of local decay rates and they can be physically interpreted as a superposition of these local decay rates^{145–148}. A β value closer to 0 represents a more heterogeneous distribution in the decay rates and a β value closer to 1 represents a more homogeneous distribution in the decay rates. When $\beta = 1$, a single exponential decay is recovered. The important metric for analyzing photophysics from the stretched exponential is the average lifetime, or τ_{avg} ¹⁴⁹. The average lifetime for a single PL decay, given by Eq 3.2, considers the characteristic lifetime (τ_c) and the distribution factor (β) to give an average lifetime of that distribution.

$$\tau_{\text{avg}} = \frac{\tau_c}{\beta} \Gamma\left(\frac{1}{\beta}\right) \quad (3.2)$$

where $\Gamma\left(\frac{1}{\beta}\right)$ is the gamma function.

Previous studies have shown the NV⁻ center's PL lifetime is susceptible to myriad influences including its location relative to the surface of the diamond crystal¹⁵⁰, the orientation of the center's dipole¹⁵¹, the refractive index of the surrounding medium^{152,153}, and perturbations from adjacent defects¹⁵⁴. The surrounding medium in this investigation is FCC argon which has an index of refraction of $n = 1.5$ at ~ 5 GPa and eventually saturates at $n = 1.8$ in the range of 15–25 GPa¹⁵⁵. Because PL rate scales with local n^2 , we would expect a $(1.8/1.5)^2 \sim 44\%$ increase in the PL decay rate at the upper limit, if the quantum yield for emission was unity. The observed blue shift in the emission of the ZPL from ~ 1.95 eV to ~ 2.1 eV would also be expected to increase the PL rate, but by a ratio of the cube of the emission energies, or only another $\sim 25\%$. Taken together, we estimate that the refractive index change, and the blue shift, could together account for at most a lifetime decrease of 1.8X if the measured lifetime was equal to the PL lifetime. The change in argon's refractive index is not large enough to explain the observed change of lifetime with pressure. However, since the photoluminescence quantum yield for NV⁻ in our nanodiamond is almost certainly less than 1, and since the average lifetime is reduced by 3X at high pressure, we conclude that

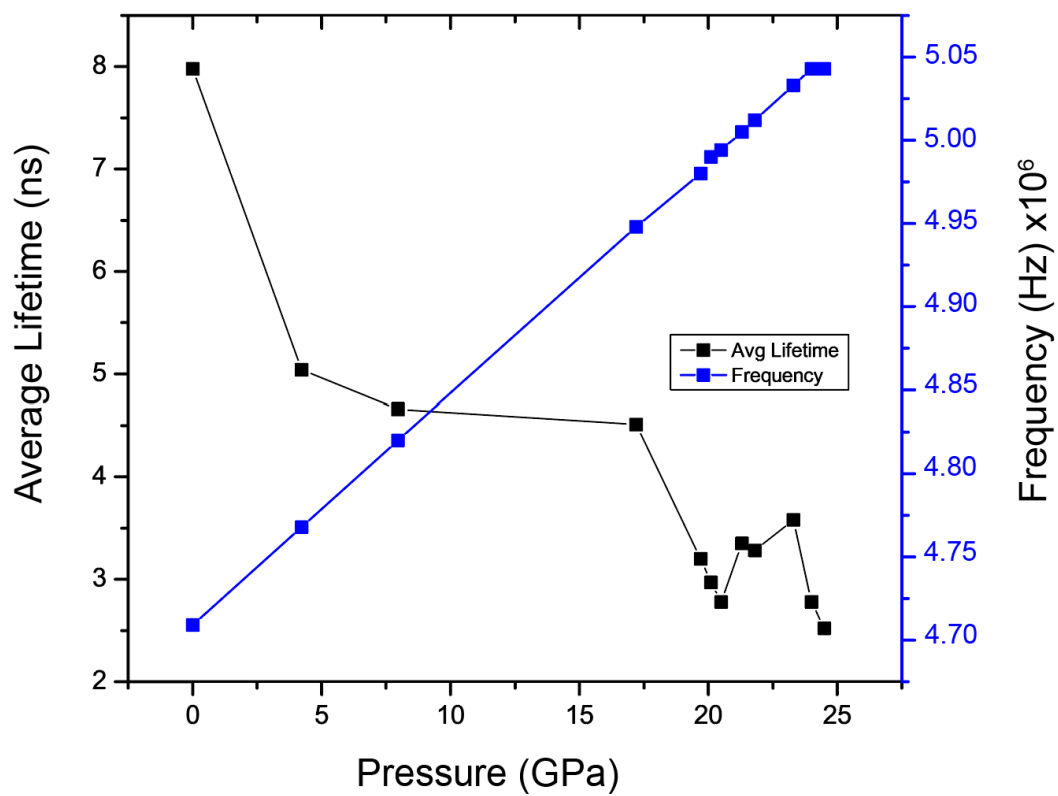


Figure 3.6: Comparison of the experimental NV- average lifetime and the frequency of the oscillating radiative dipole with pressure.

refractive index changes alone are unable to account for the pressure-dependent decrease in the NV- lifetime.

We propose that both the comparatively short lifetime for the NV- centers in our nanodiamonds, and the relatively large change in response to hydrostatic pressure could be explained if our samples have a relatively low quantum yield (high non-PL rate) dominated by coupling to nearby defects. In this case one would expect a PL lifetime well below that of the reported NV- PL lifetimes in nanodiamonds, which we do observe (c.f. ~ 8 ns in our samples compared to 25 ns in the literature), as well as a reduction in the lifetime and intensity under pressure as the quenching defects interact more strongly with the emissive NV- centers. Indeed, we measure a $\sim 3X$ reduction in lifetime, and as shown in Fig. 3.4b, the intensity of the NV- emission also decreases with increasing pressure.

This hypothesis is indeed consistent with reports that non-radiative pathways involving substitutional nitrogen can shorten the NV- center's PL lifetime^{143,154,156}. As discussed above, large concentrations of positively charged P_1 centers in close proximity to the NV- center can induce large Stark shifts of NV- that broaden its ZPL and also reduce its overall lifetime¹⁴³. Other literature has reported that the reduction in lifetimes are related to not only high amounts of P_1 centers, but specifically nitrogen aggregate centers, like the A aggregate¹⁵⁷, a substitutional pair of nitrogen, and the B center¹⁵⁸, four substitutional nitrogen surrounding a vacancy^{154,156}. In Monticone *et al.* the authors propose that the NV- PL lifetime data changes when it is next to a dipole (A center) or a quadrupole (B center)¹⁵⁴. The B-center has not been observed directly in HMT-doped nanodiamonds and future work will be directed at detecting its UV photoluminescence transition (ZPL, $\lambda = 235$ nm)¹⁵⁹, or vibrational transitions¹³⁰ at 780, 1003, 1098, 1175 cm^{-1} via either micro-FTIR, infrared photothermal heterodyne imaging spectroscopy^{160,161}, or low-loss aloof EEL spectroscopy.¹⁶²

Figure 3.6 shows aberration corrected, high-resolution TEM images of HMT-doped nanodiamonds recovered from the DAC. Figure 3.6a illustrates a representative BF-TEM

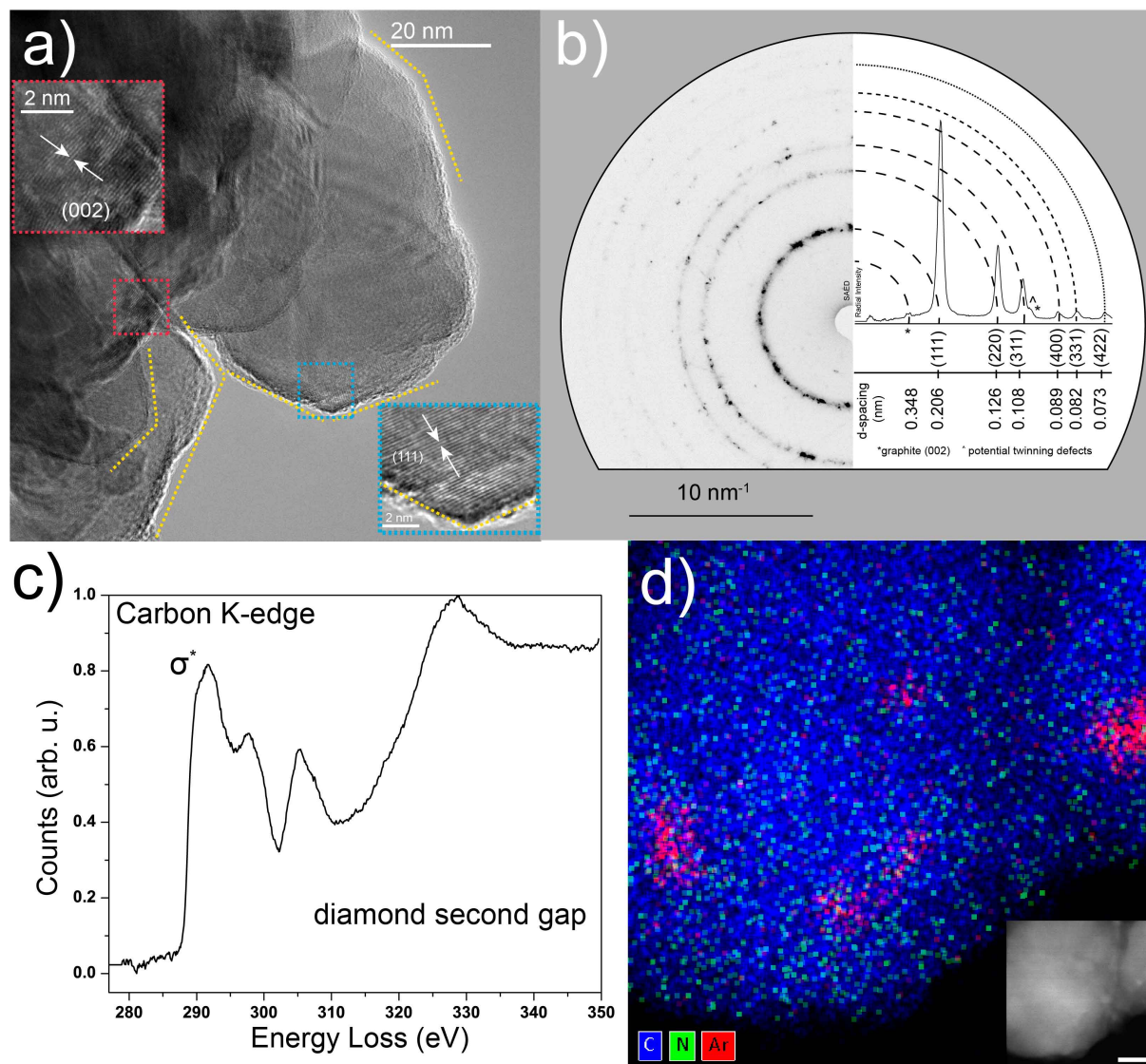


Figure 3.7: (a) BF-TEM image of the nanocrystalline diamond samples. Yellow dashed lines outline the crystallographic facets of the nanodiamond samples. The blue inset shows a uniform crystallinity (111). The red inset portrays a graphitized surface. (b) SAED and radial intensity plot of the BF image in (a). The pattern was indexed to cubic diamond with the crystallographic reflections and the corresponding d-spacing indicated in the panel. (c) Carbon K-edge spectrum of the as synthesized nanodiamond samples illustrating the σ^* transition and the second gap of diamond. (d) RGB elemental color map showing the spread of elements within a nitrogen doped nanodiamond sample. The inset is a STEM-HAADF image which further illustrates the microstructure of the HPHT synthesized diamond. The scale bar in the inset is 5 nm.

image of the synthesized nanocrystalline diamond. The diamond grains are approximately 100 nm in diameter with surfaces defined by (111) Miller facets (yellow lines) which have also been reported for ball-milled HPHT-nanodiamonds. The inset at the lower right shows (111) Miller planes of diamond's cubic lattice. Domains with graphitic (002) planes are observed as shown in the red inset at left in Fig. 3.6a. Fig. 3b presents a radially integrated, indexed select-area electron diffraction (SAED) data set that confirms the formation of polycrystalline nanostructured diamond. The (002) plane of graphite is also observed using SAED with a d-spacing of 0.348 nm. The peak at a d-spacing of approximately 0.105 nm could potentially be due to twinning defects in diamond, but requires further investigation. Figure 3.6c demonstrates the carbon K-edge spectrum of the photothermally converted material. The σ^* transition and the second gap of diamond are observed in this spectrum, which further serves to verify that the converted material is diamond. As seen in Fig. 3.6, the EEL spectra were collected from the converted material and show sp^3 σ and double plasmons. Mie theory was used to interpret the plasmon responses of the recovered nanodiamonds as a function of their radii.

