

High performance thermoelectric materials using solution phase synthesis of narrow bandgap core/shell quantum dots deposited into colloidal crystal thin films

Final Report, June 2005

I. Introduction and objectives of Phase 1

Thermoelectrics is the science and technology associated with thermoelectric converters, that is, the generation of electrical power based on the Seebeck effect and refrigeration by the Peltier effect. The attractive features of thermoelectric devices are their long life, low maintenance, they have no moving parts, they can be miniaturized, they do not produce emissions that might be harmful to the environment, and they are highly reliable.

Thermoelectric generators are used to provide electrical power in medical, military, and deep space applications where their desirable properties outweigh their relatively high cost and low operating efficiency. In recent years there also has been an increase in applications for thermoelectric coolers for use in infrared detectors, optical communications, and computing. The widespread use of thermoelectric components is presently limited by the low figure-of-merit of presently known materials.

The objective of the Phase 1 proposal was to demonstrate a new route to the realization of highly efficient bulk thermoelectric materials through engineering material structures at the nanoscale. Furthermore, the intent of our continuing work is to create these nanostructured materials using cost effective processes that will eventually lead to viable commercial products and fill a market need. In particular, interest lies in the application of nanotechnology to design thermoelectric materials whose intrinsic electrical and thermal properties are far better than the properties of traditional bulk thermoelectric materials.

Thermoelectric materials are used to create electrical power when a thermal gradient is placed across them. Optimal thermoelectric materials have an important intrinsic property measured by the Seebeck coefficient S , and require a delicate balance between electrical and thermal conductivities, σ and κ respectively, at a temperature T according to

$$ZT = \frac{S^2 \sigma T}{\kappa}. \quad (1)$$

Aside from a select few small band gap semiconductors/semimetals including, but not limited to, Pb(S,Se,Te), Bi(S,Te), and their alloys, most bulk materials have either large

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phonon and electrical transport coefficients (metals) or low phonon and electrical transport coefficients (insulators). It thus turns out that the best conventional thermoelectric materials at present, for instance $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, have a $ZT \sim 1$ at 300 K. On the other hand, the discovery of materials with $ZT \sim 2$ or greater would enable efficient power generation and general heating/cooling applications, and would have immense impact on military and commercial applications.

The difficulty of finding a route for improving thermoelectric materials through increasing σ/κ has suppressed advances in these technologies over the past few decades. Recently, however, Dresselhaus and other researchers have proposed that the bulk ZT limit can be overcome by focusing on the Seebeck coefficient, S . It has been suggested that S can be enhanced when physical dimensions in the devices are smaller than the spatial extent of the electron wavefunction. In this case the density of states, and therefore ZT is substantially increased. In practice, such a scenario can be achieved by growing nanoscale structures of low bandgap semiconductors/semimetals, for example quantum wells or quantum wires. The structures are able to conduct charge carriers but due to their small size, they scatter phonons more strongly than the bulk forms of the same material. Despite the exciting results, the methods used to create these structures such as molecular beam epitaxy (MBE) are incredibly expensive and can only be used on relatively small, rigid, and planar substrates.

Such potential advances in thermoelectric material properties hold the promise of both reducing cost and increasing conversion efficiency. The recent wave of new methodologies for material manipulation and fabrication on the nanometer scale inspires an alternative strategy for fabricating nanostructured thermoelectrics. Evident Technologies, Inc. is using its core competency in quantum dot synthesis, quantum dot surface modification and quantum dot composites to create cost effective, high ZT thermoelectric materials that self-assemble onto inexpensive flexible substrates. The focus of our research has been the preparation of viable quantum dot superlattices for thermoelectric applications. It is insufficient simply to assemble quantum dots into an ordered lattice, which can be achieved, for example as shown by Murray and co-workers at IBM. In that case the electron mobility is severely compromised because the transport is limited to a percolation mechanism.

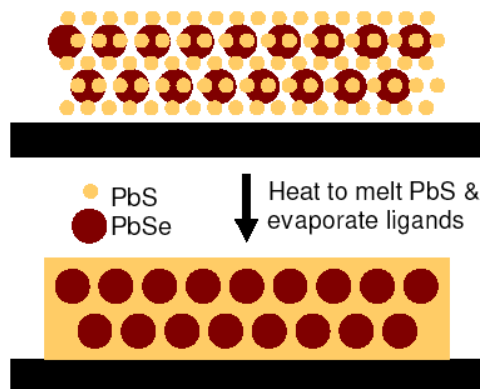


Figure 1

It has been proposed by Balandin and Lazarenkova that one should aim to prepare a material in the “electron transmitting-phonon blocking” regime, which means that the quantum dots interact sufficiently strongly with each other that mini-band formation facilitates carrier transport. To accomplish this it is necessary to remove the surface-protecting ligands from the quantum dots in order to permit them to approach each other to close separations, simply because the electronic coupling between quantum dots is strongly distance-dependent. We have taken this process a step further by using size-dependent physical properties of the quantum dots. Using the fact that small quantum dots have melting points significantly lowered from those of the bulk material, we were able to demonstrate the feasibility of melting small quantum dots in a binary self-assembled superlattice, Fig. 1, thus forming a nanostructured semiconductor host matrix, thus potentially optimizing miniband formation and hence carrier mobility.

