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Synthesis and characterization of protective aluminides, borides, and carbides

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This project funds fundamental, exploratory research into the synthesis and characterization of new chromium-based aluminides, borides, and carbides for high temperature protective applications. These materials are characterized by strong covalent bonds, metallic nature, and propensity for forming stable, protective Cr_2O_3 and Al_2O_3 scales. Typical properties include high hardness and resistance to thermal shock and fracture. We have compiled libraries of prospective compounds, we have grown numerous high quality single crystal samples, and we have performed careful measurements of crystallographic structures as well as functional properties. To date, we have discovered two new compounds – $La_{21}Cr_{8-2a}Al_yGe_{7-y}C_{12}$ and Cr_4AlB_4 – and characterized three other compounds that were not previously understood – $Cr_{55}Al_{232-\delta}$, $Cr_{3.1}Ni_{0.93}Al_{14.7}$, and $Bi_2CrAl_3O_9$. This work has so far yielded three peer-reviewed publications with undergraduate student authorship and some fifteen presentations at scientific meetings, with the majority given by undergraduate students.

IMPACT OF THE RESEARCH

Crystal structure of $La_{21}Cr_{8-2a}Al_yGe_{7-y}C_{12}$

Early in this project, we grew single crystals of $La_{21}Cr_{8-2a}Al_yGe_{7-y}C_{12}$, a new compound and the first Cr-based example of its structure type. The structure is composed of three sub-units arranged a polyatomic analog of the Heusler structure. A La_9Ge_6 sub-unit is centered on a La atom, which is octahedrally coordinated by Ge and enclosed within a cube of La. Adjacent $La_{12}Al_bGe_{1-b}$ sub-units consist of a central Al or Ge atom coordinated by six equally-spaced triangular La plaquettes. Most interestingly, the final sub-unit with composition $Cr_{4-a}C_6$ takes the form of four vertex-linked, tetrahedrally arranged plaquettes of CrC_3. This geometrically-frustrated configuration of a $3d$ transition metal could lead to magnetic frustration and a host of interesting magnetic ground states, as have previously been observed in pyrochlores and related compounds [1]. We recently published our work on this compound [2].

Hardness, oxidation resistance, and low thermal conductivity of $Cr_{55}Al_{232-\delta}$

Focusing on the oxidation resistant properties of Al-rich scales, we grew high quality single crystals of $Cr_{55}Al_{232-\delta}$, an icosahedral quasi-crystalline approximant. We carried out characterization of crystal structure, hardness, fracture toughness, oxidation resistance, scale characterization via scanning electron microscopy, high temperature thermal conductivity, and high temperature thermal expansion. We found high hardness, robust oxidation resistance, and low thermal conductivity – all promising for high temperature protective applications. Fracture toughness at room temperature was only modest, however, motivating our search for related materials. $Cr_{55}Al_{232-\delta}$ is unique in its combination of high oxidation resistance and hardness, as well as with its low density and thermal conductivity. We recently published our work on this compound [3].

Composition, low thermal conductivity, and high hardness of $Cr_{3.1}Ni_{0.93}Al_{14.7}$

We investigated the properties of $Cr_{3.1}Ni_{0.93}Al_{14.7}$ to improve upon the strengths of $Cr_{55}Al_{232-\delta}$ while addressing its limitations. We first resolved several contradictions in the literature regarding its composition and crystallographic space group. Our Vickers micro-hardness indentations reveal striking improvement over $Cr_{55}Al_{232-\delta}$ with hardness $H = 6.9$ GPa and a lack of visible indentation fractures, speaking to substantially improved fracture toughness. Oxidation resistance is similarly improved by an order of magnitude, while electronic conductivity in this compound is reduced by nearly two orders of magnitude from $Cr_{55}Al_{232-\delta}$, suggesting corresponding reduction in thermal conductivity. This work led to a contributed talk [4], and we are preparing a manuscript.

Cr_4AlB_4

We discovered Cr_4AlB_4, an entirely new member of the layered MAB-phases, boride analogs of the refractory MAX-phase machinable refractory ceramics. We have determined the quasi-one dimensional crystal structure of this material and carried out electrical resistivity ρ measurements, revealing non-Fermi liquid behavior with $\rho \propto T^3$, a property shared by the quasi-one dimensional Cr pnictide superconductors. Our work on this compound is ongoing.

$Bi_2CrAl_3O_9$

We have grown high quality single crystals of $Bi_2CrAl_3O_9$ and carried out diffuse reflectance spectroscopy that reveal two band edges at 1.32 and 1.55 eV with spin-split Cr-$3d$ bands. Magnetic susceptibility measurements suggest a Cr^{3+} state with strong Cr-O hybridization and the potential onset of order at $T = 79 \pm 3$ K. Density functional theory calculations suggest the importance of Mott-Hubbard physics in determining the gap and magnetic ground state. This work led to a contributed talk [5], and we are preparing a manuscript.

Temperature control and data acquisition system

To characterize the transport properties our materials, we developed a automated instrument control software package with an easy to use GUI. The software is designed to be modular and interfaces directly with a lock-in amplifier, various preamplifiers, and temperature control instrumentation. Electrical transport measurements can be automated with temperature precision to 10^{-3} K. We provide the program and GUI freely upon request, and we published our work on this software in peer-reviewed conference proceedings [6].

IMPACT ON MY CAREER

The funds provided with this project permitted me to take on greater research challenges than would have been otherwise accessible with the start up funds available at a primarily undergraduate institution. The resulting publications and presentations will support my impending application for tenure. As a direct result of the research productivity of this project, I was invited to join as Senior/Key Personnel in a US Department of Energy, Energy Frontiers Research Center, which will fund our research in this field for the next four years. Preliminary data developed during this project has also supplemented my application for an NSF CAREER award.

IMPACT ON THE STUDENTS

Over the first two years of this project, we supported eleven undergraduate students, several of whom were supported for the entire two years. Three students from populations historically underrepresented in STEM fields received additional support the New York State Collegiate Science Technology Enrichment Program CSTEP. Eight students are economically disadvantaged and receive substantial financial aid that permits them to attend college. The stipends these students received from PRF permitted them to work in a laboratory related to their intended career paths rather than take retail jobs to make ends meet. As part of our outreach activities, we also invited a high school student to join us.

This project generated thirteen student poster and oral presentations at local, state, and national meetings including the FSC Celebration of Scholarship [7–12], the SUNY Undergraduate Research Conference [13, 14], the International Energy and Sustainability Conference [15, 16] the CSTEP Conference [17], and the Emerging Researchers National Conference [18, 19]. All presentations acknowledge PRF funding.

Three of the supported students have since graduated and have embarked upon graduate education in pursuit of a Ph. D. in Electrical Engineering at Stony Brook University, an M. S. in Materials Design & Innovation at the University of Buffalo, and an M. S. in Civil Engineering at Manhattan College. A fourth graduate is now a test engineer at a global safety consulting firm. The majority of students supported by this project have not yet graduated but have similar plans.

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