DOE award #: DE-FG02-06ER46333 (Texas A&M University)

Project title and PI: "Low-Temperature Synthesis Routes to Intermetallic Superconductors," Raymond E. Schaak (PI)

Date of report: May 14, 2007 (covering the period Aug 16, 2006 through May 11, 2007)

Brief description of accomplishments:

Program Scope

Over the past few years, our group has gained expertise at developing low-temperature solution-based synthetic pathways to complex nanoscale solids, with particular emphasis on nanocrystalline intermetallic compounds. Our synthetic capabilities are providing tools to reproducibly generate intermetallic nanostructures with simultaneous control over crystal structure, composition, and morphology. This DOE-funded project aims to expand these capabilities to intermetallic superconductors. This could represent an important addition to the tools that are available for the synthesis and processing of intermetallic superconductors, which traditionally utilize high-temperature, high-pressure, thin film, or gas-phase vacuum deposition methods. Our current knowledge of intermetallic superconductors suggests that significant improvements could result from the inherent benefits of low-temperature solution synthesis, e.g. metastable phase formation, control over nanoscale morphology to facilitate size-dependent property studies, robust and inexpensive processability, low-temperature annealing and consolidation, and impurity incorporation (for doping, stoichiometry control, flux pinning, and improving the critical fields). Our focus is on understanding the superconducting properties as a function of synthetic route, crystal structure, crystallite size, and morphology, and developing the synthetic tools necessary to accomplish this.

This research program can currently be divided into two classes of superconducting materials: inter-metallics (transition metal/post transition metal) and metal carbides/borides. Both involve the development and exploitation of low-temperature synthesis routes followed by detailed characterization of structures and properties, with the goal of understanding how the synthetic pathways influence key superconducting properties (Tc, Hc, Jc) of selected target materials. Because of the low-temperature methods used to synthesize them and the nanocrystalline morphologies of many of the products, the superconductors and their nanocrystalline precursors are potentially amenable to inexpensive and large-scale solution-based processing into wires, coatings, films, and templated or patterned structures with nanoscale and microscale features. Also, because of the new synthetic variables that play a key role in the low-temperature formation of intermetallics, the possibility exists to discover new superconductors.

Recent Progress

During this first (partial) year of funding, we have focused on ensuring that we can routinely generate superconducting materials using newly developed and modified low-temperature synthetic strategies. This work involved both synthetic development and characterization of the

superconducting properties for a selected set of superconducting intermetallics, as proposed. Our initial targets were chosen to ensure that phases which are known to be superconducting as bulk solids synthesized using traditional high-temperature methods are also superconducting when made using low-temperature methods. (This is important, because such "control" studies are often ignored during synthetic development work, yet are critical for ensuring that useful materials can be formed.) Our initial targets were NiBi, Bi_2Pd, and $BiIn_2$, and all were found to be superconducting with T_cs matching those reported previously (Figure 1). Of these, only NiBi has been previously reported to form by low-temperature methods.

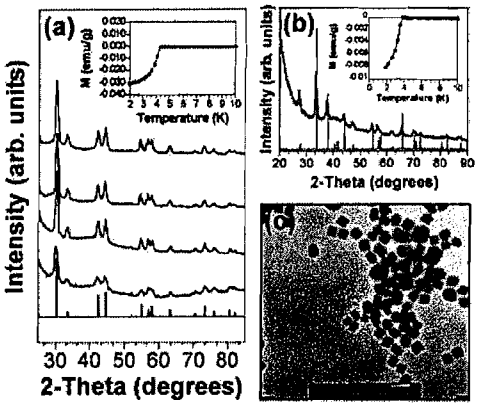

Figure 1. (a) XRD (bottom to top: simulated, 260 °C for 1, 3, 5, and 7 h) and magnetization data for NiBi; (b) XRD, magnetization, and (c) TEM data for Bi_2Pd.

NiBi is a strategic first target for this project, because it is a known superconductor that can be made by multiple low-temperature and high-temperature techniques, including arc melting, powder metallurgy, solvothermal methods, polyol synthesis, and other methods for comparison purposes. Our lowest-temperature protocol involves the synthesis of NiBi directly in solution at 260 °C for 3 h using a modified polyol process (Figure 1a). Upon annealing at 550 °C for 3 h, it becomes superconducting with $T_c = 4.2$ K (Figure 1a). The degree of crystallinity can be systematically modified using a range of solution and powder annealing protocols (Figure 1a).

Superconducting Bi_2Pd can also be synthesized as uniform nanocubes using a modified polyol process (Figure 1b,c). Bi_2Pd is a bulk superconductor as-synthesized in solution at 280 °C for 3 h with no additional annealing necessary. Interestingly, the published phase diagram for the Bi-Pd system shows two Bi_2Pd polymorphs. Both have been reported to be superconducting, but the 4.2-K superconductor is the high-temperature polymorph, stable only above 380 °C. We are able to access this polymorph below 280 °C. This provides evidence that we can access metastable intermetallic superconductors as bulk solids using our low-temperature strategies, one of the hypotheses of our original proposal.