The STEM-EDS elemental map shown in Fig. 3.7d demonstrates the recovered HMT-doped nanodiamonds have a composition consisting primarily of carbon, nitrogen, and argon. As seen in this panel, nitrogen incorporates homogeneously into the diamond samples after HPHT diamond growth. Quantitatively, the atomic percentage of nitrogen in this sample was approximately 0.5%, about five times greater than non-doped samples synthesized under similar conditions. This evidence, in combination with the photoluminescence spectra from Fig. 3.4b discussed above, further confirms that the molecular dopant, HMT, provides the rich source of nitrogen to the amorphous CA. Argon recently has been reported to incorporate within nanodiamond grown at HPHT conditions⁸⁶. Figure 3.7c also illustrates a map of argon impurities in the HPHT diamond lattice. Overall, argon is observed to incorporate homogeneously, however larger inclusions with higher concentrations of argon are also observed in these samples. The source of argon comes from the liquid argon used

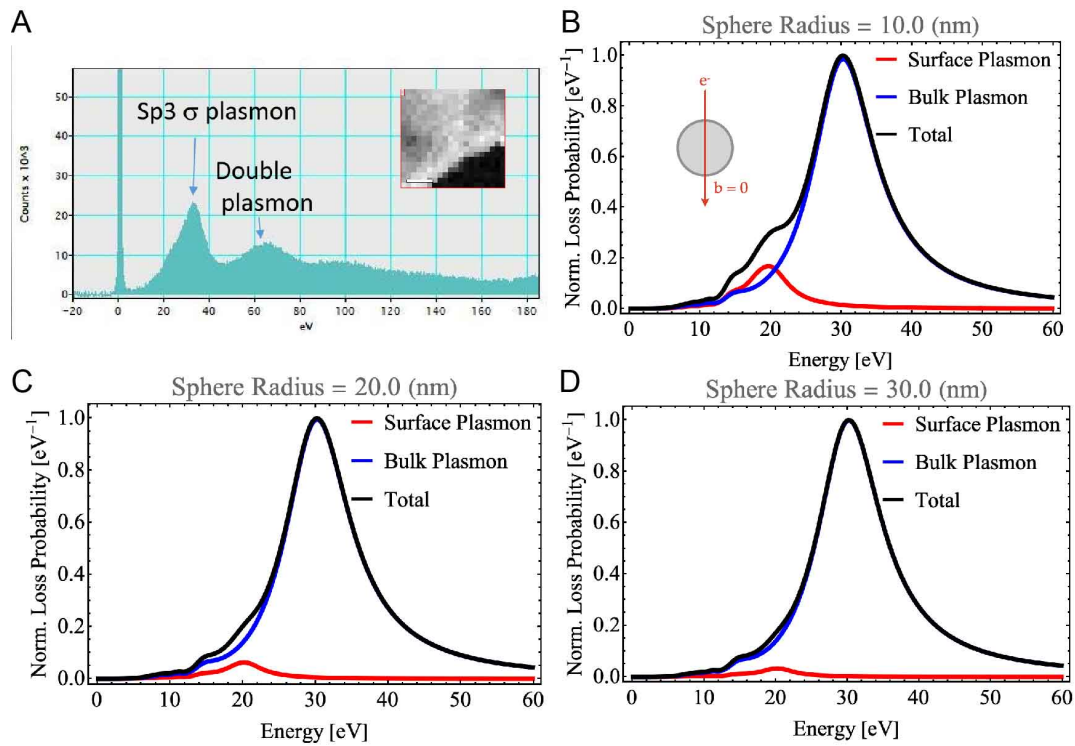


Figure 3.8: EEL spectrum of HMTND. (A) Experimental point spectrum. (B), (C), (D) Electron beam driven Mie theory of nano-diamond spheres of varying radius at the impact parameter $b = 0$ (inset in B) showing both surface and bulk plasmon responses with one quantum of excitation

as a hydrostatic pressure medium, which fills the pores of the HMT-CA. As the DAC was taken up in pressure, the argon solidified, as discussed above. During photothermal heating and diamond formation, the pores of the amorphous CA collapse, potentially trapping local pockets of argon in the diamond lattice. However, the atomistic microstructure of potential argon defects within the diamond lattice remains an open question.

Ab initio quantum cluster calculations were performed in order to clarify the vibrational or electronic transitions of argon split-vacancy point defects in nanodiamond, as well as potential B-centers. The resulting vibrational and electronic absorption spectra are plotted in Figure 3.9. Given the difference in composition and in structure between the diamond systems reported (pure diamond, B-aggregate doped diamond, and argon split-vacancy doped diamond) the vibrational spectra are expected to exhibit unique responses. The infrared (IR) absorption spectra are plotted in Figure 3.9 (a,c,e), and as can be seen the three systems all have a diamond IR response at 1330 cm^{-1} matching well with experiment.^{163–165} This indicates the structures and methods used provide experimentally valid information. See Ref. 117 for a detailed examination of the vibrational properties of the pure diamond cluster. The nitrogen B-aggregate system has a noticeably increased response in the $\sim 900 - \sim 1200\text{ cm}^{-1}$ energy region. These responses correspond to T_2 vibrations of the aggregate-center coupled with the diamond lattice. Of particular note is the peak which can be noted in Figure 3.9(c) at $\sim 1095\text{ cm}^{-1}$ which has been noted to arise due to the B-center previously in literature.¹⁶⁶ Also notable is the peak at $\sim 980\text{ cm}^{-1}$ also due to a T_2 vibration of the B-aggregate within the diamond lattice. This peak also correlates with a noted response of the B-aggregate system at 1003 cm^{-1} , though red-shifted as the host diamond is quantum confined.^{166,167} For a more in-depth examination of B-aggregate doped nanodiamonds please see Ref. 168. The argon containing diamond has a response at ~ 1090 and $\sim 1070\text{ cm}^{-1}$ corresponding to E type vibrations of the diamond lattice. Ar-specific responses occur at $\sim 300\text{ cm}^{-1}$ where they mix with the diamond lattice breathing modes. The low-energy infrared absorption spectra are shown inset into the heavy spectra in Figure 3.9(a,c,e).

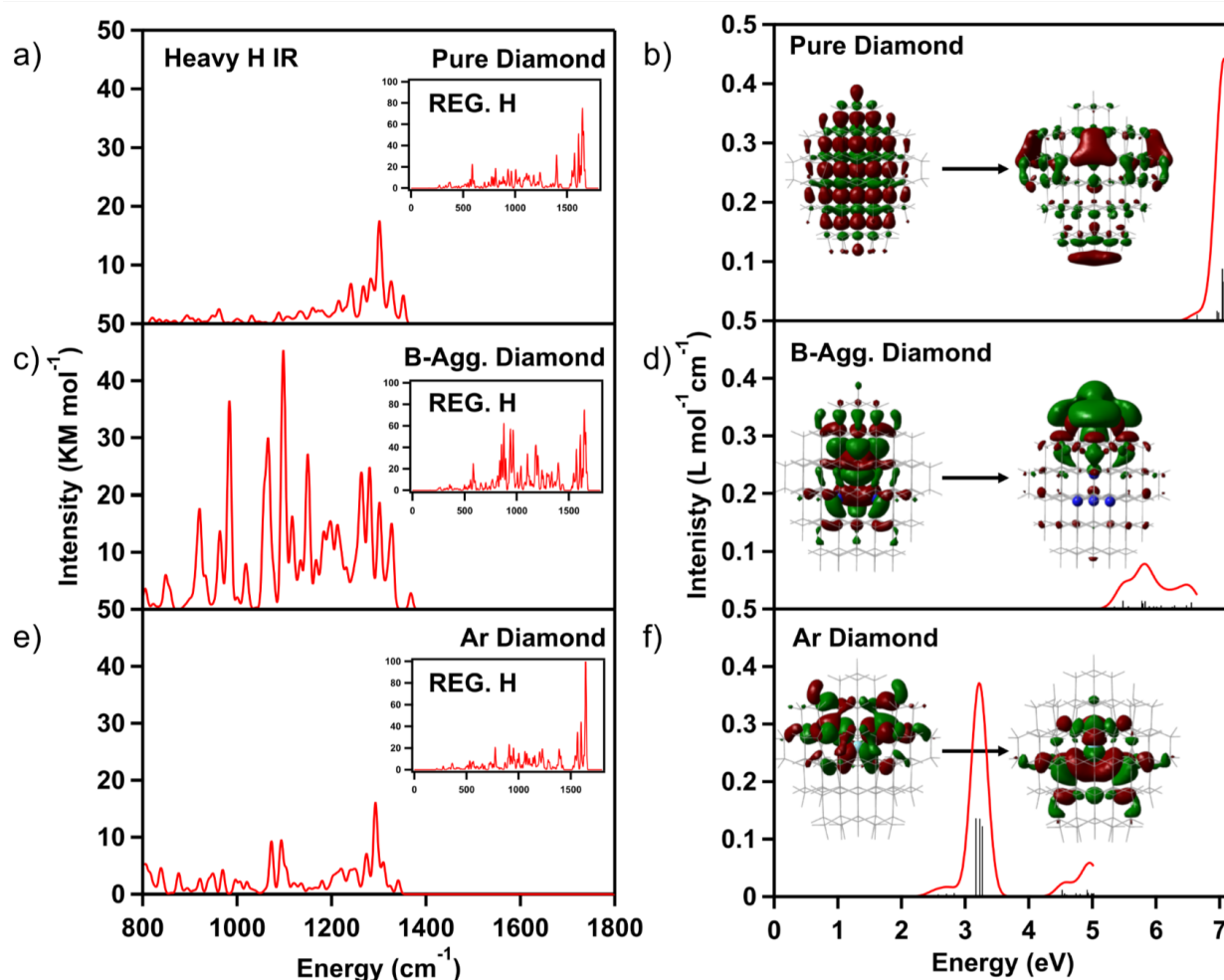


Figure 3.9: *Ab initio* absorption results at the B3LYP/6-311G(d) level of theory for the ~ 1.2 nm diamond systems. From top to bottom there are the vibrational (left; a,c,e) and optical (right; b,d,e) absorption spectra for the pure diamond (a,b), the B-aggregate doped diamond (c,d), and the argon-doped diamond (e,f). The theoretical spectra have had gaussian broadening applied (full width half maximum value of 4 cm⁻¹ and 0.12 eV for the vibrational and optical absorption spectra, respectively), with the electronic transitions marked with black lines. In the case of the vibrational absorption spectra, the spectral window shown originally overlaps with H-C-H bending modes, to isolate the carbon and dopant contributions the mass of the hydrogen has been artificially increased (100 amu). The insets are of the spectra without the artificially massed hydrogen, not shown are C-H stretching modes (~ 3000 cm⁻¹ +) which are not of interest in this study. The insets for the UV/Vis spectra are the natural transition orbitals responsible for the first transitions plotted with an isovalue of 0.02.