In summary, we have made use of the unique properties of nanocrystalline semiconductors—state-of-the-art synthetic methods for controlling size and customizing semiconductor composition, the size-dependence of the melting point, and the ability of these materials to self-organize with precision—to demonstrate the feasibility of a new manufacturing protocol for viable quantum dot superlattices designed for thermoelectric applications.

II. Summary of the Aims of the Proposal & summary of the Research Results

Research results-

- PbSe/PbS core-shell quantum dot colloidal synthesis was unsuccessful due to temperature constraints on synthesis which result in quantum dot aggregation and uncontrolled precipitation in solution.
- Successful synthesis of 2 compositions of colloidal quantum dots composed of small bulk bandgap semiconductors (PbS and PbSe respectively)
 - Quantum dot material systems were selected because of their use as *bulk* thermoelectric materials and melting properties
 - Quantum dot diameters were also selected to impact size dependent melting point depression. It is known that small quantum dots melt at a lower temperature than large quantum dots and substantially lower than bulk quantum dots of the same material system.
 - 2 monodisperse populations of each quantum dot material system were synthesized, each having 2 mean diameters (<2nm and 2.5nm PbS, 8nm and 10nm PbSe)
- Successful demonstration of thin and thick films colloidal quantum dots assembled onto or cast into a variety of substrates including refractory metal boats, glass, and polyimide (Kapton) films.
 - Films comprising a single type of Quantum dot were assembled (i.e. PbS or PbSe) through a process where the solvent was eliminated from a QD dispersion resulting in the controlled precipitation of the QDs onto the selected substrate.

- Films of binary Quantum Dot mixtures at several ratios were assembled (i.e. PbS and PbSe mixtures) through a process where the solvent was eliminated from a QD dispersion and resulted in the controlled precipitation of the QDs onto the selected substrate.
 - ~1mm thick films were produced in the refractory ceramic boats and on low melting point polymer films indicating that large area thick films can be fabricated on inexpensive substrates.
- Successful demonstration that the organic ligands which surround the quantum dots for colloidal stabilization can be subsequently removed from assembled quantum dot films through low temperature heating under vacuum.
 - FTIR measurements indicate the lack of organic materials in heat treated quantum dot solid film samples
- Successful demonstration that films comprising a single type of quantum dot (i.e. PbSe or PbS quantum dots) can be solidified through a heating process whereby the temperature is significantly lower than the bulk melting temperature of the same material in bulk form (350°C)
- Successful demonstration that binary quantum dot films (i.e. PbSe and PbS quantum dot mixtures) can be solidified through a heating process whereby the small quantum dots melt (the larger quantum dots do not melt) at temperature is significantly lower than the bulk melting temperature of the same material in bulk form.
- Electrical conductivity of solidified quantum dot samples was low, presumably due to nanoscale voids remaining the films after the sintering process.

III. Experiments and Results

The synthesis of PbSe/PbS core-shell nanocrystals originally proposed remains extremely challenging without any notable success. The shelling process is best done by slowly adding the two reagents into a hot solution of the core nanocrystals which contains appropriate stabilizing ligands. By controlling the temperature and the rate of addition, the shell material epitaxially grows onto the core particle. All efforts to synthesize PbSe/PbS resulted in an insoluble aggregation of the materials. Likely this is due to the overly strong reactivity between Pb and S. As soon as the surface of the nanocrystal is sulfur rich it reacts with a neighboring nanocrystal containing a Pb rich surface resulting in aggregated particles resembling bulk material. Efforts to utilize different sulfur precursors and lower concentration levels to control the reactivity were unsuccessful. The recent results of Lifshitz and co-workers along the lines of these core/shell synthesis efforts indicate that the shell turns out to be an alloy of PbS and PbSe, which is not the material of choice for the first stage of our project.

An alternative strategy was developed to provide comparably structured materials and simplifying the processing thus eliminating the need for the pyridine ligand exchange, Task 2. This strategy utilizes the significant changes in the physical properties of materials that emerge on the nanometer length scale. It is well-known that electron-phonon coupling, and as a result the melting point and other properties, are strongly influenced by the size and shape of small metal or semiconductor nanoparticles [A.

Tamura, K. Higeta, & T. Ichinokawa, J. Phys. C (1982), 15, 4975]. Results have been recently reported in the literature, for example, experimental observations of the melting point depression of CdS [Goldstein et al, Science (1992), 256, 1425] and theoretical studies of CdS [Zhang et al, Semicond. Sci. Technol (2001), 16, L33]. The melting point of semiconductor nanocrystals is significantly depressed with decreasing particle size. For instance, bulk CdS melts at ~1400°C whereas CdS nanocrystals 7 nm in diameter melt at ~1150°C, while those 3 nm in diameter melt at just 600°C.

Based on this phenomenon, our manufacturing process involves combining very small nanocrystals of PbS (bulk mp 1118°C) with large nanocrystals of PbSe (bulk mp 1078°C). Heating the mixture to a temperature just high enough to melt the PbS provides a nanostructured honeycomb matrix of PbS interspersed with PbSe nanocrystal islands, Figure 1. The organic ligands are stripped in the process because their boiling point under vacuum is below the melting point of the PbS nanocrystals. This modification eliminates the necessary pyridine ligand exchange, which would be required if annealing the originally proposed core-shell nanocrystals on account of insufficient heat to strip the ligands resulting from the synthesis.

