R1-C.1: Understanding Heterogeneity of Energetic Materials

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II. PROJECT DESCRIPTION

Core funding for this project ends in Year 3 per the outcome of the Biennial Review process. Currently funded students will be supported via the ALERT Science and Engineering Workforce Development Program (SEWDP) (formerly known as the ALERT Career Development Grant Program) so as to not impact their degrees. Results of the student work will be reported in a special section of the ALERT Year 4 Annual Report.

A. Project Overview

The project at Texas Tech is centered on the heterogeneity of energetic materials. We seek to understand the structure of energetic materials and how that structure influences kinetic and thermodynamic properties. In addition, we have developed novel tools to determine thermodynamic parameters of high explosives. These two projects are discussed separately as: (1) Heterogeneous and mock energetic materials, and (2) Determination of thermodynamic parameters of explosives based on optical methods.

An important aspect of funding on this project, with so many participants, is that in 2015 and 2016 two graduate students were awarded internal fellowships covering 100% of their expenses (Baghi and Ramirez). We were able to leverage this unexpected funding to place additional students on the project (Fondren and Charles).

A.1. Heterogeneous and mock energetic materials

The scope of this work has investigated methods to produce a diverse range of materials which exhibit predictable properties with respect to morphology and structure. To this end, we have explored a synthetic methodology which can be used to control the texture, composition, and z-number of inorganic materials. Last year, we explored how the complex structure of inorganic materials can be modified by inducing a bimodal pore structure. These structures are proposed to allow for texture determination in X-ray screening due to the diverse heterogeneity observed in the same chemical structure.

During this year of the project, we focused our studies to produce mock materials with inherent heterogeneity that exhibited physical properties which can be modulated. Iron based systems (Fe_3O_4) that exhibit novel magnetic behavior at the nanoscale were synthesized, where the iron di-cation is substituted for an alternative transition metal di-cation; the Scanning Electron Microscopy (SEM) image of the cobalt substituted material is shown in Figure 1. To probe conductive behavior, a series of materials of Indium tin oxide (ITO) were made, where the mass percent of tin (Sn) in the material was systematically increased to determine the effect on conductivity. The material that has 17 mass percent tin with respect to indium is shown in Figure 1.

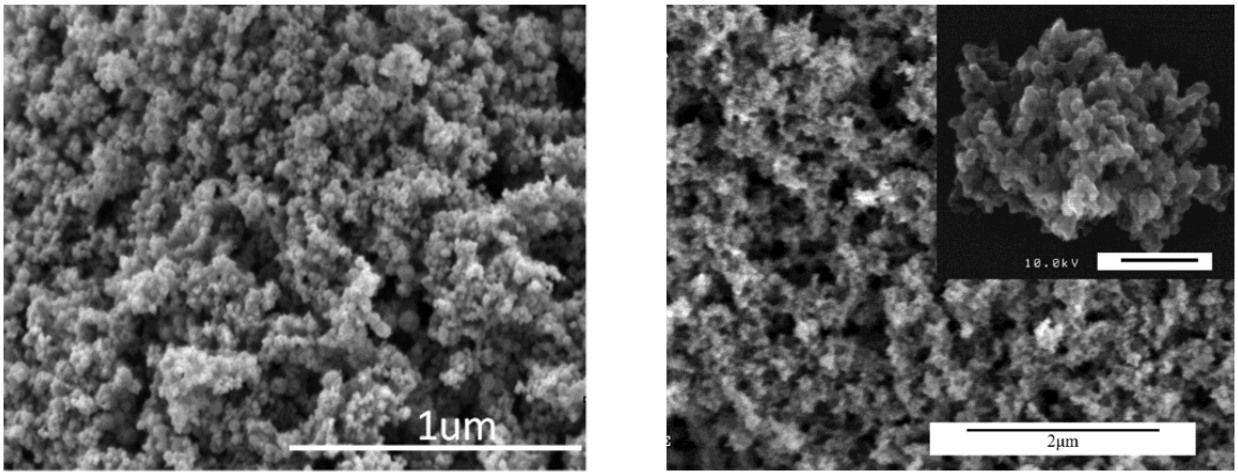

Figure 1: SEM of metal oxide aerogels: A) Conducting Indium Tin oxide; and B) Magnetic CoFe2O4 (Inset TEM image showing nanocrystaline structure).

