New Quantum Materials: The Search for Topological Thermoelectrics and Topological Superconductors

Overview

Quantum materials have properties that can revolutionize sustainable energy technologies and quantum computing. Every material has a band structure and is made up of atoms described by quantum mechanics. However, quantum materials specifically refers to those materials whose properties cannot be approximated by a classical description; such materials can host various entangled electronic phases including superconductivity, magnetism, thermoelectricity, and topological phases. **The focus of my group will be on the design, synthesis, and low temperature characterization of crystalline solids with emergent quantum phases.** My philosophy is centered around finding connections between different subfields in condensed matter to identify new ground for exploration that will motivate future fundamental research with relevance to technology.

The foundation of chemical engineering is built on the ideas of material balance and energy balance. On this foundation gained in my early training, I have built expertise in the chemistry and physics of quantum materials. My search for novel materials will be guided by the overlap of electronic properties, shown in Fig. 1. **Unconventional superconductivity** appears in the vicinity of magnetism [1, 2], and thermoelectric performance can be enhanced with short-range magnetic order [3]. We will study **materials with a known *magnetic* ground state and tune their properties in search of a high thermoelectric figure-of-merit zT and unconventional superconductivity**. The topology of the electronic band structures is important, and topologically non-trivial electronic states, containing knots or twists, result in topological materials, such as topological insulators and Dirac/Weyl semimetals.

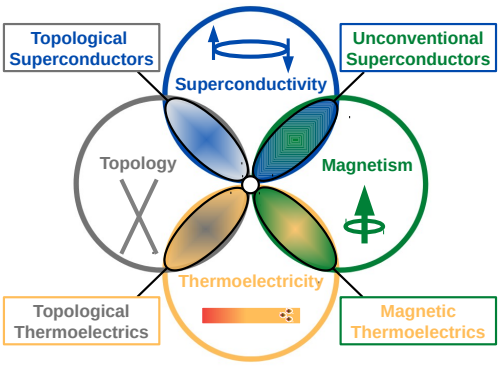

Figure 1: Various properties of quantum materials, and emergent quantum states at the overlap.

Topological thermoelectrics are those materials with topologically non-trivial states that contribute to their high thermoelectric efficiency. A key challenge in the field of thermoelectrics is to decouple the electrical conductivity from the thermal conductivity, with the goal of achieving a "phonon-glass electron-crystal" (PGEC) [4]. The brute-force "classical" methods to improve thermoelectric efficiency include introducing ionic disorder to scatter phonons without scattering electrons, and some success was achieved in my work on copper chalcogenides [5, 6]. However, a more elegant and inherently "quantum" path towards achieving PGEC in a material may be found in topological insulators such as Bi_2Se_3 [7], where the electronic conductivity is robust against disorder due to topologically-protected electronic states [8]. Some topological materials have been demonstrated to violate the Lorenz number, and this should be utilized in the search for efficient thermoelectrics [9]. However, despite tremendous efforts, these materials seem to have hit an intrinsic limit in terms of thermoelectric efficiency [10]. Also, doped topological insulators such as $Cu_xBi_2Se_3$ [11] are some of the leading candidates for realizing **topological superconductivity**, but these doped crystals suffer from low superconducting volume fraction [11], likely due to inhomogeneity of the intercalated Cu atoms. To overcome these challenges we need new families of topological materials where we can grow high-quality single crystals with new techniques, such as high-pressure synthesis.

Previous Work

I have worked on synthesis of many materials, including chalcogenides, antiperovskite oxides (Fig. 2), bismuthates, irridates, ruthenates, cuprates, silver oxides, high-entropy oxides, and pnictides, using a wide variety of synthesis methods, including flux, vapor transport, floating zone, electrochemical, and high-pressure. We synthesized a new phase of $AgSbO_3$ with strong Sb-O hybridization [12] and identified a new topological Weyl semimetal $\mathbf{Ag_2BiO_3}$ using high-pressure high-temperature methods [13]. We highlight the similarity between Ag_2BiO_3 (space group $Pnn2$) and the perovskite type bismuthate $BaBiO_3$ (space group $I2/m$), both with nominal "Bi^{4+}" state that disproportionates into two distinct sites. Suppression of the disproportionation in Ag_2BiO_3 (space group $Pnna$) will stabilize a Dirac semimetal state and can even lead to superconductivity. At UBC, we have grown **high-quality superconducting cuprate and Fe(Se,Te) crystals using flux method and $\mathbf{(Ba,K)BiO_3}$ crystals using electrochemical growth**, and helped my collaborators measure x-ray absorption of superconducting $(Ba,K)SbO_3$ synthesized at high-pressure [14].