The PbS and PbSe nanocrystals were prepared via a solution phase synthesis. Although the specific details of the synthesis are proprietary, the routes are similar to published methods. [C. B. Murray, S. Sun, W. Gaschler, H. Doyle, T. A. Betley, C. R. Kagan, *IBM J. Res. Dev.* **2001**, 45, 47; M. A. Hines and G. D. Scholes, *Adv. Mat.* **2003**, 15, 1849] In general, the lead precursor is heated in high boiling point hydrocarbon solvents. This solvent mixture contains organic molecules with a coordinating functional group off the end of a long chain hydrocarbon. The coordinating group binds to the lead while the long hydrocarbon chain provides solubility of the complex and ultimately stability as a surfactant ligand on the nanocrystal. A solution of either the sulfur or selenium precursor is rapidly injected into the reaction vessel containing the hot lead complex. The colorless reaction solutions turn dark brown indicating nucleation and growth of the nanocrystals. The reaction is stopped by rapidly cooling the mixture. The size of the nanocrystals is tuned by modifying reaction parameters such as concentration, temperature, and growth time before cooling.

The PbS and PbSe nanocrystals are precipitated out of the reaction mixture by adding polar solvents such as methanol, butanol, and acetone. The particles are collected as a powder and can be redispersed into a variety of organic solvents. The nanocrystals of different materials have the same solubility properties and can be readily mixed together for preparation of the nanocrystal composite films.

Absorption spectroscopy is the primary tool used for characterization of the nanocrystals upon reaction completion. The position of the first exciton peak and its width are direct indicators, respectively, of the average size and size dispersion of the nanocrystals. The further the peak is blue-shifted from the bulk band gap energy, the smaller the particle diameter. Concurrently, the narrower and more symmetric in shape the peak is the tighter and more uniform the size distribution. The absorption spectra for the various PbS and

PbSe samples used to prepare the composite films for thermoelectric characterization are pictured in Figure 2.

This information is quantified by TEM imaging. TEM also provides information on the shape and crystalline quality of the particles. TEM samples are prepared by placing a drop of dilute nanocrystal solution onto a carbon coated copper grid and either allowing the solvent to evaporate fully or wicking away the excess. The proper parameters, notably concentration and solvent choice, result in an ordered self-assembled monolayer of nanocrystals on the grid. Figure 3 displays the TEM images of the PbS and PbSe samples used for film preparation. Figure 4 is a HRTEM image of PbS and clearly indicates the high crystalline quality of the nanocrystals, which are rock salt crystal structure.

The nanocrystal composite films were prepared by mixing together solutions of PbS and PbSe of different sizes. Composites containing small PbS (2.5 nm) and big PbSe (8 nm) as well as small PbSe (< 2 nm) and big PbS (10 nm) were investigated. The PbSe and PbS were mixed in ratios of 1:2 and 2:1 by weight. Additionally, films of pure PbS and pure PbSe were prepared for comparison to the composite films. The mixed nanocrystal solution was deposited dropwise onto the substrate allowing for solvent evaporation between drops. The substrates utilized were glass cover slips, ceramic boats, and polyimide sheets. The glass cover slips turned out not to be suitable. The composite films delaminated off of the surface after processing. The ceramic boats similar in design to a mold additionally demonstrate that the process is readily adaptable to the preparation of bulk materials. The use of polyimide sheets (Kapton 500 VN) as a substrate demonstrates that processing on flexible plastic components is possible.

The samples were loaded into a quartz furnace tube and heated to 200°C under vacuum. It is reported in the literature that these same ligands undergo desorption from FePt particles at ~200°C [Perez-Dieste et al, Appl Phys Lett (2003) 83, 5053]. Under vacuum this temperature is above the boiling point of the ligands. The ligands, which are an oily liquid at room temperature, are removed from the particle surface and condense in the cooler portions of the tube outside of the furnace. The samples were heated at 200°C for approximately 18 hours after which the samples were heated to 350 °C then slowly cooled to room temperature. The long heating duration was chosen to achieve adequate removal of the organics, especially in the thick ceramic boat samples. FTIR confirms this with the presence of organics in samples heated for only a few hours and drastically reduced amounts in samples heated for 18 hours. A firm conclusion confirming the lack of organic in the samples cannot be made at this point on account of instrument issues and difficulty in obtaining a proper spectral background. The temperature 350 °C was chosen because below it films of pure 2.5 nm PbS nanocrystals appear to melt while no apparent change occurs with the 8 nm PbSe nanocrystals. These samples are pictured in Figure 5. As well, pictures of the thin films on polyimide are provided in Figure 6.

The samples were sent to Dr. Larry Olsen at Pacific Northwest National Laboratory for characterization of the electrical properties. Unfortunately, most of the samples sent for characterization were too resistive to measure the electrical conductivity. Although for

three of the samples characterized the sheet resistance was measurable but the calculated resistivities were too large by several orders of magnitude to permit measurement of the Seebeck coefficient.