The maximum conductivity of the ITO materials synthesized is ≈ 900 times higher than the previous mesoporous ITO materials prepared via sol-gel technique by Nazar [1]. The specific conductivity of the materials enhanced nonlinearly by increasing the Sn concentrations, reaching to a maximum at 17%. Increasing the Sn doping provides free electron carriers, which are responsible for the conducting property. Moreover, the higher Sn content increases the crystallite size, as was also observed in SEM images and power X-ray diffraction (PXRD) results. Larger particles contain a fewer number of grain boundaries, which behave as barriers against the electron moving, and are responsible for the charge scattering in the materials. Hence, a lower resistivity was obtained for the materials with larger particle sizes. Furthermore, the void spaces in the fluffy morphologies of the materials with lower tin content act as electron traps and defects in the structures. Therefore, there is higher resistivity compared to the more dense structures observed in the materials with higher tin content. However, it should be noted that increasing the tin content beyond 17% of Sn, results in a decrease in observed conductivity, which is related to the formation of tin-oxygen associates that were revealed to be present in trace quantities as crystalline SnO_2 phase in the PXRD pattern. Although this specimen possesses higher Sn^{+4} in the microstructure compared to the other ITO samples, the presence of excess SnO_2 in the material acts as an impurity in the material, and reduces the electrical conductivity. These results verify that dopant percentage, crystallite size, and the morphology of these mesoporous ITO materials have significant impact in the conductivity properties exhibited. Overall, the SEM, PXRD, and physisorption data demonstrated strong evidence consistent with the observed conductance values, as shown in Figure 2 on the next page.

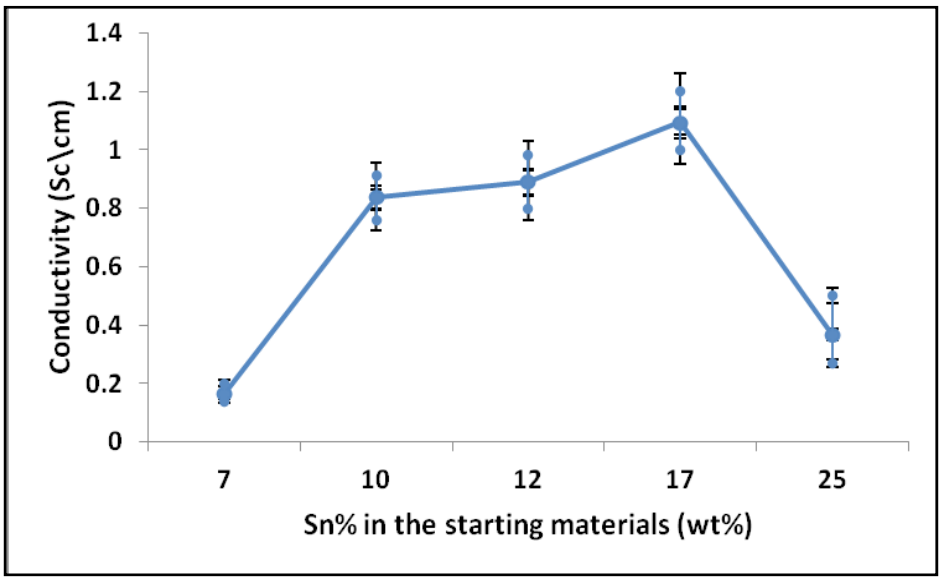

Figure 2: Conductivity of the mesoporous ITO materials annealed at 600°C.

The purpose of this work is to elucidate how mixtures of materials affect the final composition of a composite explosive. By understanding the chemistry and physics controlling the heterogeneity of a mock compound, the work's results can be expanded to explosives which are often mixtures/composites.

In addition to mock materials, we also investigated how synthetic conditions affect the heterogeneity of organic explosives. As an example, the crystallization of a secondary explosive, 2, 4, 6-Trinitrotoluene (TNT), can exist on one of two polymorphs: Monoclinic or orthorhombic. To modify the heterogeneity of TNT, crystallization studies were implemented to determine the factors which favor one polymorph over the other. We found that the morphology and polymorphs of TNT generated were influenced by both solvent and temperature. Precipitated TNT crystals with different morphology is shown in Figure 3 on the next page. The resulting crystals were analyzed by single-crystal XRD, which gave the polymorphic information of the crystals with the unit cell parameter. At lower temperatures, all the crystals exhibit a monoclinic crystalline structure, which is in agreement with that previously observed in the literature [2]. At a higher temperature (40^0C), crystals grown from methanol and ethyl acetate exhibit an orthorhombic unit cell, which has not been previously observed in the literature.