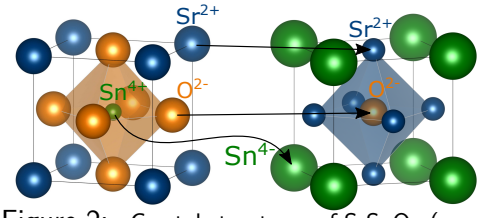

Figure 2: Cyrstal structures of $SrSnO_3$ (perovskite oxide, left) and Sr_3SnO (antiperovskite oxide, right), highlighting ionic states of atoms. The Sn^{4-} state makes Sr_3SnO a topological Dirac-semimetal.

In Kyoto, I found superconductivity in the highly air-sensitive **$Sr_{3-x}SnO$** [15] containing the unusual Sn^{4-} state revealed in Mößbauer spectroscopy [16], crystal structure of the antiperovskite oxide Sr_3SnO and typical perovskite oxide $SrSnO_3$ are shown in Fig. 2. We observed in bulk $Sr_{3-x}SnO$ evidence for **Dirac electrons** using NMR [17] and signs of **unconventional superconductivity** in muon spin relaxation (μSR) [18], then studied thin-films of Sr_3SnO using β-NMR in search of chiral surface states [19].

Topological properties have been realized in the class of materials with **2D square-nets** in their structure, where these properties can be predicted through simple chemical considerations [20], and recently we have demonstrated a non-trivial drumhead surface state in ZrSiTe [21]. At UBC, I have expanded the work on the square-net family of compounds to further elucidate the origin of their topologically non-trivial states. Specifically, I synthesized **metal antimonides $M\mathbf{Sb_2}$** (M = Ca, Sr, Eu, Yb, crystal structure shown in Fig. 3) with distorted square-nets. We have characterized the semimetallicity and superconductivity of $CaSb_2$ [22], and studied the superconductivity using μSR [23]. Antimonides have promising thermoelectric properties [24] and host topological states [25]. I will study the $M\mathrm{Sb_2}$ family of materials with the aim of achieving **topological thermoelectricity**.

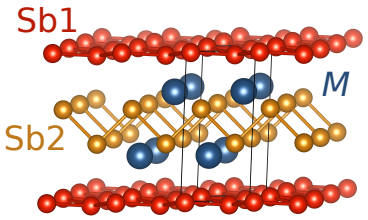

Figure 3: Crystal structure of $M\mathrm{Sb_2}$ highlighting the two different Sb chains. Sb1 chains form a distorted square-net.

Recently, I discovered superconductivity and electron-phonon drag in non-centrosymmetric semimetal $LaRhGe_3$ [26]. We have also been working on high-entropy materials, studying the properties of magnetic spinel oxides [27]. This emergent field offers a new perspective on the tunability of stability and properties of materials using entropy [28, 29, 30]. My recent work demonstrates a novel concept of charge-entropy stabilization in the selenide (Ag,Sn)Se, with 2+/4+ fluctuations on Sn, by utilizing Mößbauer spectroscopy and X-ray photoelectron spectroscopy (XPS) [31]. Furthermore, I have worked on materials with high-mobility of electrons, where electron-electron interactions are dominant, resulting in viscous/ballistic electron flow. To this end we study the high-mobility oxides ReO_3 and $PdCoO_2$ [32], where we can apply chemical engineering concepts to quantum materials. Having studied many quantum materials has allowed me to develop a holistic skill-set, which will help me in searching for new emergent quantum phases.