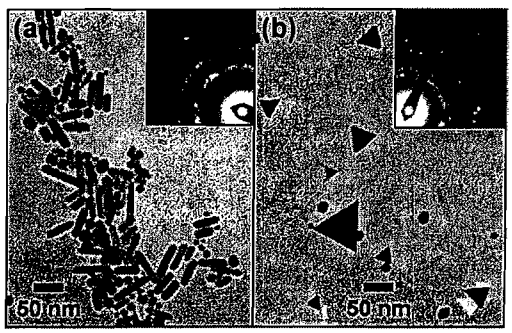

Figure 2. TEM and SAED data for (a) β-Sn nanorods and (b) In nano-triangles.

We have developed several solution chemistry strategies for converting nanocrystalline metals into intermetallics (including new and metastable structures), and this provides another potential low-temperature pathway to intermetallic superconductors. Thus, we spent some time preparing nanocrystalline elemental superconductors using similar protocols. Figure 2 shows TEM images of superconducting β-Sn nanorods and In nanotriangles, which can be used as templates for the formation of shape-controlled Sn- and In-based intermetallic superconductors.

As an alternative low-temperature strategy for synthesizing intermetallic superconductors, we have developed a new approach that combines our solution chemistry methods with more traditional metallurgical ideas. To do this, we utilize a polyalcohol solvent (e.g. tetraethylene glycol with a boiling point of ~ 300 °C), and add to it bulk metal powders in stoichiometric ratios. One of the components must be a metal having a melting point close to or below that of the boiling point of the solvent (e.g. Sn, Ga, In, Bi). Since the solvent is weakly reducing, oxidation is minimized, so the reactions do not need to occur in a sealed system (e.g. in sealed evacuated silica tubes). Also, bulk-scale samples are accessible, and the product morphologies often mimic those obtainable via arc-melting, e.g. ingots that can be crushed into smaller crystallites (Figure 3). So far we have succeeded at accessing Ni_3Sn_4, $NiGa_4$, BiIn, $BiIn_2$, $CoGa_3$, $FeGa_3$, $CoSn_3$, Cu_6Sn_5, $FeSn_2$, NiBi, and InSb at temperatures below 300 °C and with no additional annealing (Figure 3). Of these, $BiIn_2$ is a known superconductor, and we find it to be superconducting as-made (Figure 3). The formation of NiBi using this method is also very important, because it allows us to make comparisons with NiBi synthesized using other low-temperature methods. We also have preliminary data suggesting that $NbGa_3$ forms using this strategy, providing evidence that the intermetallic Nb-Ga and Nb-Sn superconductors might be accessible using this low-temperature chemistry, as proposed.

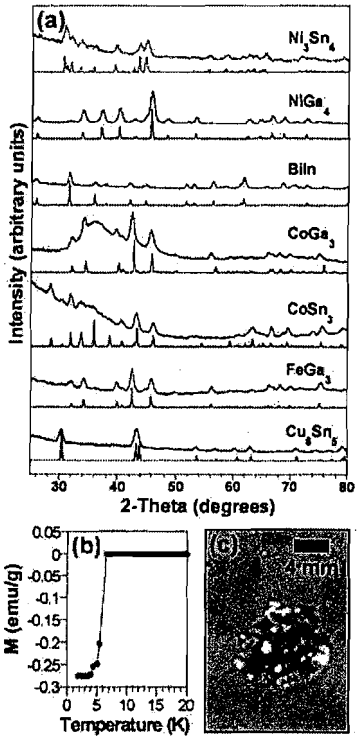

Figure 3. (a) XRD data for intermetallics synthesized via the polyol-mediated reaction of metal powders. (b) Magnetization data and (c) digital photograph of superconducting $BiIn_2$.

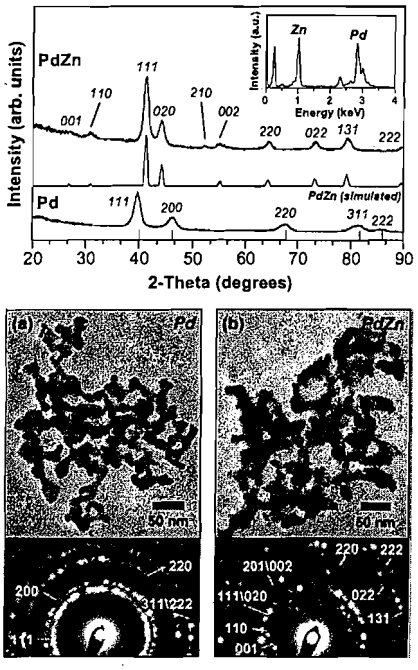

Figure 4. Nanocrystalline PdZn (b) formed by reacting pre-formed Pd nanoparticles (a) with diethylzinc. Top: XRD and EDS data.