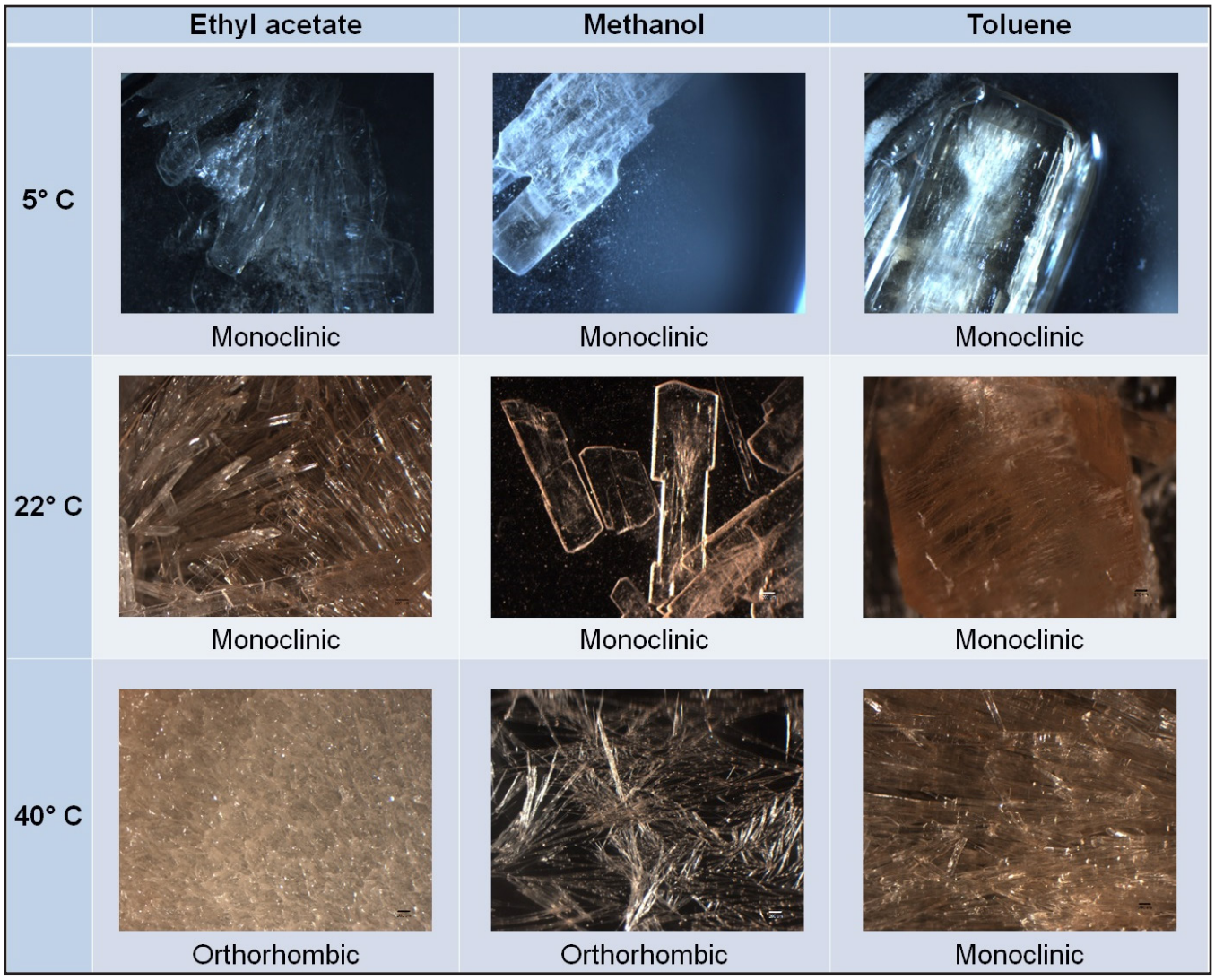

Figure 3: Morphology and polymorphism of TNT crystals produced by a solvent evaporation method at different temperature.