In Figure 3.9 (b,d,f) there are the UV/VIS absorption spectra for the pure, B-aggregate doped, and argon doped diamonds, respectively. As is readily apparent, the three systems do not have very similar absorption features. In the case of the pure diamond, the absorption feature beginning at ~ 6.8 eV corresponds to a band to band transition. Bulk diamond has a band gap of ~ 5.5 eV meaning that the 6.8 eV response is significantly blue-shifted due to quantum-confinement effects associated with simulated nanodiamonds.¹⁶⁹ Nanodiamonds containing B-aggregate systems have absorption features beginning at ~ 5.3 eV that are red-shifted from the pure diamond band to band transitions. These features arise as the B-aggregate introduces occupied levels within the band. Thus the excitations consist of transitions between the aggregate-localized energy levels and the unoccupied diamond band. The isosurfaces for the corresponding molecular orbitals are plotted in the inset to Figure 3.9 (d). This agrees well with experimental work where it has been claimed that the B-aggregates were responsible for the N9 absorption band which occurs at 5.26 eV.¹⁶⁶

The argon split-vacancy⁸¹ can be seen to be an electrically active defect as it gives unique absorption features from the pure diamond system. The presence of the Ar split-vacancy introduces argon 3p accepting orbitals into the band gap which are able to mix with the diamond lattice, which has been noted in previous theoretical work.¹¹⁸ Excitations to these from the degenerate Ar-centered HOMO and HOMO-1 give rise to the initial transitions at 2.3 eV, with the first transition of this character is plotted in the inset of Figure 3.9 (f). It can be noticed that there is a significant difference in intensity for the initial states at ~ 2.3 eV when compared to those occurring at ~ 3.2 eV. This is caused by a difference in the overlap between the departing and arriving orbitals involved in the transition, located within the supporting information are the Natural Transition Orbitals for the transition at 3.17 eV, and through comparing this transition with that inset into Figure 3.9 the difference in localization can be noted. This indicates that it may be necessary to look for absorption features of the Ar split-vacancy above ~ 3 eV, this allows for separation from the nitrogen B-aggregate (~ 5.3 eV)¹⁶⁶ or the NV⁻ (1.9 eV) centers.

3.3 Conclusions

Despite major advances in creating point defects in diamond based on single homoatomic dopants, creating point defects in diamond with control over both the defects stoichiometry and stereochemistry remains an outstanding challenge. HMT, as a molecular dopant, provides a rich source of nitrogen to the amorphous CA that, when converted to diamond through HPHT synthetic conditions, can create significantly more NV⁻ point defects as compared to undoped samples. STEM-EDS mapping demonstrates the homogeneous incorporation of nitrogen and confirms that the nitrogen from HMT incorporates into the diamond at approximately 0.5 at%, whereas undoped samples have <0.1 at% nitrogen. In trying to create more complex aggregates in diamond, like the B aggregate, future experiments will pyrolyze HMT-CA samples under the molecular dopants thermal decomposition temperature to maintain the molecules desired stereochemistry. Further, spectroscopies probing the micro environment of the synthesized diamond material taken out of the DAC chamber, like μ -FTIR, can demonstrate the formation of B aggregates without skewing the data with the presence of type 1a anvils. The stable presence of argon in the diamond lattice of these samples opens up a synthetic avenue to incorporation of other noble gases, like xenon, which has excellent properties as a single photon emitter^{170–173}. Combined these results highlight that molecular doping provides a mechanism to control dopant incorporation, including over concentrations of dopants and influence their optical properties. These are the first steps toward realizing full control of heteroatomic doping via molecular dopants.

Chapter 4

SOLID STATE REFRIGERATION AT GPA PRESSURES

As of the date of this dissertations publication, this work is currently in preparation for submission

Although solid-state laser-refrigeration recently has been demonstrated to reach cryogenic temperatures in vacuum, to date the solid-state laser refrigeration of materials at elevated pressure conditions has remained unexplored. Here we demonstrate the laser cooling of ytterbium-doped yttrium-lithium-fluoride ($10\%Yb^{3+}:YLiF_4$, or Yb:YLF) $\sim 17K$ below room temperature at pressures >4 GPa in a diamond anvil cell using lithium fluoride and ice-VII as a quasi-hydrostatic pressure media. Temperature measurements are quantified using a ratiometric-thermometry approach involving a Boltzmann fit to excited states distribution through $4f-4f$ Stark-level transitions from the Yb^{3+} ions that occur between the $^2F_{5/2}$ and $^2F_{7/2}$ manifolds. At pressures between 7 and 12 GPa the YLF grains are observed to undergo a martensitic phase transition from a tetragonal scheelite phase (space group $I4_1/a$, $Z = 4$, No. 88) to a monoclinic fergusonite phase (space group $I2/a$, $Z = 4$, No. 15) which modifies the crystal field splitting of the ground- and excited- state manifolds, but is observed to not eliminate laser cooling. Solid-state laser refrigeration at extreme pressures could allow researchers to use rapid photothermal cycling to explore temperature-dependent properties of materials, including electronic-structure phase-transitions, without the need for external cryostats.

Laser heating within a diamond anvil cell (DAC) has led to a range of significant

advances towards the understanding of both the fundamental properties¹⁷⁴ and also the synthesis of materials at extreme conditions. Since Takahashi & Bassett’s original work in the late 1960s using laser heating to synthesize diamond from graphite¹⁷⁵, laser heating at extreme conditions has enabled scientists to study matter at conditions relevant to planetary interiors^{176,177} and also to synthesize a wide variety of new materials with unique phases and compositions^{86,178,179}. Controlling the temperature within DACs has also led to recent reports of metal-hydride materials with superconducting phase transitions near room temperature^{180–182}.

In contrast to laser heating, solid-state laser refrigeration at extreme conditions has remained unexplored. The refrigeration of condensed phases was reported first in 1995 through the use of a metal-fluoride glass that was doped with trivalent ytterbium ions¹⁸³. During solid-state laser refrigeration, a material is refrigerated through anti-Stokes fluorescence¹⁸⁴. A laser, with low optical entropy, excites electronic levels within ytterbium ions which then couple to optical phonons provided by the host lattice. This phonon-mediated excited-state upconversion is followed by the spontaneous emission of high-entropy photoluminescence that transports heat away from the material. Myriad materials have been shown to laser cool in the last two decades. The transition from amorphous glasses to crystalline ceramics such as ytterbium-doped YLiF_4 (Yb:YLF) has had a major impact on the minimum achievable temperatures. Cooling from room temperature to cryogenic temperatures (~ 90 K) in vacuum has recently been demonstrated¹⁸⁵. More recently, solid-state laser cooling in liquid water has led to the first experimental demonstration of cold Brownian motion¹⁸⁶ since Einstein’s seminal 1905 paper on isothermal Brownian motion¹⁸⁷.

To date it has not been clear whether solid-state laser refrigeration is possible within a DAC due to the requirement for blue-shifted, anti-Stokes photons to escape and transport heat from the host material. Laser refrigeration within a DAC poses potential challenges for laser cooling considering the high optical index of refraction of diamond ($n = 2.5$), a large amount of metallic materials within a DAC could prevent the escape of anti-Stokes

photoluminescence, and the large conductive heat load, especially when the particles are in contact with the diamond, which has a high thermal conductivity. Additionally, high pressure phase transitions are known to occur for YLF^{188,189}, which can lead to significant changes to the crystal-field (Stark) levels of lanthanide ions. In particular, increasing the splitting of the ground state manifold at high pressures could decrease the efficiency of phonon-mediated upconversion¹⁸⁴.

Here we report the first experimental demonstration of solid-state laser refrigeration of both individual Yb:YLF microcrystals and bulk Yb:YLF at pressures > 11 GPa, opening up new experimental possibilities for the rapid photothermal control of the temperatures of matter at extreme conditions. We observe that Yb:YLF in the scheelite phase cools > 20 K below room temperature at a pressure of ~ 4 GPa for both the single crystal and bulk. At pressures above 7 GPa the tetragonal scheelite phase undergoes a martensitic second order phase transition to a monoclinic fergusonite phase with increased crystal field splitting. Despite the phase transition, laser refrigeration > 5 K below room temperature is observed for the fergusonite phase for both the single crystal and bulk, opening up a new range of potential applications of laser cooling in high pressure science. Finally, future avenues to optically refrigerate Yb:YLF in the fergusonite phase are discussed.

4.1 Methods

4.1.1 YLF Synthesis

All reagents were purchased from Sigma Aldrich and utilized without further purification. The hydrothermal synthesis used to synthesize Yb:YLF nanocrystals was taken from Roder et al with some modifications¹⁸⁶. Approximately 0.585g (2 mmol, analytical grade) EDTA was dissolved in 10 mL Millipore DI water and 0.28 g LiOH, and heated to 80°C while stirring. After the EDTA dissolved, 1.8 mL of 1.0M (1.8 mmol, 99.999 purity) Yttrium

chloride hexahydrate ($\text{YCl}_3 \cdot 6\text{H}_2\text{O}$) and 0.2 mL of 1.0 M (0.2 mmol) Ytterbium chloride hexahydrate ($\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$) was added to the solution with continuous stirring. This mixture was denoted as solution A. In a separate container, denoted solution B, 0.105g (4mmol, analytical grade) LiF and 0.34g (8mmol, analytical grade) of NH_4HF_2 were dissolved in 5 mL of Millipore DI water and heated to approximately 70°C with stirring for 1 hour. After the hour, solution B was added dropwise to A with continuous stirring to form a homogeneous white suspension. After 30 minutes, the combined mixture was then transferred to a 23-mL Teflon-lined autoclave (Parr 4747 Nickel Autoclave Teflon liner assembly) and heated to 180°C in a Thermo Scientific Heratherm General Protocol Oven (65 L) for 72 hours. After, the autoclave was taken out of the oven and allowed to naturally come to room temperature. The product, Yb:YLF, was sonicated and centrifuged at 4000 rpm with ethanol and Millipore DI water three times each. The final white powder was then dried in the oven at 60°C for 12 hours followed by calcination in at 300°C for 2 hours using a ThermoScientific Lindberg/Blue M tube furnace.

4.1.2 Diamond Anvil Cell Preparation

A Merrill-Basset and modified Bx90¹⁹⁰ diamond anvil cell (DAC) were employed for spectroscopic experiments. Standard, type 1a diamonds with a culet size of 0.350 mm served as the anvils, which indented an Inconel 718 gasket to roughly 100 μm in thickness. A hole was drilled in the center of this indentation with a 0.155 mm copper wire using electric discharge machining (EDM). Annealed ruby chips and crystals of Yb:YLF were placed into the homemade chamber using a Marzhauser Wetzlar, type MCL-3, nanomanipulator equipped with a tungsten needle. Yb:YLF samples were placed directly in contact with the bottom culet. Ground lithium fluoride was poured into the chamber to serve as the hydrostatic pressure medium. For experiments where the pressure transmitting medium was water, the DAC was submerged in DI water. For both experimental designs, it is unclear whether the Yb:YLF samples moved or reoriented themselves upon sealing and pressurizing the cham-