As proposed, we are also working toward incorporating elements whose soluble precursors are difficult to reduce to zero-valent metals using the common reducing agents used in the types of chemical syntheses that we and others most often utilize. Our key elemental targets from a superconductivity perspective are Mg and Nb, and we are currently developing strategies for incorporating these elements into intermetallics using solution-chemistry techniques. As a first step toward this goal, however, we explored the formation of Zn-based intermetallics, since Zn^{2+} is not easily reducible using either polyalcohol solvents or $NaBH_4$. Using diethylzinc as a zero-valent molecular zinc source, we are able to convert pre-formed metal Au, Pd, and Cu nanoparticles into Au_3Zn, AuZn, PdZn, and Cu_5Zn_8 nanoparticles (Figure 4). This provides an important stepping stone to our proposed work with Mg and Nb intermetallic superconductors, since the chemistry developed for the Zn system is likely to be portable to these more electropositive systems.

Finally, as a first step toward accessing the metal carbides and borides described in our proposal, we have learned how to make phase-pure Ni_3B using polyol chemistry at temperatures below 300 °C (Figure 5). Boron is known to incorporate into Ni when preparing Ni nanoparticles using $NaBH_4$ in water, but polyol chemistry provides greater synthetic flexibility, and also yields Ni_3B directly in pure crystalline form. This is in contrast to the formation of metal borides using other methods, which usually produce amorphous solids and require annealing to crystallize.

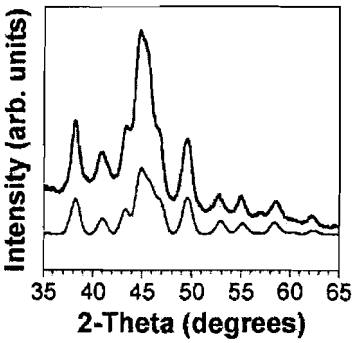

Figure 5. Experimental (top) and simulated (bottom) XRD data for Ni_3B (polyol).

As a side project, our synthetic explorations inspired some developments in an area outside of the original focus of our proposal, but highly germane to the issue of synthetic advances related to superconductivity. We discovered a multi-step solid-state pathway for accessing perovskite-type $Eu_2Ti_2O_7$ at 750 °C and ambient pressure, which is facilitated by exploiting a solid-state precursor ($EuTiO_3$) that contains the same structural motif that is present in the desired product (Figure 6). Perovskite-type $Eu_2Ti_2O_7$ has previously been synthesized only by high-temperature high-pressure techniques (> 2000 K, 4 GPa).[6] We find that perovskite-type $Eu_2Ti_2O_7$ is active for second harmonic generation with efficiencies of 80 × SiO_2. We anticipate that similar chemical transformations will provide access to high-Tc oxide superconductors with unique features, such as texture, non-equilibrium structures, enhanced critical fields, etc.

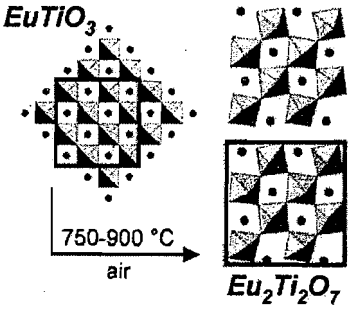

Figure 6. Schematic describing the low-temperature ambient-pressure synthesis of the SHG active perovskite $Eu_2Ti_2O_7$.

List of papers acknowledging DOE support (in print and submitted only):

- N. Henderson, J. Baek, P.S. Halasyamani, and R.E. Schaak, "Ambient Pressure Synthesis of SHG-Active $Eu_2Ti_2O_7$ with a [110] Layered Perovskite Structure: Suppressing Pyrochlore Formation by Oxidation of Perovskite-Type $EuTiO_3$," *Chem. Mater.* **2007**, *19*, 1883-1885.

- R.E. Cable and R.E. Schaak, "Solution Synthesis of Nanocrystalline *M*-Zn (*M* = Pd, Au, Cu) Intermetallic Compounds via Chemical Conversion of Metal Nanoparticle Precursors," submitted to *Chem. Mater.*

List of people working on the project:

Name	Status	Level of support
Ting-Hao Phan	Graduate Student	Full
Nathan Henderson	Graduate Student	Partial (10%) – will convert to full in FA07
Robert Cable	Graduate Student	Partial (10%)

Brian Leonard	Graduate Student	Partial (10%)
Yolanda Vasquez	Graduate Student	Partial (10%)
Zachary Schaefer	Graduate Student	Partial (10%)
Xiaole (Joy) Chen	Postdoc	Partial (25%)
Matthew Sanders	Undergrad. Student	No financial support (for-credit research)