An alternative approach to induce crystallization is via crash precipitation. Again, our studies have indicated that temperature affects the type of crystalline polymorph exhibited, as shown in Table 1 on the next page. For the majority of conditions, the TNT crystalized within the monoclinic space group agrees with the data of Gallagher and Sherwood [3]. Most interestingly, at 40°C, the situation changed dramatically when we observed that the state of the resultant TNT product was drastically affected by the initial TNT solution concentration and the TNT solution to water mixing ratio. As shown in Figure 4 on the next page, altering the mixing ratio resulted in either the TNT precipitating out of solution to yield TNT crystals with an orthorhombic space group or, alternatively, to inducing crystallization of the TNT to precipitate as a super-cooled TNT melt; under some conditions no precipitation was observed. The super-cooled TNT melts were highly sensitive, and small changes in temperature and perturbation, resulted in the TNT melt, converted to a crystalline solid. The summary of the different phases induced by crash precipitation using a TNT solution in Acetone are shown in Figure 5 on the next page.

Solution temperature (°C) / Water temperature (°C)	5	22	40
5	Monoclinic	Monoclinic	Monoclinic
22	Monoclinic	Monoclinic	Monoclinic
40	Monoclinic	Monoclinic	Two immiscible layer (Orthorhombic)

Table 1: Polymorphism of TNT crystals produced by crash precipitation method at different temperature by dilution of solution with DI water at 1:1 ratio.

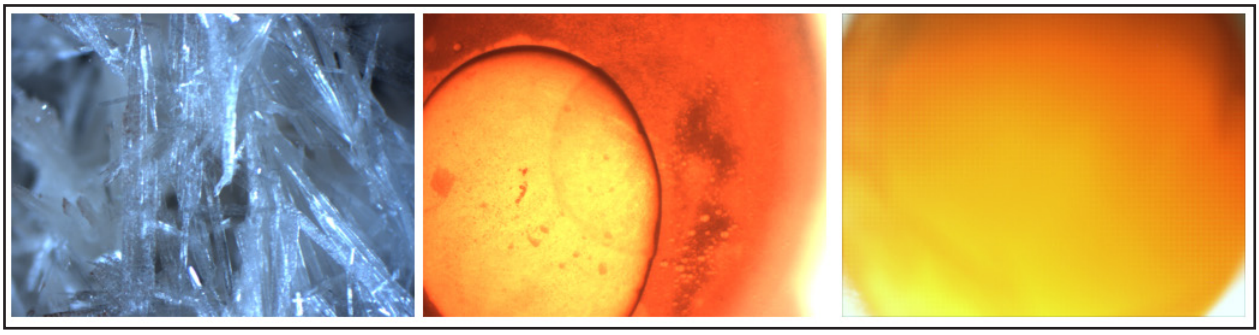

Figure 4: Three different observed situations after mixing TNT solution and DI water both at 40°C: (Left) Precipitation of solid TNT crystal; (Center) Precipitation of super cooled TNT melt; and (Right) No precipitation.