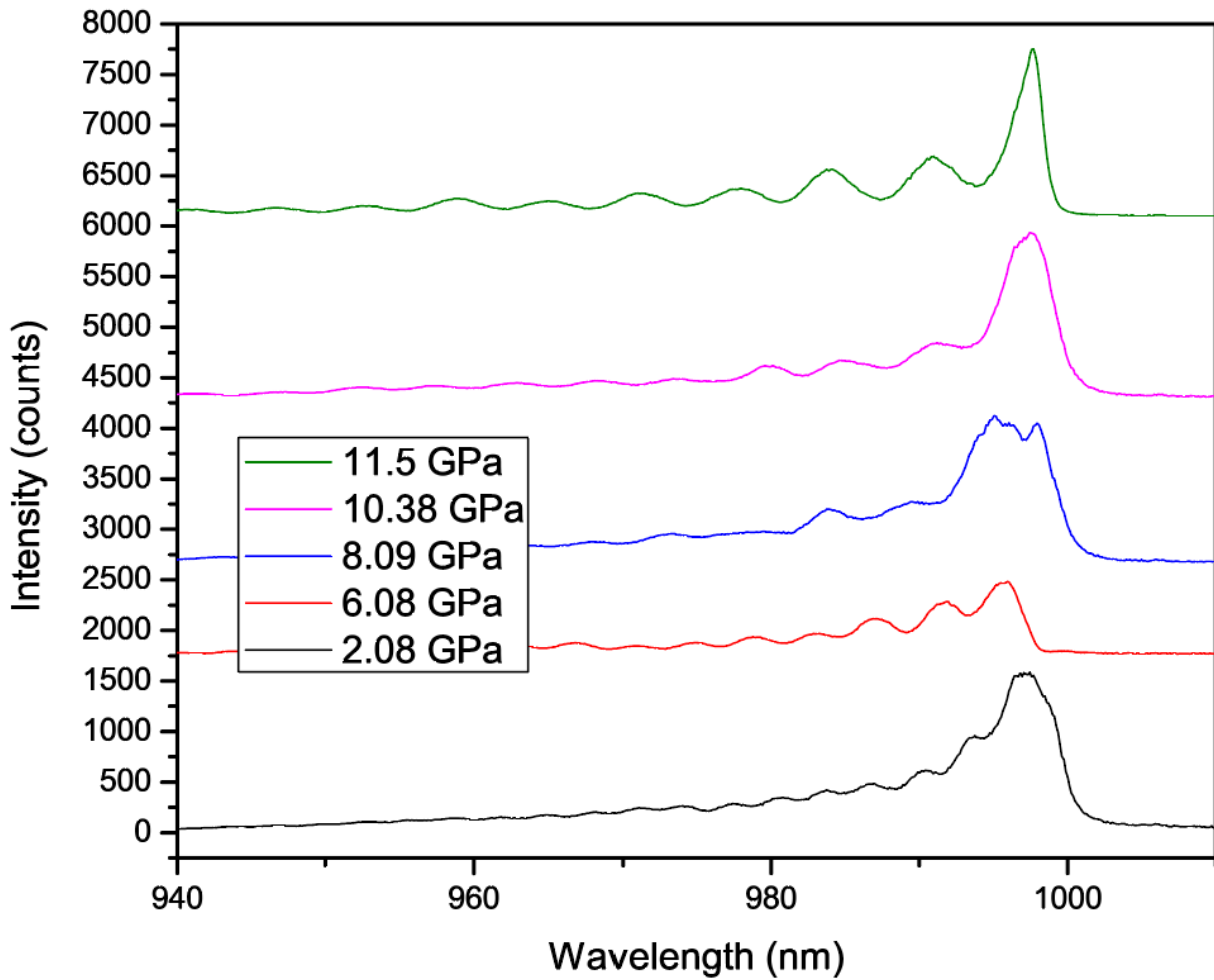


Figure 4.1: Analysis of FP fringes in background and full spectrum

ber. Utilizing the anvil culets as a Fabry-Perot interferometer, see 4.1 and section 5.1.6 for more details, it was determined that at the sealing pressure, 2.38 GPa, the gasket thickness was approximately 100 microns in diameter.

Figure 4.10 exhibits a stark difference in error bars. The reduction in error in Fig. 4.10B and Fig. 4.10D arise from the different detectors used to collect emission signal.

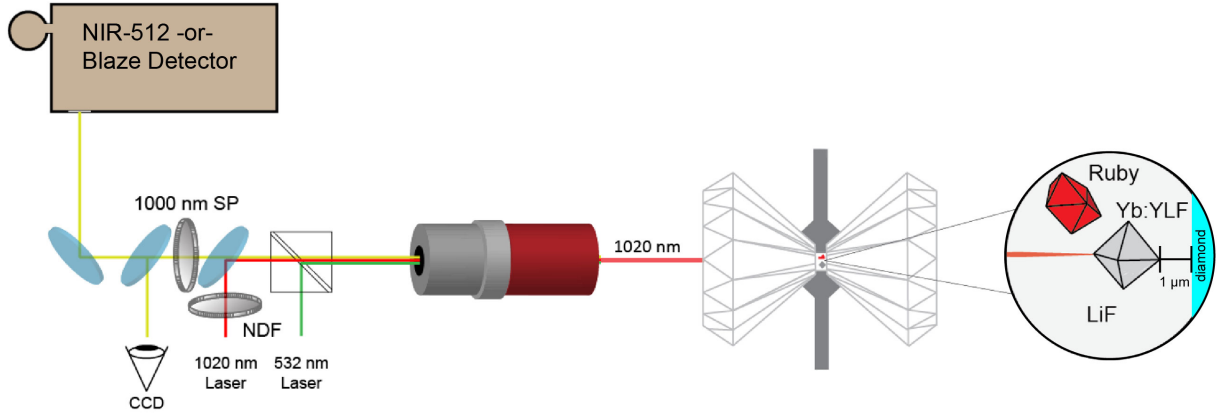


Figure 4.2: Optical Schematic of Experimental Design

4.1.3 Spectroscopic Measurements

A CW QPhotonics 1020 nm diode laser (Model: QFBGLD-1020-400, Part: Bo2-J13, polarized extinction ratio: 18 dB) was utilized to pump the Yb^{3+} fluorescence through a Mitutoyo 50x objective (NA: 0.55, WD: 13.0 mm, half-angular aperture: 33°), as seen in Fig. 4.2. The diode laser itself is not modified to exhibit a certain polarization, nor was the incident beam directed through optics to control its polarization. To obtain the luminescence spectra for radiometric analysis, the laser irradiance was controlled via a series of neutral density filters (NDF), with there being five increasing irradiances in all. A total of six spectra were collected for each irradiance. The 1020 nm light was focused into a Merrill-Basset type or Bx90 type DAC chamber and the forward scattered light was directed through a 1000nm SP into a Thor Labs camera or into a Ocean Optics NIR-512 detector for the single micro-crystal experiment or a Princeton Instruments SpectraPro HRS-500 spectrometer with a thermoelectrically cooled Princeton Instruments Blaze 100HR camera. For collection of Yb^{3+} s full emission spectrum, 1020 nm laser irradiation was pulsed, the 1000 nm SP and the NDF were removed, and a shutter was placed in front of the spectrometer. Ruby fluorescence, excited

with a 532 nm source, was utilized to measure the pressure inside the DAC chamber. The sample chamber was aligned to a 532 nm Coherent laser and a custom made QPhotonics 1020 nm diode laser. The 532 nm laser was utilized to determine the pressure of the strain affected ${}^2T_1 \Rightarrow {}^4A_2$ Cr^{3+} ruby R1 line. The 1020 nm laser was used to excite the Yb^{3+} photoluminescence.

4.1.4 Temperature Calibration of Yb:YLF Particle

To determine the quantitative amount of cooling for a single Yb:YLF particle and the bulk measurements, a temperature calibration was performed.

For the single particle Yb:YLF samples in Ice-VII and LiF: a thermocouple was secured against the DAC's stainless steel gasket holder to measure the temperature. Once secured, fiber glass wool was gently tamped into the open spaces between the DAC's two metal plates and glass, microscope cover slips were taped over the opening where the Inconel 718 seats meet the metal plate. When the DAC was securely placed on a butterfly mount and aligned to the Thorlabs camera, resistive heating tape was wrapped around the DAC and butterfly mount to supply the heat. The lowest laser irradiance was held constant while the temperature was varied because the particle was assumed to be at room temperature at the lowest laser irradiances. A total of six spectra were collected for each temperature (six temperatures in total); and, the ratio was calculated, as seen in Fig. 4.3.

For the experiments involving the DAC chamber filled with aggregated Yb:YLF samples: a thermocouple was secured against the DAC's stainless steel gasket holder to monitor the temperature. Once secured, the Bx90 type DAC was inserted into a thermoelectric cooler apparatus (TEC) modified from Noguchi's & Okuchi's¹⁹¹ original design. A water circulatory machine was attached to the TEC to regulate the temperature more effectively.

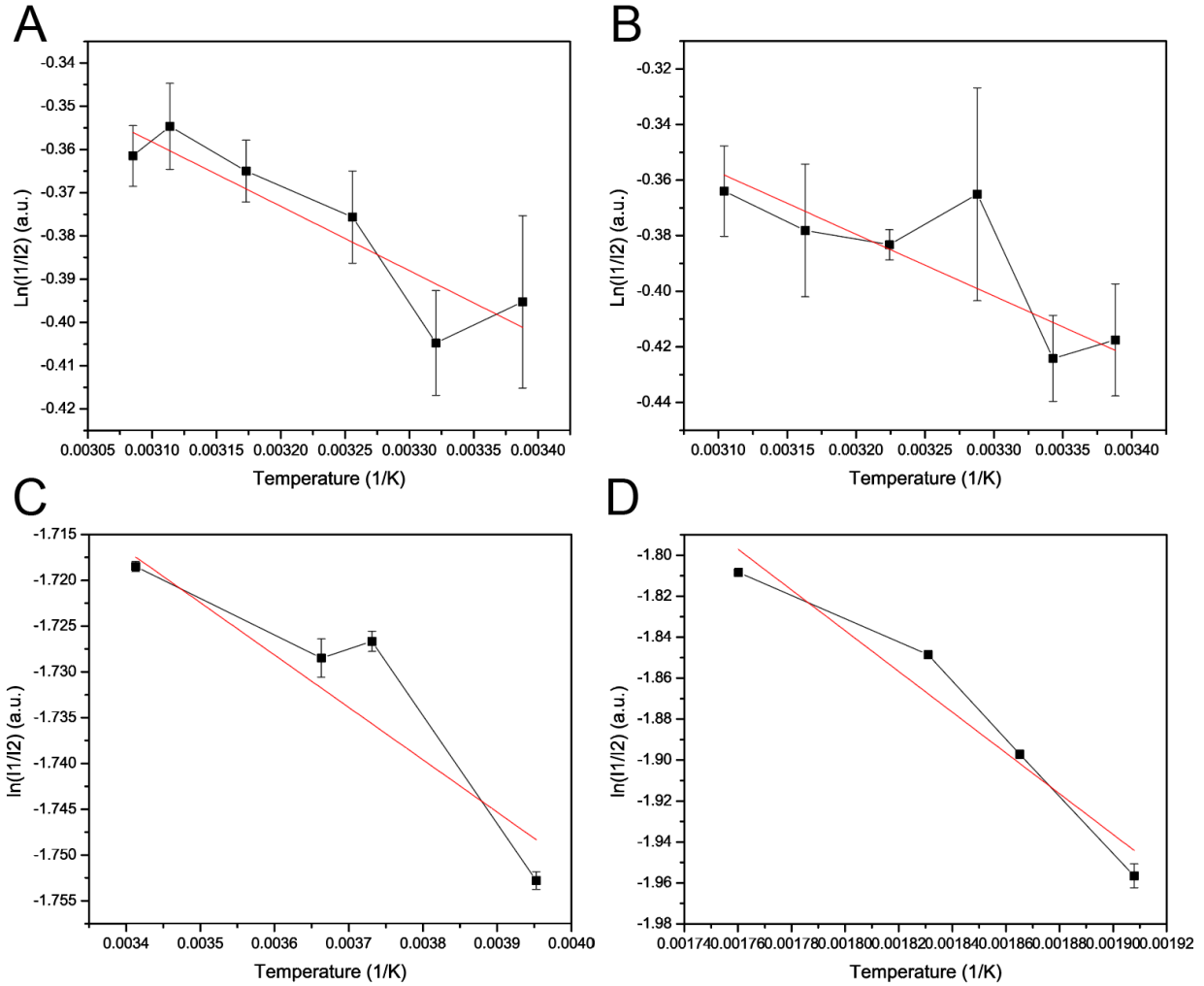


Figure 4.3: In situ temperature calibration for the (a) scheelite and (b) fergusonite phase for single particles of Yb:YLF. *In situ* temperature calibration for the DAC chamber filled with Yb:YLF particles in the (c) scheelite and (d) fergusonite phase.