Future Projects

I will search for superconductivity in Ag-based materials using high-pressure synthesis, including the Ag oxides/fluorides. One target is superconducting perovskite oxides containing silver, where under high-pressure silver can replace alkali metals in oxides. The silver oxides are more stable than their alkali metal analogues and some are Dirac/Weyl semimetals. Another target is superconducting silver fluorides. The proposed family of high-pressure phases containing AgF_2 (shown in Fig. 4) can host superconductivity, analogous to superconductivity in the CuO_2 based materials [33]

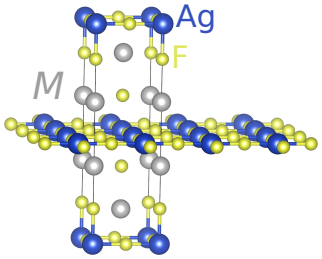

Figure 4: Crystal structure of layered silver flouride, M_2AgF_4, a proposed new family of superconductors.

I will explore the magnetic and thermoelectric properties of natural superlattices, such as misfit structures $[(MX)_{1+\delta}]_m(TX_2)_n$**.** These misfit structures are layered compounds containing two building blocks, MX rocksalt layers and TX_2 dichalcogenide layers. Compounds reported inlcude M = Sn, Pb, Sb, Bi, La, Ce, Sm, Tb, T = Ti, V, Nb, Ta, Cr, and X = S, Se [34, 35], which offer a vast map for exploration and expansion to include new elements. I will explore magnetic order in relation to the 2D limit in isolated TX_2, and enhancement of thermoelectric efficiency due to phonon scattering at the superlattice interface. This will bridge together the work on exfoliated and bulk TX_2 materials.

I will investigate topolgical superconductivity and thermoelectricity in the $M\mathbf{Sb_2}$ family, and explore their topological properties in light of Sb-Sb distortions in these materials. In this family of antimonides, the distortion of Sb-Sb bonds into zigzag chains gives rise to non-symmorphic space group of the crystal structure, and the emergence of nodal-line state in their electronic structure. My work will focus on the superconducting pairing mechanism and identifying any connection to topology in $M\mathrm{Sb_2}$.

Rationale for Experimental Techniques

In my lab, we will study the interplay between crystal structure, electronic structure, and physical properties in new topological thermoelectrics and superconductors. To successfully study various materials one needs a variety of synthesis and characterization tools. We will utilize electrical and thermal transport, μSR, and X-ray spectroscopy to study materials in my lab. On the synthesis front, **I plan to combine state-of-the-art crystal growth methods with high-pressure synthesis.**

Having the niche of high-pressure synthesis techniques in my lab will enable exploration of new range of parameter space for synthesis. While it is common knowledge that most materials show a wide variety of distinct phases in their temperature-pressure phase diagram, conventional synthesis routes cannot make effective use of the pressure dimension

and solely rely on temperature, deeply limiting the possible phases. This is especially important for superconductors, because the phase with the highest transition temperature for a specific ratio of elements is sometimes only stabilized at high pressures. However, high-pressure synthesis allows us to **add another dimension to the phase diagrams** and expands the number of crystalline materials we can make. By applying pressure to the constituent elements and by providing energy, in the form of heat, we can form high-pressure phases distinct from those formed at ambient conditions. These metastable phases can be "quenched" before removing the pressure from the reaction vessel and retrieving the sample. Quantum materials discovered using high-pressure synthesis include Ba_2CuO_4 [36] and $KBiO_3$ [37]. **While the need for high pressure is widely recognized, a key challenge in the field has been to grow single crystals of high-pressure materials that are large enough for devices and physics experiments**, such as angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscope (STM). The lack of experimentally synthesized crystals has kept our understanding of such high-pressure materials limited despite the novel properties they host.