Planned activities for next year:

Our immediate plans, in line with our goal of understanding how the synthetic pathway influences the key superconducting properties for our new low-temperature routes, are to (a) synthesize NiBi, Bi_2Pd, and $BiIn_2$ using several distinct routes (low-temperature powder, low-temperature solution, traditional high-temperature), (b) measuring Hc and Jc for all samples, and (c) characterizing the microstructure and nanostructure in detail (electron microprobe, STEM), focusing on the characterization and identification of impurities, percolation networks, and grain size. Efforts to carefully control size, shape, and dispersity of key superconducting intermetallics (looking toward possible size-dependent property studies) will also be explored. We will simultaneously focus on the Nb-Ga system, building on our preliminary evidence that $NbGa_3$ forms using our new low-temperature polyol strategy. The first challenge will be to synthesize Nb_3Ga, and while we do not expect this (or other Nb-rich intermetallics) to form using simple one-pot reactions, we will approach this from other pathways, for example by reaction of $NbGa_3$ with reactive Nb precursors ($NbCl_5$ under strongly reducing conditions, zero-valent and low-valent organometallic Nb complexes). We will approach the Nb-Sn system in a similar manner.

We will also expand significantly on our initial work with metal borides and carbides. Building on our successful formation of Ni_3B, we will explore the formation and physical properties of other binary metal borides using low-temperature solution strategies. We will also use nanocrystalline Ni_3B (and other related borides that we anticipate being able to prepare) as a reactive low-temperature precursor to ternary metal borides, in analogy to "nanocrystal conversion chemistry" routes that we have reported previously. For example, by reacting nanocrystalline Ni_3B with activated magnesium (work in progress), we should be able to form $MgNi_3B$, the boron analogue of the non-oxide perovskite superconductor $MgNi_3C$. While $MgNi_3B$ is not expected to be superconducting, other similar targets may be. We have already begun work to access Mg-based intermetallics using chemistry described in our proposal, and we will continue in that area. As a longer-term goal, we will also work toward preparing YNi_2B_2C and YPd_2B_2C (T_c = 23 K, previously inaccessible in pure form) using a combination of the strategies outlined above, as well as new techniques in development.

Exploratory synthesis using our unique low-temperature techniques, as well as testing of all synthesized samples for superconductivity, is an ongoing discovery-based aspect of this work that will continue in an effort to identify new superconducting solids.

Updated list of other support (all "current"; no pending proposals at this time):

National Science Foundation (DMR/Solid State Chemistry): "CAREER: Low-Temperature Solution Synthesis of Intermetallic Nanomaterials." [$551,588: 2006 – 2011]

This grant describes the development of fundamental chemistry aimed at synthesizing intermetallic nanocrystals and understanding the reaction pathways that allow them to form. The chemical systems under development in this work are limited to those whose metal salt precursors are reducible using $NaBH_4$. Some of this work clearly forms the chemical basis for the synthetic techniques used in the DOE grant, but the synthetic development in the DOE grant is distinct, requiring different chemistry for the necessary targets. There is no superconductivity work in the NSF grant and no rigorous property testing or synthesis-structure-property relationships.

Department of Energy (BES/Materials Sciences & Engineering): "Low-Temperature Synthesis Routes to Intermetallic Superconductors" [$311,981: 2006 – 2009]

This grant describes the exploitation and expansion of recently-developed synthetic strategies, as well as significant new synthetic development (both bulk and nanoscale) using new chemistry, aimed at generating improved superconducting materials, accessing metastable intermetallic superconductors as bulk powders, and discovering new superconducting materials. The targets are largely early transition metal, alkaline earth metal, and boride/carbide systems that are not included in the NSF grant. The focus of the DOE grant is on superconductors and understanding synthesis-structure-property interrelationships.

Arnold and Mabel Beckman Foundation (Beckman Young Investigator Award): "A New Polymer-Assisted Galvanic Approach to Hollow Multi-Metal Nanospheres for Biomedical, Plasmonic, and Fuel Cell Applications" [$264,000: 2006 – 2009]

This grant provides seed money for developing and expanding our efforts in generating hollow multi-metal nanostructures using modified galvanic displacement reactions. Our studies are also expanding into bio-templated synthesis. In all cases, the focus is on the exploration of catalytic transformations (CO, formic acid, methanol oxidation reactions for fuel cells).

American Chemical Society (Petroleum Research Fund – Type AC Grant): "New Structures of Old Elements: Low-Temperature Solution Routes to Metastable Polymorphs" [$80,000: 2006 – 2008]

This grant allows us to expand our low-temperature synthetic efforts into elemental (not multi-metal) systems. The focus is on elemental systems where several distinct allotropes are known, but only one is typically accessible under