Physical characterization of the sample films by TEM and EDX was performed by Prof. Greg Scholes at The University of Toronto. The PbSe/PbS composites after processing were embedded in polymer for microtombing and imaging by TEM. The EDX provides qualitative compositional analysis and confirms the presence of Pb, S, and Se (Figure 7). Additionally it indicates the presence of C and O. Both the organic ligands on the nanocrystals and the embedding polymer contain these elements so therefore these results cannot be used to assess whether or not the ligands have been fully removed during processing. EDX can also be used as an imaging tool and provide spatial resolution of by collecting x-rays of a characteristic energy for a given element. For our samples collecting a Se x-ray would provide evidence to confirm the presence of PbSe quantum dots within the surrounding PbS structure. Unfortunately due to time constraints we were unable to obtain this EDX imaging but will be able to provide these results in the Phase II proposal. The conclusion drawn from the TEM images is that the composite films, although crystalline, contain structural discontinuities and voids. The images are presented in Figure 8 along with a small area diffraction pattern. The diffraction rings are cleanly spaced indicating crystallinity but the presence of rings rather than discrete spots, which would be present from diffraction off a single crystal, indicates that the composite is highly polycrystalline.

Although this work has demonstrated the feasibility of a new manufacturing process for the preparation of nanostructured composites, the characterization results of the electrical properties do not yet indicate successful preparation of a thermoelectric material. The discussion must turn towards possible explanations for the poor electrical properties of the films.

In order for there to be good electrical transport properties within the films the samples need to be highly crystalline. The process relies upon melting the small PbS nanocrystals to subsequently envelop the interspersed larger PbSe nanocrystals, which do not melt. One question raised is whether upon removal of the stabilizing organic ligands from the particle surface do the small PbS nanocrystals sinter together forming a highly non-uniform yet bulk-like material thus modifying the low melting point of the PbS? If so, then the melting point of the resulting PbS matrix would in principle be higher than the embedded PbSe nanocrystals. Without melting, the PbS matrix would likely be polycrystalline or possibly amorphous. Discussed previously, the TEM images indicate that the samples appear non-uniform and porous as a bulk material yet polycrystalline in structure. One possible route to improve the crystallinity of the material would be introducing pressure into the experiment rather than preparing the samples under vacuum. Alivisatos has conducted extensive research investigating the phase transition of CdSe quantum dots under high pressure from wurtzite to rock salt crystal structure.

An additional issue would be if upon formation of bulk-like PbS whether or not organic ligands remaining in the film are trapped and cannot diffuse out of the matrix. These

bulky highly insulating organics would result in poor electrical transport properties. The FTIR data supports that extending heating of the samples under vacuum virtually eliminates organic ligand from the sample. The question that needs further exploration is whether the processing can be improved by utilizing smaller ligands than those currently resulting from the synthesis. If the ligands are not fully desorbed and removed with the vacuum, they could additionally be removed by heating to temperatures sufficient to decompose the organics. The by-products formed would be small sized molecules which would more easily diffuse out of the bulk or be trapped within interstitial voids that might not interfere with charge transport. The disadvantage to this route is that such high temperatures could induce vast diffusion and alloying of the PbSe nanocrystals into the PbS matrix destroying the integrity of the nanostructured composite.

One final possibility to comment on is the introduction of dopant metal atoms for improved charge transport. In bulk thermoelectric materials p- and/or n- dopant atoms are incorporated to improve transport. Although, the basis of this work is to develop a nanostructured thermoelectric material utilizing semiconductor quantum dots, which in theory offer unique electronic properties owing to quantum confinement and thereby do not necessarily require the same properties as a traditional bulk TE material. Future work would certainly entail breaking of the 1:1 stoichiometry currently in place for PbSe/PbS composite.

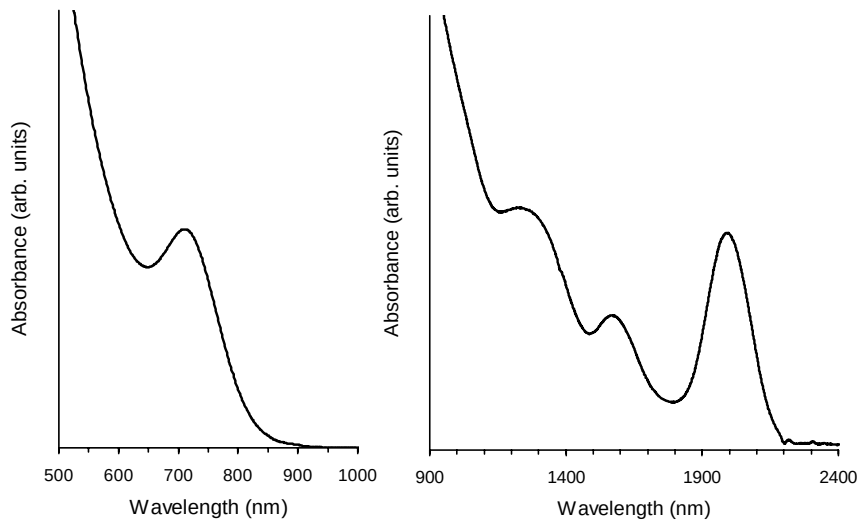


Figure 2: Absorption spectra for the PbS (left) and PbSe (right) nanocrystals used to prepare nanocomposite films.