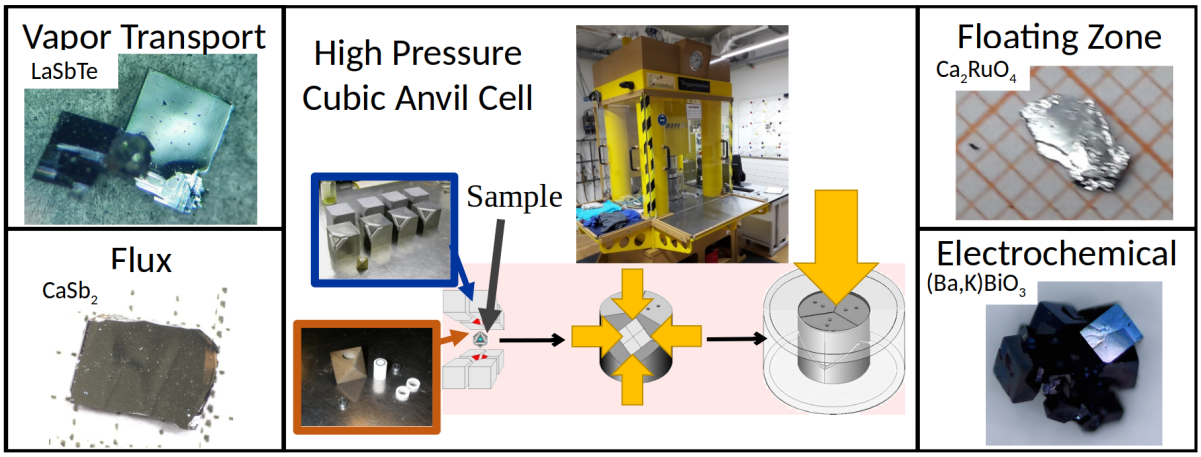

Figure 5: Crystals I have grown: Topological crystalline insulator, LaSbTe, vapor transport (top left), Superconducting Dirac nodal-line semimetal, $CaSb_2$, self-flux (bottom left), Mott Insulator, Ca_2RuO_4, floating zone (top right), unconventional superconductor, $(Ba,K)BiO_3$, electrochemical (bottom right), and high-pressure synthesis setup with cubic-anvil cell at MPI-Stuttgart (center).

However, recently some progress was made in integrating crystal growth techniques into high-pressure synthesis, and this is demonstrated with work on hexagonal boron nitride crystals [38]. Utilizing recent technical advancements in anvil cell design [38], I propose elevating the conventional growth methods of flux growth to work at high, GPa-level pressure. In particular, I will incorporate an **octahedral anvil cell with a Walker-type press** (center of Fig. 5) and a belt press. These type of presses can achieve pressures up to 20 GPa and temperatures of up to 1400 °C, and, most importantly, have a large sample space of up to 100 mm^3. With the large sample space I will be able to synthesize large, high-pressure grown samples **suitable for everything from device-level transport to neutron and muon experiments.** Besides searching for new, high-pressure stabilized phases of materials, my lab will utilize different methods to synthesize crystals of new quantum materials, including those shown in Fig. 5.

Synergy with American University of Sharjah (AUS)

I look forward to collaborations with members of the Department of Physics at AUS working on theory and experiments involving quantum materials and devices. Bulk crystal growth techniques and high-pressure apparatus I propose to build will enable new collaborations with faculty in the area of energy materials, thermodynamics, and phase transformations. I look forward to collaboration with faculty working experimentally on thin-films, photonics and sensing, and those working on theory of metamaterials.

My research will benefit from the available facilities at AUS. For bulk synthesis, I will utilize synthesis equipment such as box furnaces, tube furnaces, quartz sealing station, and glovebox. As my lab expands, it will include a floating zone furnace, arcmelter, and high-pressure synthesis machine; I will evaluate the properties of materials synthesized in my lab with a broad range of techniques, including heat capacity, magnetic susceptibility, thermal transport, and electrical transport, with visits to user facilities for μSR, neutron diffraction, and X-ray spectroscopy experiments. My lab will provide research groups at AUS with high-quality single crystal samples.

To complement the work at AUS, I plan to maintain my collaborations at CLS (XPS, XAS), TRIUMF (μSR, β-NMR), University of British Columbia (STM, ARPES, Theory), Kyoto University (NMR, Mößbauer spectroscopy), University of Tokyo (high-pressure measurements), ETH Zurich (Theory), and MPI-Stuttgart (Theory and X-ray Spectroscopy). Finally, by building on my robust background in quantum materials, I hope to expand on the quantum materials research at AUS and bring it to new heights.

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