4.1.5 *Analysis of Hydrostaticity of DAC Chamber through Ruby*

As the pressure of the chamber was determined via the photoluminescence R_1 line, the hydrostaticity of the chamber was examined. As the pressure is increased, if the chamber is becoming nonhydrostatic, the splitting between the R_1 and R_2 lines decreases until only one peak is present. As seen in Fig. 4.4, the ruby luminescence maintains its two peaks during all of the pressures examined in this investigation. Some spectra shown a slight broadening in the line shape of the peaks, but the splitting distance was essentially constant throughout all pressure changes.

4.1.6 *Fabry-Perot Background Analysis*

To ensure that all of the peaks in the full spectrum of Yb^{3+} were real, and not due to background interference from the cavity created by the DAC culets, the background was analyzed separately from and against the Yb^{3+} full spectrum. As the pressure increases, as seen in Fig. 4.1, the length between sinusoidal peaks increases, which is interpreted as the cavity created by the DAC culets decreasing in size and tracks with Fabry-Perot theory. These peaks also appear in the range of many of the peaks seen in Yb_{3+} 's full spectrum; however, the peaks in the full spectrum do not match in wavelength to the peaks of the background spectrum.

The Fabry-Perot background analysis was also ancillary in determining the distance between the two anvil culets, and thus the thickness of the gasket during experimentation. A Matlab code was coded to fit the sinusoidal peaks at each of the pressures, as described above. It was determined that the thickness of the gasket was approximately 100 microns at the sealing pressure and decreased to about 95 microns.

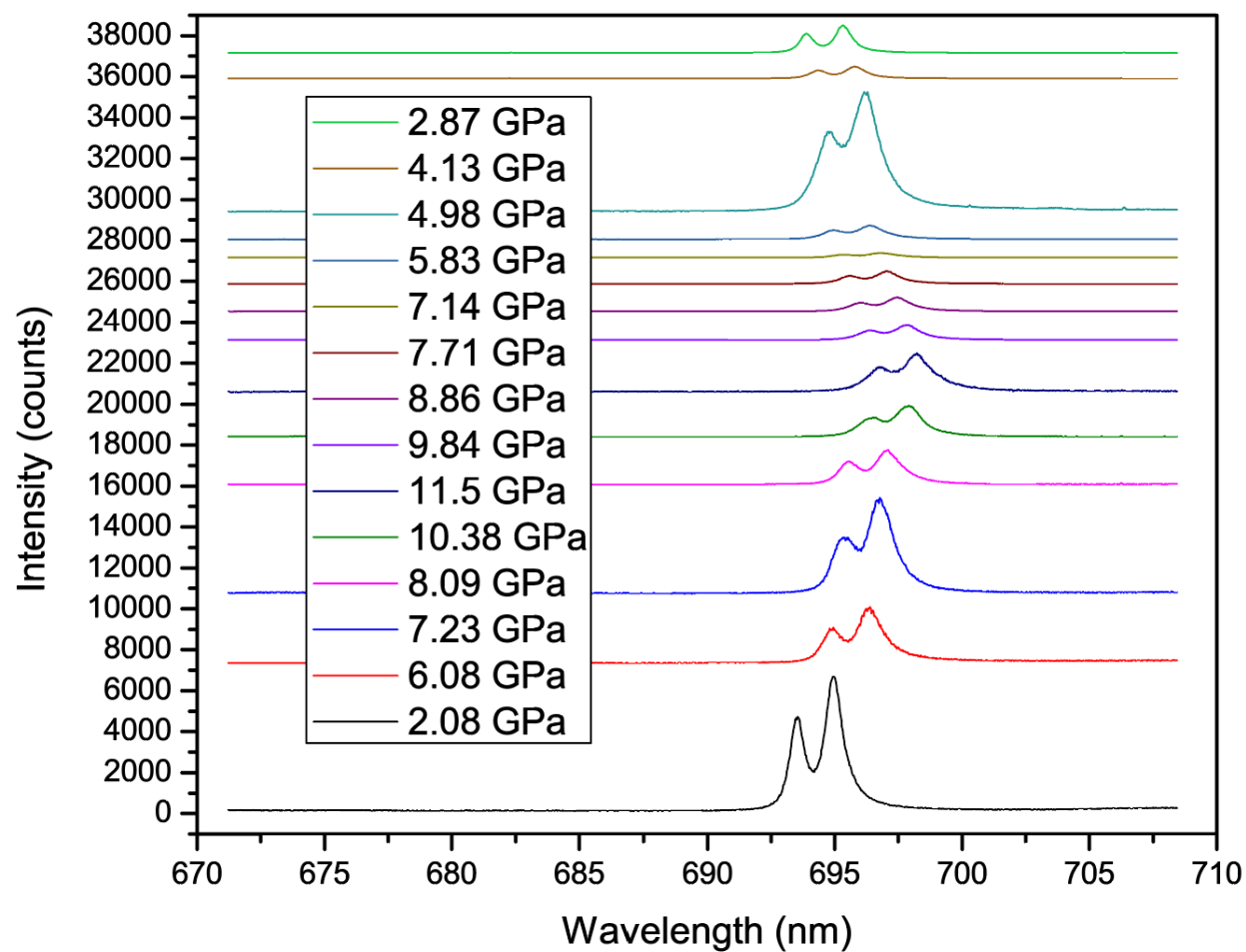


Figure 4.4: Analysis of ruby spectra illustrating quasihydrostaticity of DAC chamber

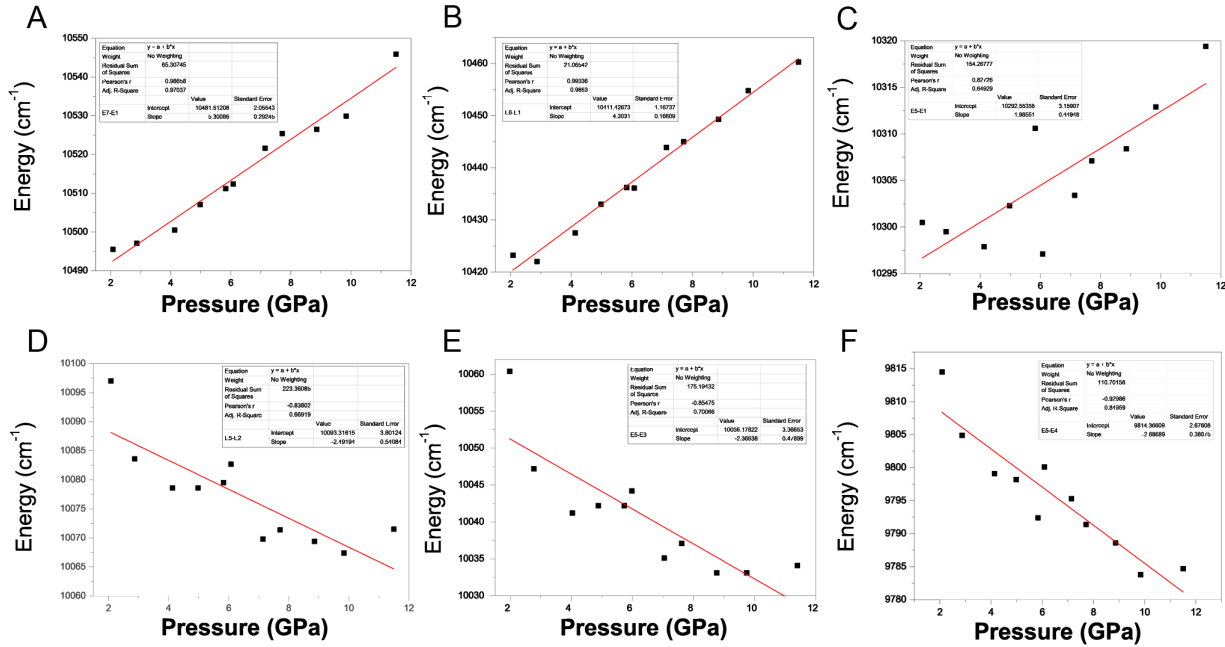


Figure 4.5: Linear trend-line fitting of the highlighted energy transitions in Fig. 2 and Fig. 3 of the manuscript

4.1.7 Fitting and Analysis of Full Spectrum Energy Transitions

After the energy transitions were fit in Python using a Levenberg-Marquadt nonlinear least squares fitting, they were plotted in Origin against each pressure point used in the study. A standard linear trend-line was fit to the data, as shown in Fig. 4.5.

4.1.8 Laser Cooling Experiments of Yb:YLF in Ice-VII

For the experiments in water, as seen in Fig. 4.11, single micro-crystals of Yb:YLF, along with ruby, were placed into a DAC chamber made of Inconel approximately 120 microns in diameter and 100 microns in thickness. Once sealed with water, as confirmed by ruby luminescence, Raman measurements of the pressure transmitting medium were collected with a Renishaw inVia system equipped with a Leica DMIRBE inverted optical microscope.

A confocal high end 785 nm excitation source was directed through a pin hole and focused with a Nikon LU Plan 50x objective (NA: 0.55, WD: 9.8 mm). Forward scattered light was collected through the objective, analyzed through an inVia spectrometer, and focused on a CCD camera. Raman measurements confirm the pressure transmitting medium changed from liquid water to Ice-VII at 4.7 GPa.

4.1.9 Numerical Heat Transfer Calculations

To explore how the heat transfer from the Yb:YLF to the diamond, three-dimensional steady state heat transfer calculations were done using COMSOL by Dr. Anupam Pant and Chaman Gupta. Two scenarios of Yb:YLF orientation relative to the surface of the bottom DAC culet were explored with COMCOL. In both scenarios, one cuboidal LiF domain of size 30x30x15 μm was sandwiched between two a diamond domains of the same sizes as shown in Figure 4.6. The purple faces were set to a constant temperature boundary condition (295 K). All external surfaces were kept at zero flux boundary condition. A Yb:YLF crystal inside the LiF domain was constructed using two square pyramids (side = 3 μm and height = 2.5 μm , each) with a common base, tilted and moved to have one face coinciding with the diamond domains top surface. In the first scenario, the coinciding face of the Yb:YLF grain was placed in direct contact with the diamond culet. The physical properties for the material domains used in the simulation are shown in Table 4.1. The simulations from this scenario indicate a change in temperature of only a few milliKelvin and demonstrate that the diamond culet acts as a heat sink. The second scenario involves translating the Yb:YLF vertically by 1 μm within the LiF domain. Results from this scenario indicate a reduction in temperature of approximately 5 K and demonstrate the same order of magnitude of cooling as those shown in 4.10. Even when the YLF grain was reoriented to have the long axis perpendicular to the diamond culet, the magnitude of cooling was approximately the same 4.6. A cooling power of 3×10^{-6} W was distributed within the Yb:YLFs volume. To take into account the gap conductance introduced due to possibly trapped air in between the roughly powdered