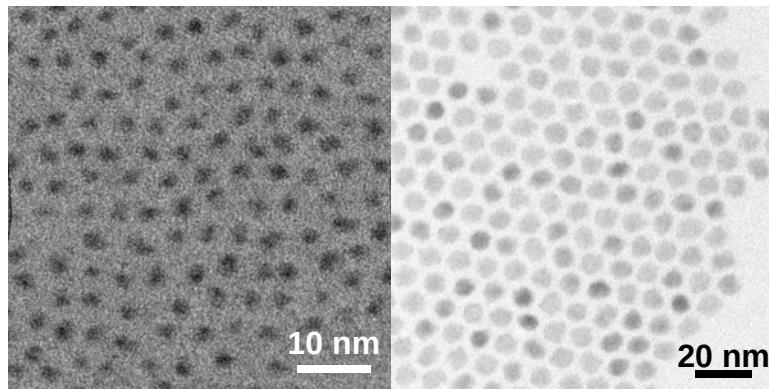


Figure 3: TEM images of colloidal nanocrystals of 2.5 nm PbS (right) and 8 nm PbSe (left).

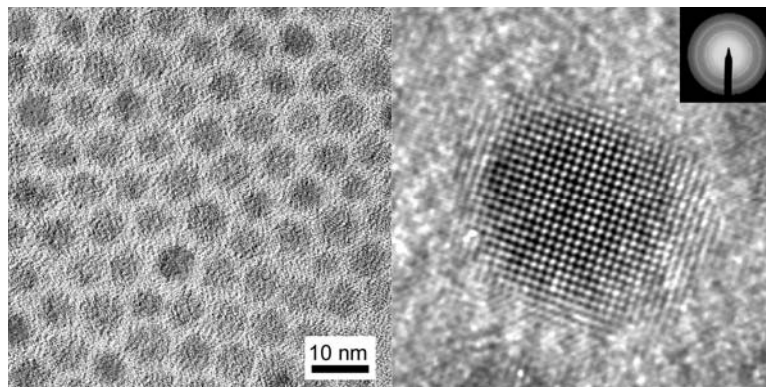


Figure 4: HRTEM image of PbS nanocrystals – (left) a highly ordered array of particles and (right) a single particle. The inset on the right is the small area diffraction pattern of the particles.



Figure 5: Ceramic boats containing films of PbSe, above, and PbS, below after heating under vacuum at 200°C then 350 °C.

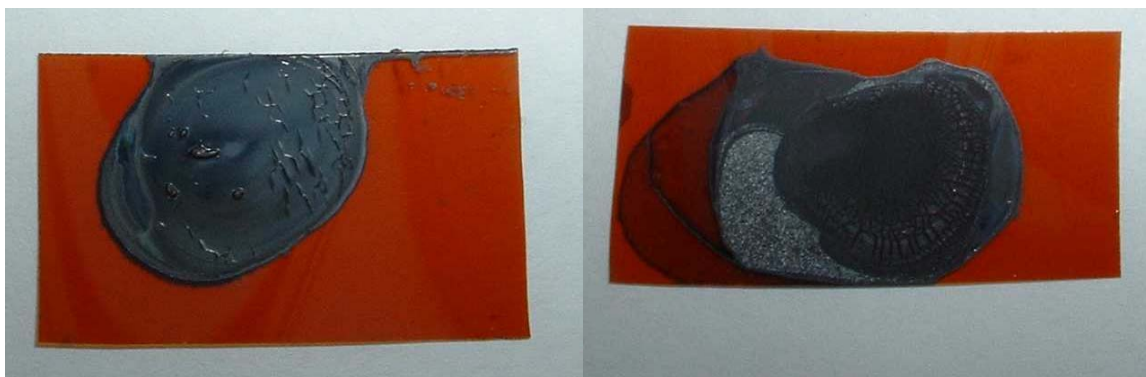


Figure 6: Films of PbSe/PbS composite on polyimide after processing. The samples correspond to the ratios of 1:2 (left) and 2:1 (right) by weight PbSe:PbS