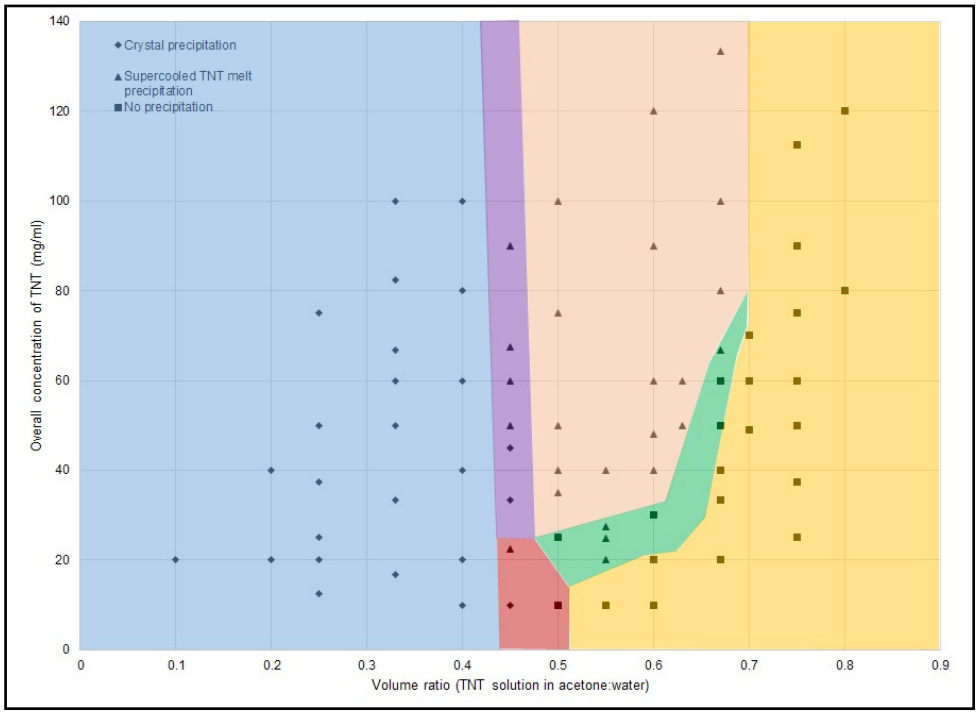

Figure 5: Dependency of phases of TNT crash precipitation on solution concentration and mixing ratio of two solvents. crystal precipitation, super cooled TNT melt precipitation no solution, two phase region between crystal and super cooled TNT melt, two phase region between super cooled TNT melt and no precipitation, three phase region.

A.2. Simultaneous determination of thermodynamic parameters for multiple compounds

Modern day analysis of thermodynamic parameters (e.g. vapor pressures, enthalpies, etc.) are mostly performed via Thermogravimetric Analysis (TGA). TGA techniques involve heating a particular sample in a TGA pan (usually made of platinum) to a relatively high temperature (below the boiling temperature) and then monitoring the rate of mass loss in real time relative the initial mass used. At a particularly high enough temperature, the total mass of the sample will completely volatize (i.e., from 100% to 0%), and the rate of disappearance depends on how fast the sample is heated (assuming a sufficient temperature for volatizing the sample is satisfied). For example, a slower heating rate yields a lower temperature at which 100% mass loss is achieved because the sample spends more time at each temperature, and, hence, vaporizes at lower temperatures.

In addition, for a composite mixture of two or more different chemicals with significantly different boiling points, a TGA curve displays two apparent mass losses at two different times (or temperatures since it is a rate). For example, a 50/50 mixture by mass may show 50% mass loss at a particular temperature, and then remain constant in mass until it reaches the next temperature to sufficiently vaporize the second chemical before returning to 0%. However, the aforementioned trend will only be observed for two chemicals with significantly different boiling points. If two chemicals with similar boiling points are used then it becomes impossible to distinguish two different vaporization events because both compounds will appear to vaporize at the same time (i.e., only one smooth curve).

The purpose of our investigation is to overcome the limitations of TGA for compounds of similar boiling points by using Ultraviolet/Visible (UV-VIS) optical spectroscopy. A major advantage of using UV-VIS is that the mass of the sample used does not need to be known as long as there is sufficient enough sample to ensure saturation of the vapor pressure relative to the atmosphere. By monitoring a maxima in the absorbance of a particular wavelength with increasing temperatures, it can be shown that the absorbance at a particular temperature can be plotted in a linear fashion to obtain the enthalpy of sublimation via the equation:

$$\ln[A(\lambda)T] = \ln\left[\frac{k\sigma(\lambda)l}{k_b}\right] - \frac{\Delta H}{k_b}\frac{1}{T}$$

where $A(\lambda)$ is the absorbance as a function of wavelength, T is the temperature in Kelvin, k is a constant (related to frequency of occurrence), k_b is boltzmann's constant, ΔH is the sublimation enthalpy, l is the path length inside the cuvette, and $\sigma(\lambda)$ is the attenuation coefficient relating the strength of absorbance per individual atom (depends on species of chemical and wavelength).