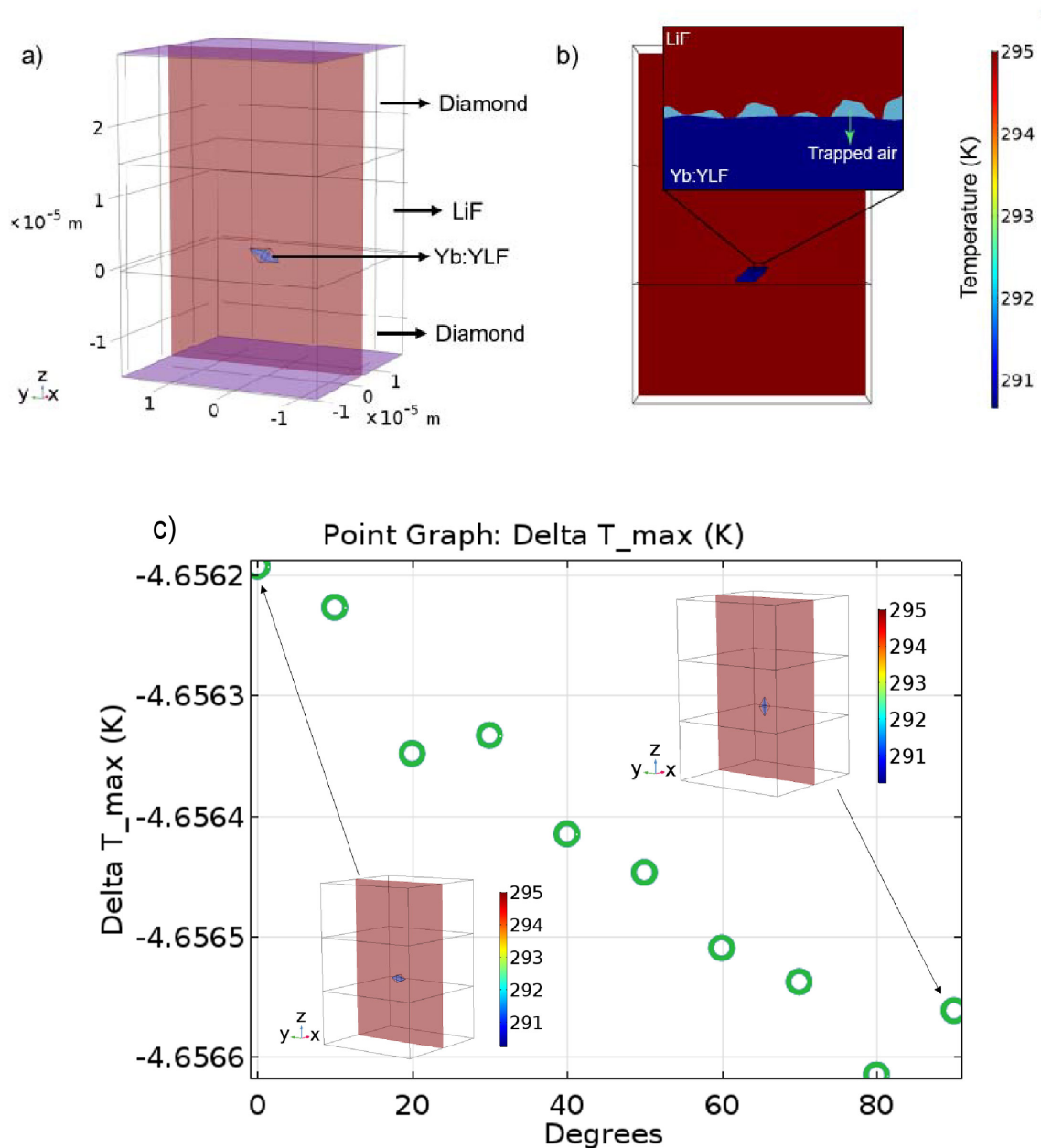


Figure 4.6: (A) COMSOL simulation of a single YLF particle in the DAC. Situated between the bottom of the YLF particle and the top of the diamond culet is 1 μm layer of LiF. (B) Temperature distribution of a single Yb:YLF particle in LiF. The inset illustrates the surface roughness of the LiF which could potentially trap pockets of air against the Yb:YLF single crystal. (C) COMSOL simulations comparing how the reorientation of the YLF crystal with respect to the diamond culet affects the cooling temperature.

Table 4.1: Physical properties of materials utilized in heat transfer simulations

Material	Density (kg m ⁻³)	Specific Heat Capacity (J kg ⁻¹ K ⁻¹)	Thermal Conductivity (W m ⁻¹ K ⁻¹)
Diamond	3510	630	2290 ¹⁹⁵
LiF	2640	1611 ¹⁹⁶	14.9 ¹⁹⁷
Yb:YLF	3980	790	6.25 ¹⁹⁸

LiF during sealing of the DAC chamber, thermal conductance of 10 KW m⁻² K⁻¹ was used at all the Yb:YLF surfaces in contact with LiF (except the one in contact with diamond), and the LiF/diamond¹⁹². At the pressures investigated in this study, molecular nitrogen, the main component of air, would solidify at a pressure of 2.5 GPa (300 K) to the β -N₂ hexagonal phase¹⁹³. To find the volume of these trapped air pockets at elevated pressures, we first assumed the air pockets trapped in between the LiF grains at ambient conditions would have a starting diameter of 1 μ m, and found the number of molecules of nitrogen from the ideal gas equation. Then, after finding the volume of the unit cell of β -N₂, we estimated the number of crystalline unit cells and their total volume. Finally, we approximated the spherical crystalline diameter from this total volume to be roughly 14 nm at 5 GPa^{193,194}. It is important to note that enlarging the size of LiF and diamond domains in order to reflect the real dimensions of the diamond anvil cell did not make a notable difference to the steady state temperatures. The temperature distribution in the Y-Z plane at X=0 is plotted in Figure 4.6b.

Results and Discussion

Merril-Basset and modified Bx90 type DACs were utilized to probe the Yb:YLF samples with increasing pressure (up to 12 GPa). As seen in Fig 4.7, LiF serves as the pressure transmitting medium as it maintains a quasi-hydrostatic environment in the desired pressure range of the experiment and is transparent to 1020 nm light, the main excitation source for this study's experiments¹⁹⁹. For one set of experiments, individual YLF micro-grains were

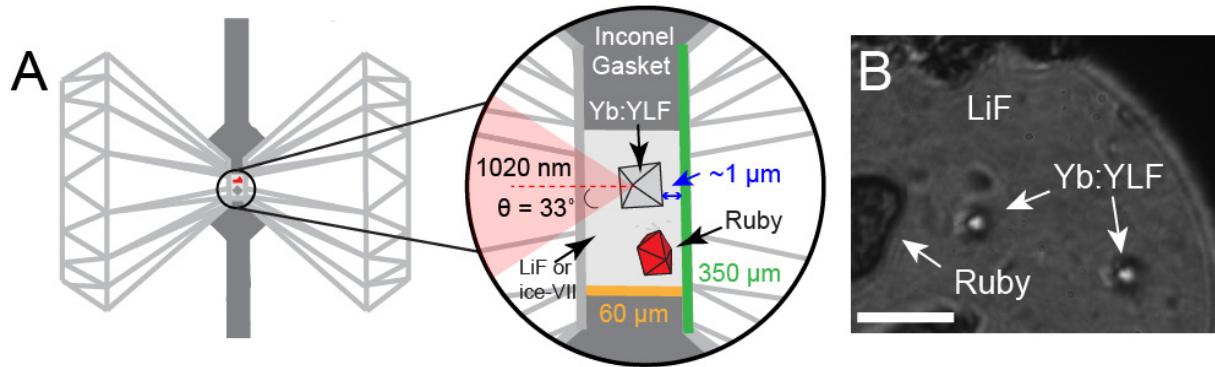


Figure 4.7: Experimental Schematic (A) An illustration of the diamond anvil cell chamber. Inside the chamber includes ruby, for pressure sensing, Yb:YLF, the sample, and finely ground LiF, the quasi-hydrostatic pressure medium. The critical angle of the microscope objective is denoted as θ . (B) an optical micrograph of the DAC chamber. Components of the chamber are labeled in white. Scale bar is 10 microns.

first transferred to the anvil culet (Fig. 4.7A). It is unclear how the YLF grains reoriented upon sealing and pressurization. YLF grains were observed to move in LiF after reaching high pressures. This is illustrated in 4.2. It is unlikely that the Yb:YLF grains remained in contact with the diamond culet after sealing as discussed in heat transfer simulations discussed in 4.6. Shown in Figure 4.10B and D is a second set of experiments, which explore the optical refrigeration of approximately half of the DAC chamber filled with Yb:YLF micro-crystals, or a bulk sample set. In both experiments, the excitation laser was focused through the opposite anvil to individual Yb:YLF grains or the bulk sample, as seen in the inset in Fig. 4.7A. Yttrium lithium fluoride is a uniaxial crystal with polarization-dependent absorption and emission spectra. A partially polarized diode laser was utilized to excite the Yb^{3+} emission. In order to account for polarization-dependent emission the DAC was returned to its original position and orientation in front of the 50x objective following every pressure adjustment. The optical micrograph shown in Fig. 4.7B illustrates the experimental chamber at the

highest pressure of 11.5 GPa. As the pressure was increased, ruby was utilized to monitor not only the pressure, but the hydrostaticity of the DAC chamber, following procedures found in Chai and Brown (1996) *et al.*¹³⁶ and seen in 4.4. By measuring the splitting distance of the R_1 and R_2 luminescence peaks as the pressure is increased or decreased, it was determined that the DAC chamber was hydrostatic over the pressure ranges investigated in this study. Therefore, any changes in photoluminescence spectra collected are due to compression only, not tensile or sheer stresses due to a nonhydrostatic environment.

The local environment of the scheelite Yb:YLF crystal contains a trivalent yttrium/ytterbium cation and a monovalent lithium cation coordinated by eight fluoride and 4 fluoride anions, respectively, as seen in Fig. 4.8A. Under ambient conditions, the quasi-tetrahedral LiF_4^{3-} sub-unit has been characterized to have ionic bonding, which is more easily compressible than the Y/Yb-F bond^{200–203}. The point-group symmetry of the trivalent cation site is S_4 . According to experimental^{188,189} and theoretical literature^{204–206}, as a YLF crystal undergoes compression in a hydrostatic environment, its phase changes from a scheelite phase (tetragonal, spacegroup $I4_1/a$) to a fergusonite phase (monoclinic, spacegroup $I2/a$), as seen in Fig.4.8A. The local symmetry of the trivalent cation site reduces to C_2 after the transition to the fergusonite phase. Raman and XRD pressure measurements^{188,189} place this phase transition pressure in a wide range pressures. Optical luminescence measurements of rare earth ions substitutionally doped into the yttrium site¹⁸⁸ have observed subtle reductions of local point-group symmetry at pressures above 10 GPa. Discontinuities in the phonon frequencies during Raman measurements, due to the stiffening of the LiF_4^{3-} bonds, indicated a structural phase transformation at 7 GPa²⁰¹. As previous papers have shown that photoluminescence from Nd and Eu ions can detect the transition from scheelite to fergusonite, we relied on these measurements for Yb, and the well known phase transition pressure of > 10 GPa, to track the phase transition of our YLF crystals. Overall, the phase transformation from scheelite to fergusonite is slow with the major structural changes occurring at < 10 GPa. All studies showed a reversible transformation from the fergusonite phase