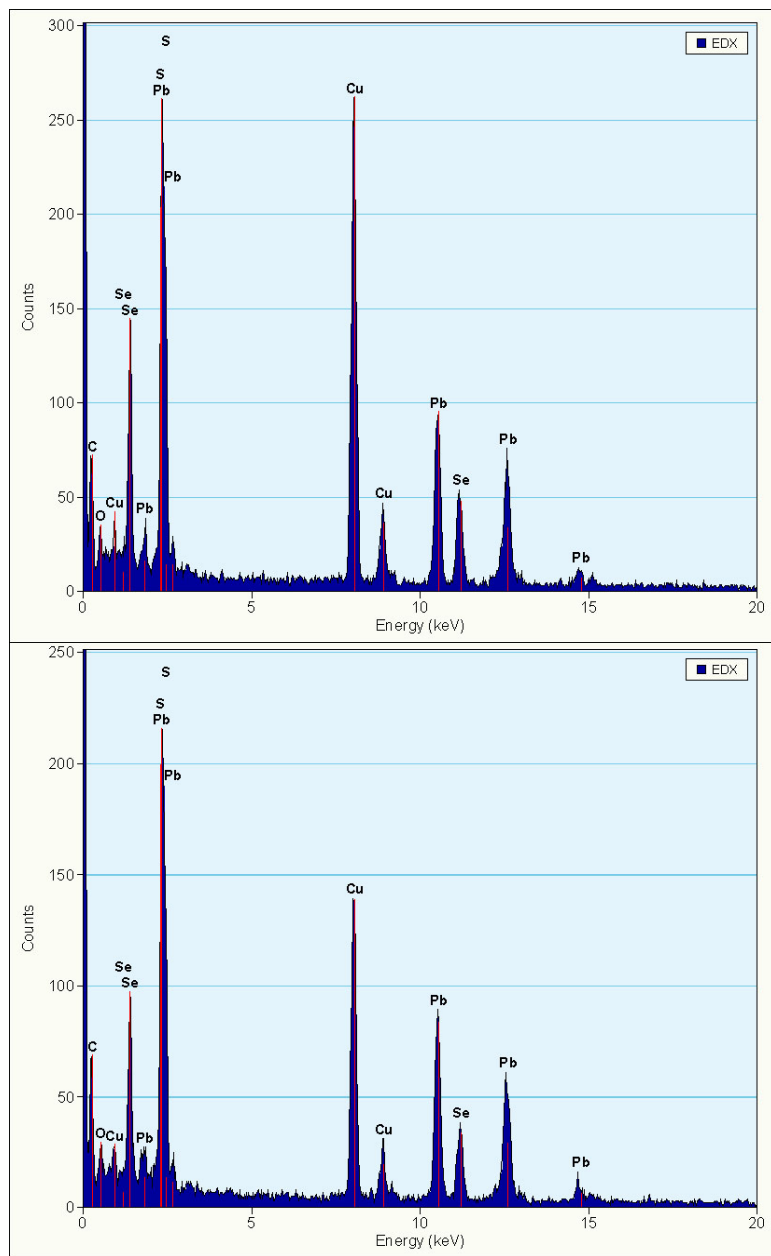


Figure 7: EDX spectrum of composite films prepared from mixtures of 1:2 (top) and 2:1 (bottom) PbSe:PbS nanocrystals.

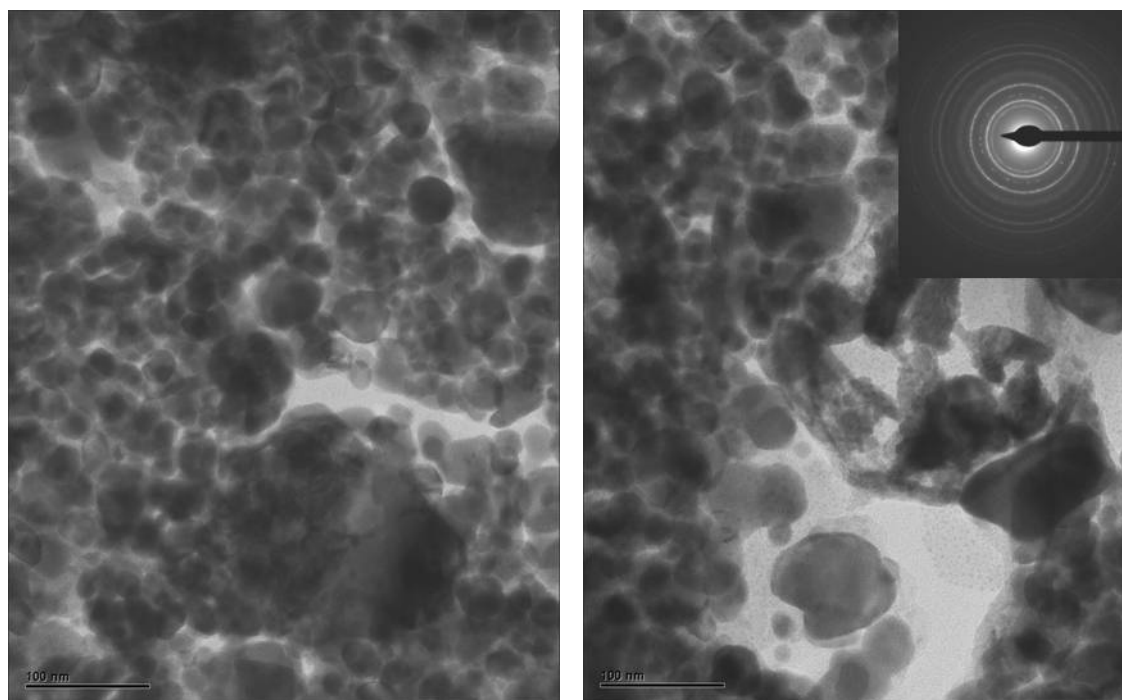


Figure 8: TEM images of PbSe/PbS composites with corresponding ratios by weight of 1:2 (left) and 2:1 (right). The inset on the upper right corner is the corresponding small area diffraction pattern for the imaged sample.