Our previous work focused on assessing the validity of simultaneously determining the enthalpy of sublimation of both benzoic acid and ferrocene. In addition, it was of interest to decrease the amount of one relative to the other to identify how small of an amount of either could be used while still observing reliable results. This method requires saturation of the vapor pressure of each chemical such that, below a certain mass, there are simply too few particles where in all molecules are in the vapor phase. While assessing the validity of these compounds, it was observed that ferrocene absorbs (to a smaller extent) in the same region as benzoic acid. According to Beer's Law, the total observed absorption at a specific wavelength can be taken as a superpositional sum of the absorbance of the individual molecular species at that wavelength. For example, if species 1 has an absorbance of 1 absorbance unit (A.U.) at 215 nm, and species 2 has an absorbance of 0.5 A.U. at 215 nm, a composite mixture should yield an absorbance of 1.5 A.U. if both are analyzed (assuming saturation conditions). Mathematically, this is represented as:

$$A(\lambda) = \sigma(\lambda)N_s l$$

or

$$A(\lambda)_1 = \sigma(\lambda)_1 N_{s_1} l$$
$$A(\lambda)_2 = \sigma(\lambda)_2 N_{s_2} l$$
$$A(\lambda)_{total} = A(\lambda)_1 + A(\lambda)_2 = (\sigma(\lambda)_1 N_{s_1} + \sigma(\lambda)_2 N_{s_2}) l$$

Therefore, it was concluded that in order to accurately distinguish between the absorbances at particular wavelengths for different chemical species, the attenuation coefficient for at least one compound must be known. In order to accomplish this, one must know precisely how many molecular absorbers are present. Recent work has focused on systematically increasing the masses of each sample, and analyzing the absorbance response at high temperatures. After reaching a maximum absorbance, the temperature of the system was decreased slightly to ensure there was not a decrease in the absorbance indicating all molecules were in the vapor phase. If sufficient mass is present, the chemicals will remain in equilibrium between the solid and vapor phases such that it does not require much mass to fill a container (i.e. cuvette) full of gas particles since they occupy a much greater space than the solid phase (see Fig. 6). If a small enough mass is added, all molecules will tend to the gas phase at sufficiently high enough temperatures, and a calibration curve can be made to relate a known mass (and, hence, number of absorbers) to the observed absorbance. By obtaining the attenuation coefficient, the total absorbance can be pieced together to indicate how much absorption is at a given wavelength due to one species or the other. For two chemicals, only one value would be needed. For 3 or more, the absorbance needs to be known for 2 out of 3, and so forth.

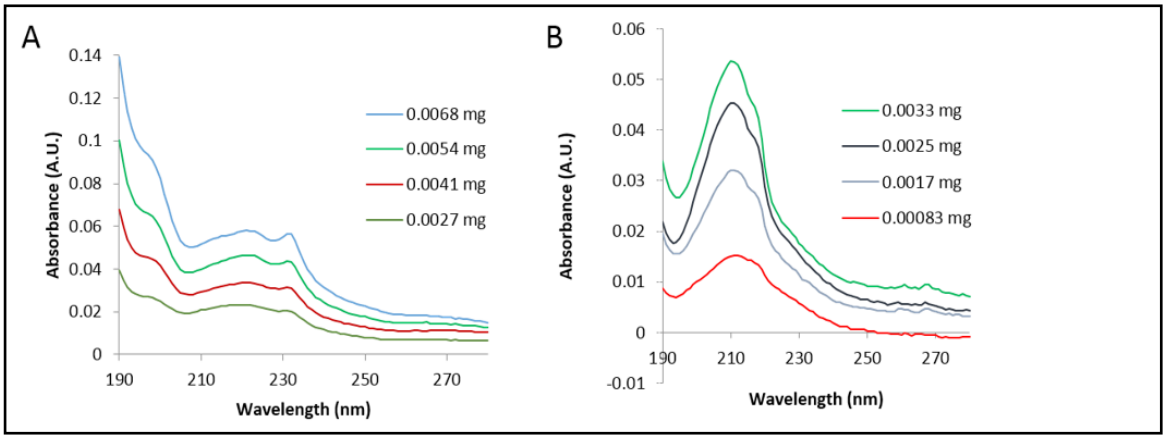

Figure 6: Calibration of absorbance with respect to mass for: A) Ferrocene; and B) Benzoic acid.

B. Biennial Review Results and Related Actions to Address

This project will be ending this year. The goal is to complete the current studies and have the students complete their degrees.

C. State of the Art and Technical Approach

C.1. Heterogeneous and mock energetic materials

Heterogeneity in both mock and real energetic materials is affected by impurities and synthesis conditions, and these can be used to control other physical properties such as conductivity. For example, the structures shown in Figure 1 have very different magnetic and conductive properties. We also demonstrated that polymorphic heterogeneity of TNT crystals is very much dependent on the condition under which the crystal is grown, such as temperature, concentration of TNT solution, and mixing ratio of solvent. The phase diagram of TNT crash precipitation can be used as a source of information to study heterogeneity of TNT crystals in

the future. The morphologic and polymorphic information of TNT crystal grown from different solvents can be used to determine the source of TNT (i.e., to distinguish between home-cooked and industrially-produced TNT).