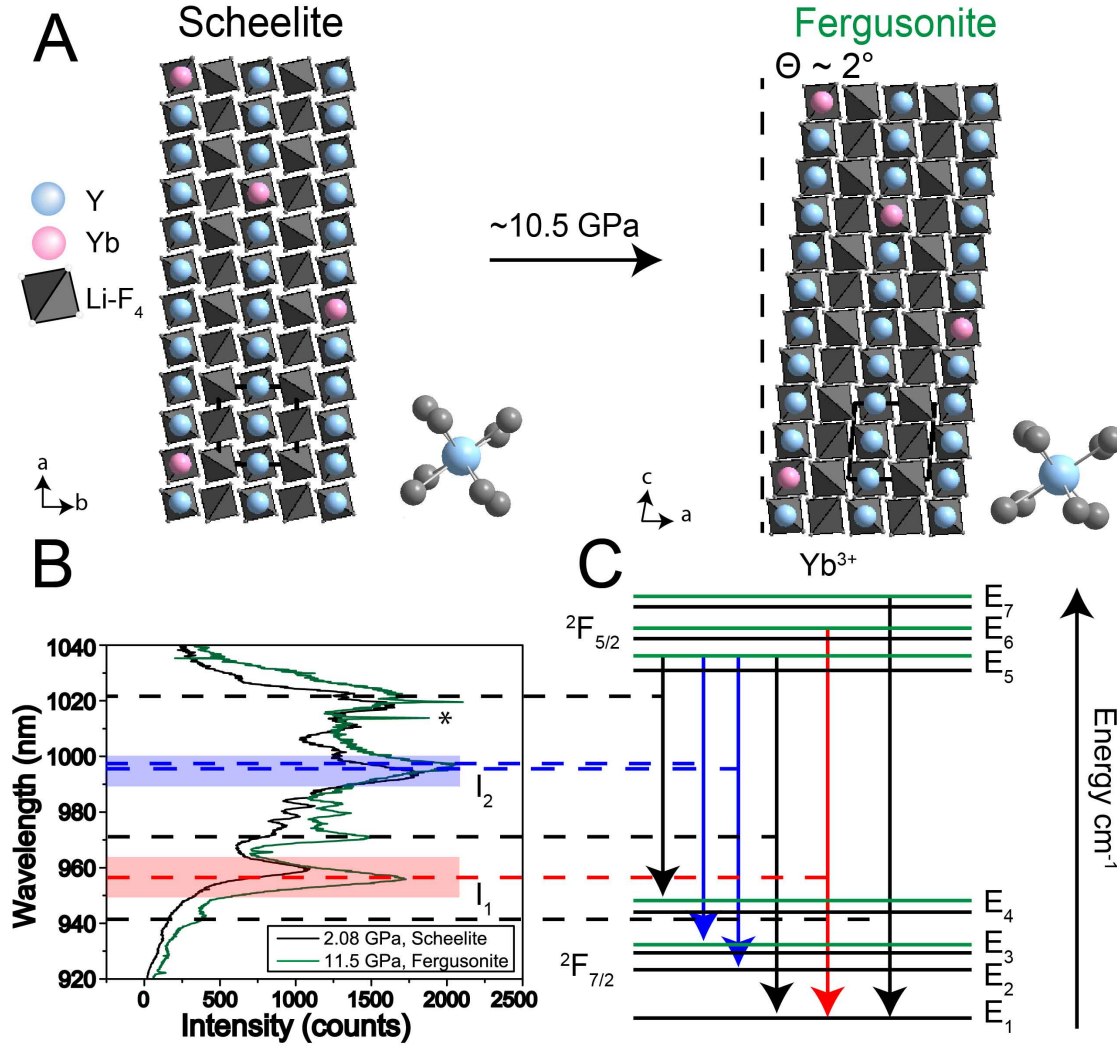


Figure 4.8: (A) The phase transition of Yb:YLF from tetragonal Scheelite ($I4_1/a$, $Z=4$) to monoclinic Fergusonite ($I2/a$, $Z=4$). The small inset illustrates the local symmetry of the Y/Yb ion next to the 8 nearest F neighbors. The local symmetry is reduced from S_4 to C_2 when transitioning from scheelite to fergusonite, respectively. (B) The full emission spectrum of Yb^{3+} ion at elevated pressure. The black line denotes the emission spectrum in the scheelite phase; the green represents the emission spectrum of the fergusonite phase. Key energy transitions are marked with a dashed line. The * denotes a cosmic ray. (C) The Stark manifold of the Yb^{3+} ion. The key energy transitions denoted in (B) are matched to their respective energy levels in the manifold. The energy transitions in blue and red represent the levels used for Boltzmann ratiometric thermometry analysis.

back to the scheelite phase when going back to ambient pressures, which is corroborated by our measurements. Theoretical calculations have predicted these phase transitions can occur at a range of pressures between 9²⁰⁷ and 5.5²⁰⁴ GPa .

Figure 4.8*B* illustrates the fluorescence spectrum of a trivalent Yb³⁺ dopant in the YLF host crystal. Based on the crystal field interactions from the host lattice, the ²F_{7/2} (ground state) and ²F_{5/2} (excited state) spin-orbit manifolds are further split into four and three Stark levels, respectively, giving a total of 12 possible transitions, as seen in Fig. 4.8*C*. The fluorescence peaks and their corresponding vibronic sidebands have been characterized by previous studies at low temperature and ambient pressure^{208,209}. From these studies, the energy transitions were derived based on the S₄ point group symmetry's reduced matrix elements and utilized to make predictions on the value of each energy level in the ground and excited state manifolds seen in Fig. 4.8*C*^{209,210}. To the best of the authors' knowledge the Yb³⁺ fluorescence spectrum in YLF has not been investigated while under compressive strain.

Increasing the pressure with the DAC is observed to have a significant impact on the crystal field levels for Yb ions in YLF. The black line in the emission spectrum of Fig.4.8*B* represents the emission when the scheelite phase is at elevated pressure (2.38 GPa) and the green line represents when YLF has already transitioned to the fergusonite phase (11.5 GPa). Overall, changes between the PL emission spectra clearly illustrate that the crystal field is being modified by the increasing strain. For example, three of the highlighted energy transitions shift in wavelength: the E₆-E₁ transition, the E₅-E_{2,3} transition, and the E₅-E₄ transition gradually blue shift, red shift, and red shift, respectively. The E₅-E₁ transition, increases in intensity as the pressure is increased. The E₇-E₁ transition both blue shifts and increases in intensity. At a pressure of around 6 GPa, a prominent new luminescence peak at a wavelength of ~970 nm is observed as shown in Fig. 4.8*B*, indicating the preliminary onset of the martensitic phase transition. Previous studies²¹¹ have linked the point group symmetry of a rare earth doped fluoride scheelite with its ligand field Hamiltonian to calculate

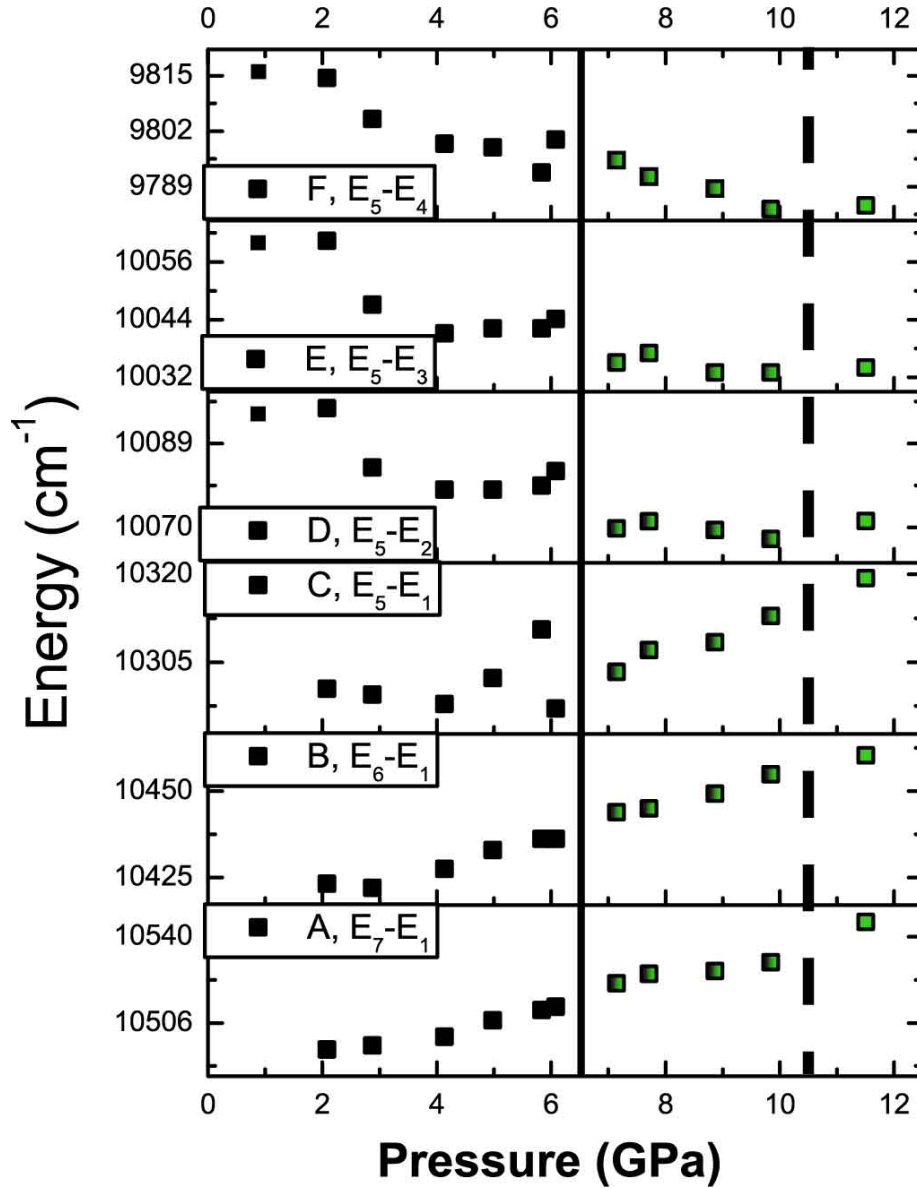


Figure 4.9: The key energy transitions highlighted in Fig. 2 over all experimental pressures. The green squares and green-black gradient squares indicate the energy transitions in the fergusonite phase and the slow conversion to the fergusonite phase, respectively. The solid line denotes the pressure (6.5 GPa) of observed, consistent discontinuities in the trend-line usually marking a phase transition. This occurs at a much lower pressure than what is previously reported in literature (10.5 GPa), which is denoted with the dashed line. (A) E_7-E_1 (B) E_6-E_1 (C) E_5-E_1 (D) E_5-E_2 (E) E_5-E_3 (F) E_5-E_4 Energy levels in the $^2F_{7/2}$ ground state and the $^2F_{5/2}$ excited state were measured and fit via Levenberg-Marquadt non linear least squares fitting.

its vibronic intensity parameters. Modification of the rare earth ion's point group symmetry with pressure can alter its surrounding ligand field and thus alter the intensities of its electronic and vibronic transitions, as can be seen in the E_5-E_1 transition ($\lambda \approx 970$) in Fig. 4.8B.

Figure 4.9 depicts the change in energy of the key transitions from Fig. 4.8B over all the pressure points investigated in this study. The emission spectra were fit with a Levenberg-Marquadt nonlinear least squares fitting in Python. With the code, the fluorescence peaks were fit to within a 0.1% error based upon the fluorescence peaks at ambient conditions from Ref²⁰⁸. As the spectra were fit at increasing pressures, the absolute energies of each level in the $^2F_{7/2}$ and $^2F_{5/2}$ manifolds were calculated based on the fitted energy transitions. These calculated energies were then checked with the E_7-E_1 energy transition, even as it blue shifted with increasing pressure. Each absolute energy level, from E_1 through E_7 , must add up to the total energy of the E_7-E_1 energy transition of the emission spectrum.