IV. Summary and Conclusion

High efficiency thermoelectric devices for efficient energy generation or cooling have been in development for several decades with relatively little success due to the inherent limitations of bulk small bandgap semiconductor material systems. Recent work by Dresselhaus and others have demonstrated that thermoelectric materials comprising small bandgap quantum dots embedded in a matrix of another small bandgap semiconductor can achieve significant enhancement of the ZT coefficient compared to traditional bulk thermoelectric materials. These nanoscale thermoelectric materials were fabricated by repeated epitaxial deposition of one semiconductor material onto an underlying semiconductor layer such that quantum dot islands are formed and subsequently buried by the following deposition step. Typically, these structures were grown using molecular beam epitaxy or other techniques that are expensive, restricted to small and flat substrates, and cannot yield significantly thick films. The inability to produce thick films using MBE is a particular drawback because the geometry of thin film confers both increased electrical resistance and increased thermal conductivity (in the transverse direction); both drawbacks for a practical device. Hence, despite the promise of these nanoscale materials applied to thermoelectric devices, the limitations of the present fabrication methods have rendered them unviable in a commercial sense.

Through the course of this Phase I project, Evident Technologies attempted to produce films derived from thermally processed colloidal quantum dots that mimic those prior nanoscale structures that have demonstrated marked improvements in the thermoelectric figures of merit. Colloidal quantum dots composed of the same bulk material systems used in traditional thermoelectric devices can be produced economically at large scale through chemical processes. Furthermore these quantum dots can be deposited as thin or thick films (on the order of or greater than a millimeter) through controlled precipitation onto a substrate. It is the company's belief that such an approach can eventually yield the desired performance metrics but at large economically viable production scales.

The initial approach revolved around the synthesis of colloidal core-shell quantum dots having a spherical PbSe core enveloped in a PbS shell. These quantum dots were to be precipitated onto a substrate through a controlled elimination of the solvents in which they were dispersed. Following precipitation, residual organics were to be removed through gentle heating followed by a higher temperature sintering step that would fuse the shells only and leave the inner core in tact. In practice the synthesis of the core-shell quantum dots proved exceedingly difficult. The growth temperatures of the PbSe core and the PbS shell are very similar resulting in uncontrolled aggregation of particles and subsequent precipitation during synthesis. After significant efforts this method was abandoned and a new method was conceived to achieve the same desired structures using a colloid approach.

The new approach relied on the observation that melting temperature is not only dependent on material composition but also heavily dependent on the size of the materials. Small particles have lower melting points than larger particles. This phenomenon is particularly apparent at the nanoscale. We proposed that by mixing

together two (or more) populations of quantum dots where one population is larger and composed of a higher bulk melting point material than the other population the smaller quantum dots in the mixture could be melted at a lower temperature than the larger quantum dots. The melt would surround the remaining quantum dot population and could be resolidified. The resulting material would contain quantum dots of one materials system embedded within a solid semiconductor matrix of another.

To this end the company synthesized four populations of colloidal quantum dots (2 sizes of PbS and 2 sizes of PbSe). It should be noted that Bismuth Selenide quantum dots were also synthesized but were not used to make subsequent films. Thin and thick films of each of those populations and several binary mixtures of those populations were deposited onto a number of different substrates including glass, refractory metal, and polyimide (Kapton) films. Thickness varied from microns to the millimetres and we believe that it is possible to create films of even greater thickness if necessary. Organic ligands used during quantum dot synthesis were driven out of the films by exposing the films to temperatures greater than their boiling point. The organic ligands do not conduct charge carriers and it is believed that residue remaining within the quantum dot films would adversely affect the respective thermoelectric performance. The presence or absence of organic ligands was determined via FTIR.

The quantum dot films were exposed to temperatures of several hundred degrees for hours to tens of hours after driving off residual organic ligands. The exposure temperature was below that of the underlying substrate, including plastic Kapton films, and significantly less than the melting temperature of bulk PbS or PbSe. Solidification of all films was observed.

Film samples were sent to Pacific Northwest Laboratory for determination for I-V characteristics and measurement of the ZT coefficient. All samples showed significant electrical resistance which prevented further investigation of ZT coefficient. TEM analysis showed a number of nanoscale vacancies that is believed to result in the low electrical conductivity. The cause of these vacancies are not know but may be a result of the conditions used to precipitate the quantum dots or the method conditions used to remove organic ligands.

The company believes that the approach can be optimized to economically produce large area thick materials having an enhanced ZT over that of conventional bulk thermoelectric materials. The method is not limited to PbSe and PbS quantum dots and can be expanded to include BiSe quantum dots or other colloidal nanoscale semiconductors. Furthermore, the distance between quantum dots within the second semiconductor matrix can be tailored using this method. In the following development phase the company would like to explore a number of parameters including the quantum dot material choices, relative quantum dot sizes and concentrations, distance and relative position from one another. Furthermore, processing conditions will be examined including the solvents, ligands, and evaporation time used to precipitate the quantum dots from solution, the temperatures and length of time at temperature used to drive off residual organic ligands and subsequent quantum dot sintering.

Outline of Plan for Phase II

We have established the feasibility of a new processing route for preparing self-assembled semiconductor quantum dot materials that have great potential as thermoelectric materials that can be cheaply produced. Recent experimental results as well as theory suggest that a new avenue towards improved thermoelectric materials is offered by nanostructured multicomposite semiconductors. A route to preparing materials with such a composition is to self-assemble colloidal quantum dots (QDs), remove organic surface materials, and anneal the material so that the QDs interact sufficiently strongly that conductivity relative to bulk materials is not greatly compromised. This latter step is important to create extended valence and conduction bands that may be thought of as Bloch states originating from periodic quantum dot “unit cells”. Balandin and Lazarenkova describe this new extended band structure as “minibands”.