C.2. Determination of thermodynamic parameters of explosives based on optical methods

The use of optical spectroscopy for determining thermodynamic coefficients was completely developed at Texas Tech [4, 5]. The only limitation to this work is that the compounds of interest must have an optical absorbance (from the infrared to the ultraviolet). The biggest advantage to this technique is that the amount of sample needed is on the order of an attogram, which is orders of magnitude less than that needed by TGA (mg), making the technique safer and more useful in forensic screening.

D. Major Contributions

D.1. Mock heterogeneous materials

Fundamental research on material properties is important to the ALERT mission. For example, there is interest in using the large void space created within the aerogels for the collection/confinement of energetic materials to enhance sensitivity of explosives detection. For example, Oak Ridge National Laboratory (ORNL) has developed a piezoelectric based explosives sensor [13]. One drawback on the ORNL piezoelectric senor is that that there is a limited surface area for the collection of explosive vapors. We have been working with Thomas Thundat (now at the University of Alberta) to incorporate the piezoelectric aerogels into his microcantilever detection scheme, which increases the surface area 10 fold.

We have also exploited the aerogel synthetic methods to prepare high surface area nitrocellulose composites. This work is focused on how various ionic impurities influence the final morphology (see Fig. 7). Therefore, it is now possible to study how the thermodynamic properties of energetic materials vary based solely on heterogeneity.

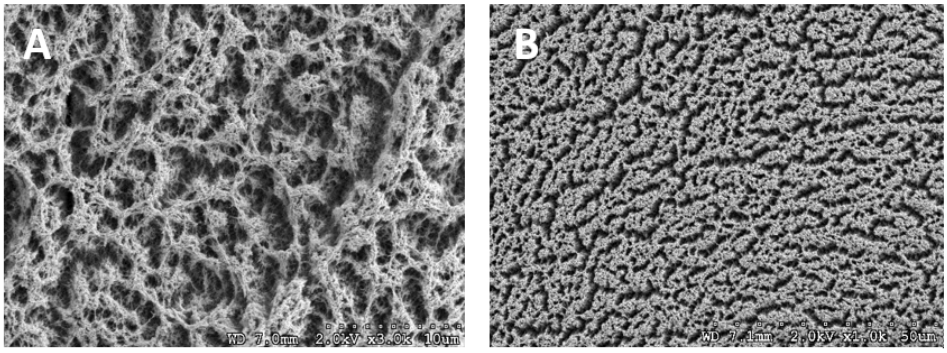

Figure 7: SEM structure of nitrocellulose aerogel: A) Impregnation with polyacrylic acid; and B) impregnation with copper ion.

D.2. Determination of thermodynamic parameters of explosives based on optical methods

We have provided experimental evidence for the diffusivity of pentaerythritol tetranitrate (PETN), research department explosive (RDX), and octogen (HMX), which agrees with theoretical values in the literature. Way Fountain (Edgewood Chemical Biological Center) had commented that “this data will go a long way to improve detection strategies” when it was presented. The current work focused on binary mixtures should further expand the information available for detection since it is the first method capable of determining thermodynamic properties of multiple materials simultaneously.

E. Milestones

E.1. Mock heterogeneous materials

Within the next year, we expect to have fully characterized texture from the metallic-based aerogels, including some novel sulfide and nitride materials. The future of the metal-based aerogels will be dependent on the needs of other ALERT thrusts/customers, where we can synthesize compounds with specific z numbers and densities to improve detection algorithms.

E.2. Determination of thermodynamic parameters of explosives based on optical methods

Through the summer of 2016, we expect to have completed and validated our studies to obtain calibration curves for ferrocene and benzoic acid. This will then allow for a more qualitative analysis for composite mixtures using Beer's Law. Once the data is validated, we will move into binary mixtures of explosives.

F. Future Plans

F.1. Mock heterogeneous materials

In the coming year, we plan to ensure that all the projects listed here are completed and the results of this work published in the scientific literature. Future plans on the mock heterogeneous metallic aerogels will be completed and the effects of dopant concentration on the magnetic and conductivity properties will be established. The effect of ionic impurity on the structure of nitrocellulose aerogels will be to elucidated to determine how the thermodynamics, kinetics, and sensitivities are affected by heterogeneity. In the next year of this project, we anticipate that we will be determining the sensitivity of the nitrocellulose aerogels by dropweight and laser ignition.