The trends in Fig. 4.9 of each key energy transition depict discontinuities at approximately 6 GPa, which normally indicates a phase transition. To reiterate, literature points to the phase transition to fergusonite at 10.5 GPa, but fluorescence experiments utilizing other RE ions show subtle structural changes as low as 5.5 GPa. The discontinuities depicted in Fig. 4.9 for each energy transition therefore illustrate similar trends. Each spectrum was fit with a linear trend-line to measure the energy shift change with increasing pressure of the transitions, as seen in SI Appendix Fig. S5. The most striking of the energy transition trends shown in Fig. 4.9, the E_7-E_1 , the E_6-E_1 , and the E_5-E_1 , illustrate an increasing energy as the pressure is increased with a slope of $5.3 \pm 0.3 \text{ cm}^{-1}\text{GPa}^{-1}$, $4.3 \pm 0.2 \text{ cm}^{-1}\text{GPa}^{-1}$, and $2.0 \pm 0.4 \text{ cm}^{-1}\text{GPa}^{-1}$, respectively. Even though the individual E_5-E_4 transition demonstrates a clear red shift in energy, with a slope of $-2.9 \pm 0.4 \text{ cm}^{-1}\text{GPa}^{-1}$, overall the energy levels in the manifold are increasing, as depicted in Fig. 4.8C. Subtle structural changes to the YLF host crystal, due to the increasing pressure, reduce the local symmetry of the Yb ion bonded to the LiF_4 tetrahedron to C_2 . Consequently, the fluorescence peaks convey very gradual shifting, either blue or red shifting, of the energy transitions as the Yb ion is responding to

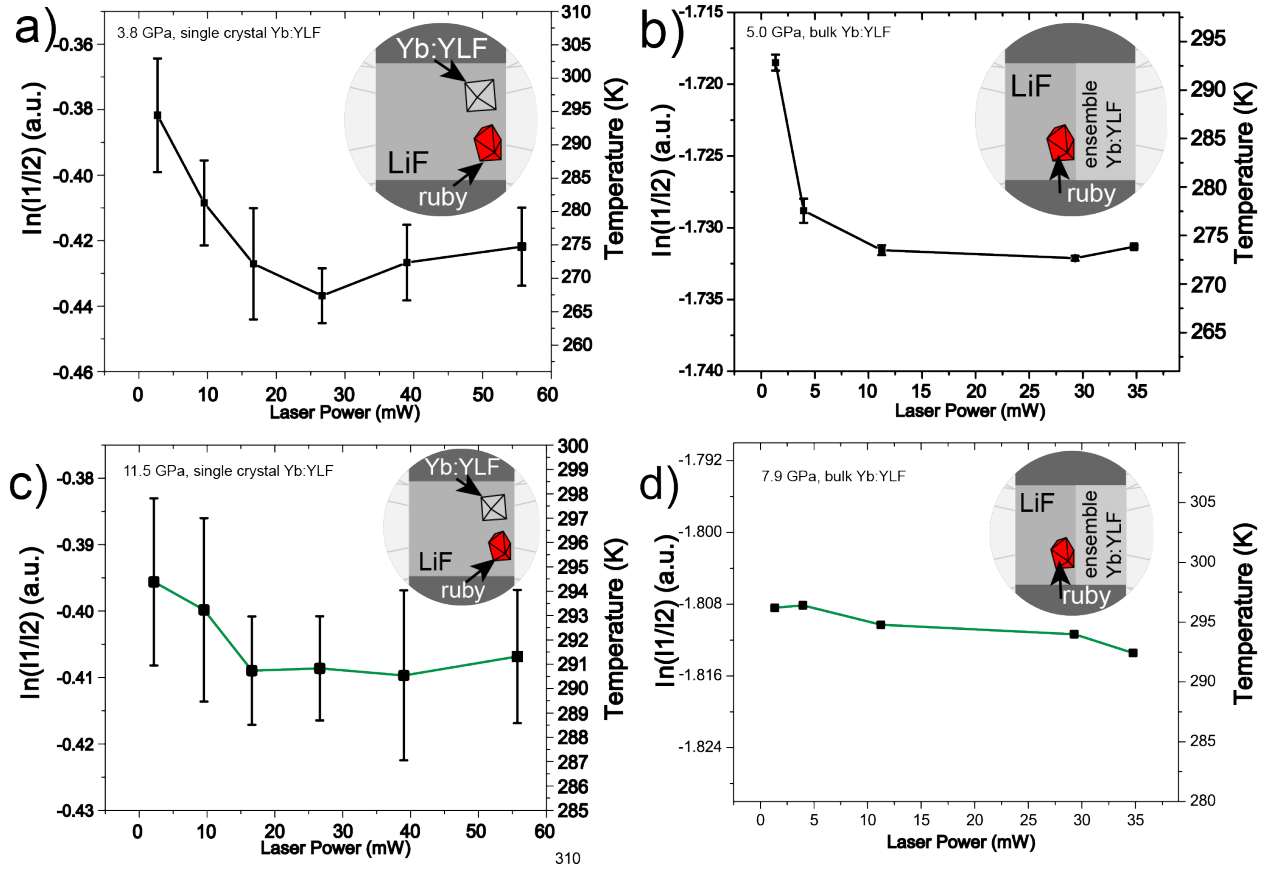


Figure 4.10: Optical refrigeration data from a Yb:YLF particle in the (A) scheelite and (B) fergusonite phase. Error bars represent the standard deviation of six separate measurements at each laser power.

the changing crystal field.

Figure 4.10 demonstrates the first measurements of solid-state laser refrigeration for the scheelite phase of YLF at various elevated pressure conditions for both the single crystal and bulk experiments. Ratiometric luminescence thermometry was utilized to measure the temperature trend of a Yb:YLF crystal inside a diamond anvil cell chamber based on the Boltzmann distribution of thermally accessible states. Two fluorescence peaks are chosen for integration, the E_6-E_1 and $E_5-E_{2,3}$ transitions, as seen in the blue and red shaded regions in Fig. 4.8B. When the laser power is varied, it is observed that the integrated

photoluminescence intensities of these two peaks change based on the internal temperature of the host crystal. As the internal temperature of the host crystal decreases, so does the probability of Yb-ions accessing higher energy configurations, which is reflected in the photoluminescence intensity. Under these circumstances, it is expected that the integrated ratio between the aforementioned emission transitions will also decrease. This trend is illustrated for the scheelite phase in Fig. 4.10*A&B*. After temperature calibration, the decreasing ratio between the two peaks could be used to quantify the temperature. A temperature decrease of approximately 20 ± 5 K below room temperature was determined for the single YLF particle in the scheelite phase at 3.8 GPa, as seen in Fig.4.10*A*. The magnitude of this temperature change is consistent with numerical finite element simulations shown in 4.6. Figure 4.10*B* also demonstrates the potential to refrigerate the bulk scheelite phase, as the ensemble was observed to cool approximately 17.0 ± 0.1 K below room temperature at a pressure of 5.0 GPa, immediately preceding the onset of the martensitic phase transition. One potential explanation for the smaller net cooling of the bulk sample is re-absorption from adjacent grains of Yb:YLF.

As discussed above, many of Yb^{3+} 's Stark manifold energy levels are modified with pressure. In particular, the E_5 - E_4 energy level red shifts as it enters into the fergusonite phase. This has major implications on the net cooling of Yb:YLF as the incident excitation of 1020 nm is no longer exactly resonant to this transition. Because the incident source is more energetic, anti-Stokes fluorescence still occurs, however, a reduction in the magnitude of cooling is observed, as seen in Fig.4.10*C&D*. For both the single crystal and bulk sample of Yb:YLF, the calibrated magnitude of cooling is much lower for the fergusonite phase than for the scheelite phase, with the former cooling by approximately 4K and the latter cooling by approximately 1.96 ± 0.02 K. As what was seen with the scheelite phase, there is a lower net cooling between the single crystal and the bulk sample. In future experiments, to verify this hypothesis, a tunable laser could be utilized to change the incident excitations source's wavelength to match the E_5 - E_4 energy level as it changes with pressure.

4.2 Conclusions

In conclusion, we have demonstrated solid state optical refrigeration for the first time at extreme pressure conditions. Both single micro-crystals and bulk Yb:YLF were placed inside a diamond anvil cell with LiF as a pressure medium. A martensitic second order phase transition of the Yb:YLF between scheelite and fergusonite phases was observed via photoluminescence spectra from Yb^{3+} ions. A decrease in the temperature of $20 \pm 5\text{K}$ below room temperature was observed for the scheelite phase for a single micro-crystal. Preliminary studies of temperature calibrated single Yb:YLF particles in water demonstrate cooling of approximately $16 \pm 5\text{K}$ below room temperature in the scheelite phase at elevated pressure 4.11. Raman measurements (4.11B) of the pressure transmitting medium, water, confirm its phase transformation to ice VII. This result illustrates the versatility of the particles cooling a variety of local environments and can potentially lead to achieving localized and fast cooling in-situ in the DAC. Specifically, utilizing these laser cooling capable particles could allow researchers to explore new territories of nucleation/crystallization and chemical fractionation kinetics at high pressures with various materials like high pressure ices that have major planetary applications^{212,213}.

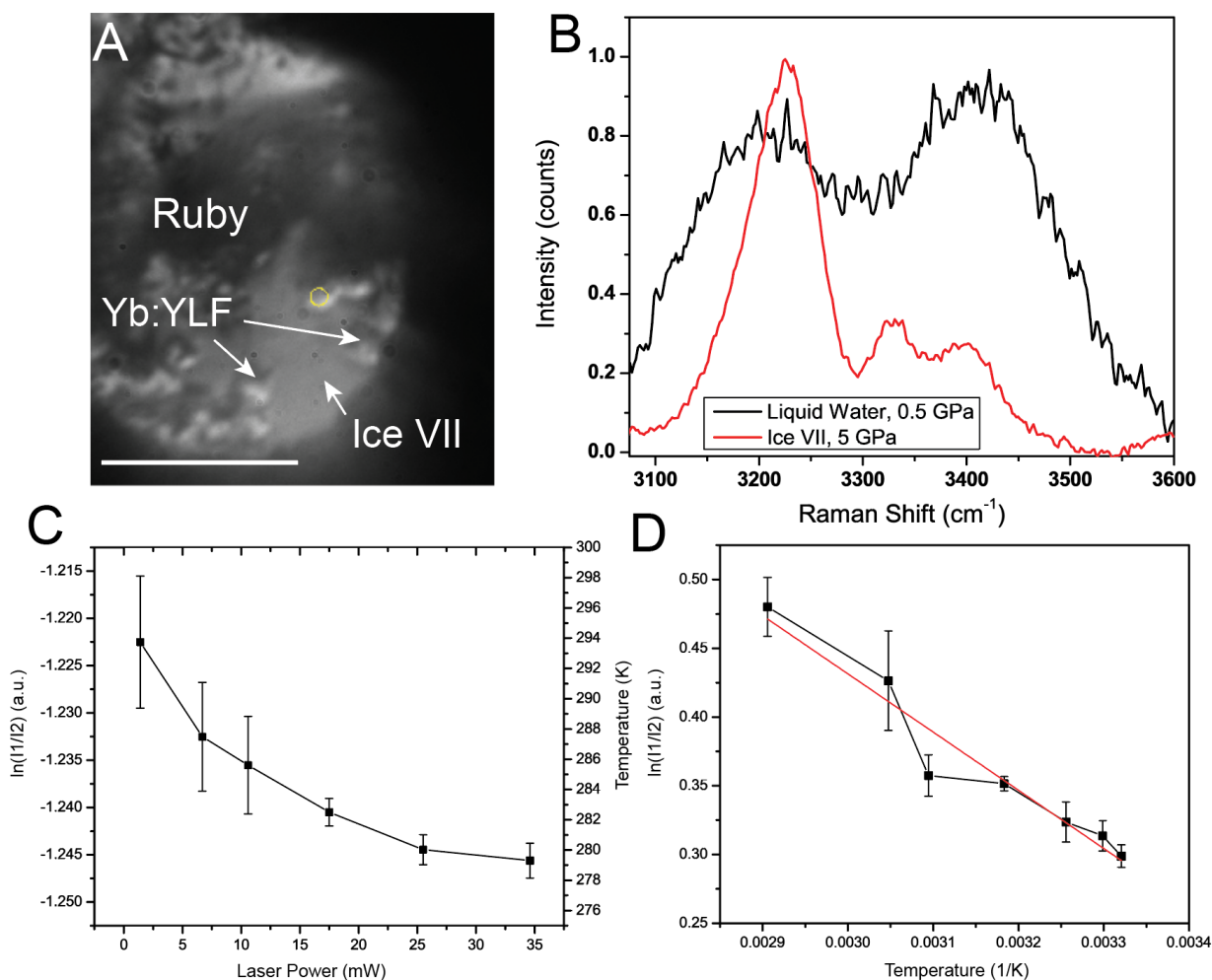


Figure 4.11: (A) Optical micrograph of DAC chamber with single Yb:YLF micro-crystals, ruby, and the pressure transmitting medium, water. At room temperature and 5.0 GPa, liquid water freezes to phase VII ice. The yellow circle denotes the position of the focused laser spot. The scale bar is 60 microns. (B) Room temperature Raman of the pressure transmitting medium at 0.5 GPa (liquid water) and 5.0 GPa (Ice VII). Demonstration of laser cooling (C) in water when a single Yb:YLF particle is in the scheelite phase at elevated pressure, 4.7 GPa. (D) Temperature calibration of the same Yb:YLF particle at 4.7 GPa.

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