We have discovered a processing route for forming such periodic states in multicomponent materials based on the size-dependence of the melting point of QDs; it is diminished markedly as a function of size. This allows controlled melting of one component (e.g. PbS) prior to others by customizing the size of the QDs self-assembled into the material. In turn, that allows more controlled fabrication of the thermoelectric material. The challenge presented by this approach, however, is that the nature of the phase transitions occurring is not understood. For example, we have shown that small PbS quantum dots can be synthesized and melt at 350°C. That process can be understood easily provided that the liquid phase also has nanometer dimensions. However, how do we describe the liquid phase formed when an array of QDs melt? A critical size parameter must evolve that will cause the melt to refreeze into a nanostructured array—probably resembling a periodic array of “necked” spheres. However, gaining an understanding of this process, “nanostructure melting”, and how to employ it to our advantage in thermoelectric material fabrication will be pursued in Phase II.

A successful outcome for Phase II will be ensured by achieving the following goals:

- (A) To understand and optimize the selected material systems that the ensuing thermoelectric materials are to be composed of.
- (B) To understand how the size of the constituent quantum dots, their relative ratios, distance from one another, and position relative to one another affects the resultant electrical and thermal conductivity.
- (C) To optimize the assembly of quantum dot films from the solution phase in order to minimize nanoscale voids that can reduce ZT.
- (D) To understand the controlled melting of periodic quantum dot arrays.
- (E) To optimize surface ligands so that they can be efficiently removed during the initial processing step.
- (F) To optimize processing condition to obtain excellent electrical transport properties in bulk-like films having thicknesses greater than 1mm.
- (G) Demonstrate enhanced thermoelectric properties of the materials and preliminary devices.

The following is a summary of the tasks we will accomplish in Phase II:

I. Empirical studies of thin films to address fundamentals of processing

A. Optimize the deposition of quantum dot thin and thick films. Parameters including the selection of solvent, evaporation rate, and surfactants will be optimized to minimize nanoscale vacancies that will lead to defects after film solidification.

B. Optimize organic groups for efficient removal during stage 1 annealing
Organic capping surfactants are required to keep the quantum dots in solution. The removal rate of those organic molecules depends on the molecular weight of the surfactant molecules and the strength at which they adhere to the quantum dot surface. Ligand exchange will be performed to replace the “standard” ligands with ligands having low molecular weight and weak adhesion to the metal atoms present on the surface of the nanocrystals. Temperature and bakeoff time will also be optimized to maximize organic residue removal. The role of film thickness will be explored on the rate at which residual organics are eliminated from the quantum dot films.

C. Investigate processing parameters: heating time, temperature, pressure
The methodology required to melt followed by freezing of one population of quantum dots in a binary quantum dot film will be rigorously examined. The role of the selection of quantum dot compositions and the size of the particles and the ensuing affect on melting parameters will be explored. Naturally, the temperature, time at temperature, and temperature ramping are leading factors in the melting and subsequent solidification of quantum dot sub-populations and will be optimized. Furthermore the team will investigate the role of pressure on the elimination of nanoscale vacancies that are a result of imperfect deposition of the quantum dots from solution. Characterization will be achieved by measuring current-voltage characteristics and physical characterization using transmission electron microscopy and small-angle X-ray scattering.

II. HRTEM investigation of melting and annealing of close packed nanocrystal arrays for single and binary compositions

A program of fundamental studies, in collaboration with University of Toronto, will be undertaken to elucidate **the mechanism and extent of nanostructured melting** by periodic arrays of QDs. Facilities important for this work include a high-resolution TEM facility, state-of-the-art X-ray diffraction instrumentation, and optical characterization.

III. Expand processing of thin films to thick films and bulk-like samples (ETI)

The TEM studies will illuminate the mechanism behind nanoscale melting and solidification. In particular, those studies will demonstrate the role of quantum dot composition size and density, as well as the affect of interstitial organic residues on the quality of solidified binary quantum dot (or ternary or quaternary quantum

dot films for that matter). Quality, in this case, is defined by the dearth of atomic and nanoscale vacancies. The company and contractors will focus on the growth of thick ($>1\text{mm}$) films having an enhanced ZT. Films of these thicknesses can be achieved with the proposed approach by the full elimination of residual organics and complete densification of those films will be challenging. That said, it is recognized that although high quality thin films may be used for scientific investigation of the thermoelectric properties of materials, practical thermoelectric devices will require large thermal gradients and low electrical resistance exhibited by thick films.

IV. Fabricate proto-type devices for testing and characterization (PNNL)

Devices will be fabricated comprised of solidified quantum dot films of varying thicknesses deposited on a further plurality of substrates. Substrate composition and the affect on resultant ZT will be explored. Substrate compositions will include a selection of materials such as polyimide (kapton), fused silica, borosilicate glass, and a variety of metals. In addition the role of electrode material and method of deposition on ensuing thermoelectric device performance will be explored.