F.2. Determination of thermodynamic parameters of explosives based on optical methods

The future plan with this project is to be able to use optical spectroscopy to identify thermodynamic multicomponent explosives. Since many homemade explosives (HMEs) have multiple components, this technique will provide useful data on both detection and characterization. We are also interacting with companies (TA Instruments, Innosense LLC) on the commercialization of this technique but no timeframe has been determined.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

The primary challenge related to homeland security is to improve efficient detection of explosives, including:

1. Improving the detection via X-ray by being able to use texture to better screen for illicit explosives. We have developed mock materials with textures from the micro to the nanoscale. We can control the overall density (0.01 to 3g/cc), and we have expanded the range of the average atomic z-number in the material from 39 previously to 49 at present.
2. Understanding what controls heterogeneity in explosives and how heterogeneity influences the thermodynamic and kinetic properties of explosives. Experiments have shown that we can modify the heterogeneity of energetic materials through solvent/chemical processing by change the temperature or the inclusion of an impurity. This year, we anticipate completing the work and obtaining initiation sensitivity data.

B. Potential for Transition

Our early work within ALERT resulted in a patent application for high energy ionic polymer based explosives. Lawrence Livermore National Laboratory (LLNL) is currently holding the patent rights, and is working with potential commercialization partners.

C. Transition Pathway

Transition of any intellectual property must adhere to the Texas Tech Office of Commercialization. A dedicated office staff handles all IP issues and faculty are not directly involved to eliminate any potential conflicts of interest.

D. Customer Connections

- Michael Shlesinger, ONR 301
  - Project to determine the effects of weak energy on energetic materials.
- Maqsood Mohammed, USAF AFMCMC, Eglin
  - Project to determine the effect of particle shape on microwave heating of organic energetic materials and metallic based energetics.
- Corey Selman, InnoSense LLC, Torrance, CA
  - Commercialization of a disposable outgas sensor for energetic materials stability and aging for the Missile Defense Agency based on technology at TTU and InnoSense.
- Way Fountain, USARMY ECBC
  - Expressed interest in diffusivity data for sensor development.

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. Course, Seminar, and/or Workshop Development
   a. All the educational and outreach activities are unfunded at Texas Tech, and are primarily ad-hoc. We have hosted workshops for local bomb squads in the Chemistry Department every biennium, the last being offered in June 2014.
2. Student Internship, Job, and/or Research Opportunities
   a. Donald Ramirez will complete his dissertation work in summer 2016, after which he will begin a position as a Research Scientist at the Pantex DoE facility.
3. Interactions and Outreach to K-12, Community College, and/or Minority Serving Institution Students or Faculty
   a. Throughout Year 3, we visited several local schools (elementary and high schools) to visit with several groups to engage them in science and engineering. In April 2016, Prof. Hope-Weeks did a demonstration at Roscoe Wilson Elementary School. This program was mean to specifically engage female students with an interest in science; the focus of this was materials and energetics in the modern world. Profs. Weeks and Hope-Weeks also gave talks at All Saints High School in December 2015, which focused on current research in the area of energetic materials.

B. Peer Reviewed Journal Articles

1. D.C. UaCearnaigh, Roya Baghi, and Louisa J. Hope-Weeks. "Sol-Gel Synthesis of a Series of First Row d-Block Ferrites via the Epoxide Addition Method." RSC Advances 6(53), 11 May 2016, pp. 48212-48221. DOI: 10.1039/C6RA05831K

C. Other Presentations

1. Other
   a. LJ. Hope-Weeks. "Porous materials: From aerogels to energetic materials." University of Louisiana, September 2015.

D. Requests for Assistance/Advice

1. From Federal/State/Local Government
   a. Multiple requests each year are associated with local bomb squads on identification or handling of explosives. Main contact is Lt. Chris Eppler, Lubbock Sheriff's Department. 806-549-8038 Continuous interaction
   b. Several requests each year from the FAA on the identification on unknown materials. Main contact Gordon D. Morris FAA Flight Standards District Office. 806-740-3812.

V. REFERENCES

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