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Exploratory Growths of the Ternary 14-1-11 Family of Thermoelectric Zintl Phases Using a Self-Flux Method

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Abstract

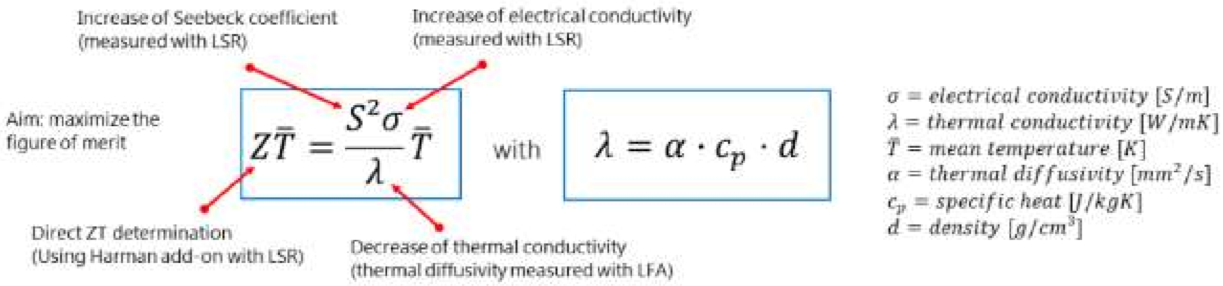
Thermoelectric Zintl phases have the ability to convert waste heat into useful electrical energy, making them valuable in various energy harvesting applications. In these Zintl phases, a high zT (thermoelectric Figure of Merit) indicates more efficient thermoelectric properties. The technique used, a self-flux method, is implemented as a relatively simple way of synthesizing Zintl phases with a higher thermoelectric Figure of Merit. This method uses an excess of reactive flux element, which acts as both a component of the Zintl phase and a reaction medium, and two other elements that are incorporated into the material. The materials with higher melting points are placed at the bottom of a quartz glass ampoule. The materials with lower melting points act as the flux and are placed on top. The flux melts and incorporates the other elements, providing a liquid solution for the ternary reactions to take place. A stoichiometric ratio of 14-1-11 was used to attempt to grow unit crystals. Preliminary results suggest new materials of $Ca_{14}In_1Sb_{11}$ and $Ca_{14}In_1Bi_{11}$ have been grown, but further testing is required to confirm the results.

Introduction

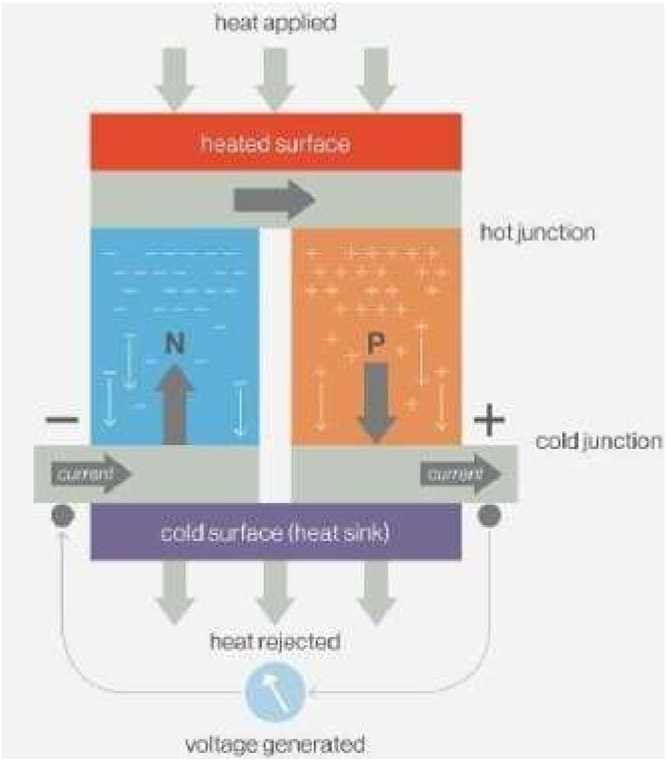
Thermoelectric Zintl phases are a burgeoning area of interest for materials scientists thanks to the variety of untested combinations of Zintl phase components. These components comprise alkali-alkaline earth metals and any post-transition metal/metalloid. Considering I am looking for novel, ternary Zintl phases, this leaves many untested material combinations to be explored. Various interesting characteristics can be found in these Zintl phases, but for now I will be exploring Zintl phases that exhibit thermoelectricity. Thermoelectricity is a highly-valued characteristic in new materials owing to the majority of heat in industrial processes being lost as waste heat. With these things in mind, this project lays out how the hunt for new Zintl phases is to be directed and how any new materials will be handled once discovered.

Theory

Thermoelectricity comprises three effects: the Seebeck Effect, the Peltier Effect, and the Thomson Effect. The Seebeck effect is the phenomenon where two conductors of different material at different temperatures will produce an electric potential difference between them. Different materials have different efficiencies at turning supplied heat into voltage, and this efficiency is denoted as the Seebeck coefficient, S[1].



(Fig. 1: Seebeck & Peltier effect equation[2])



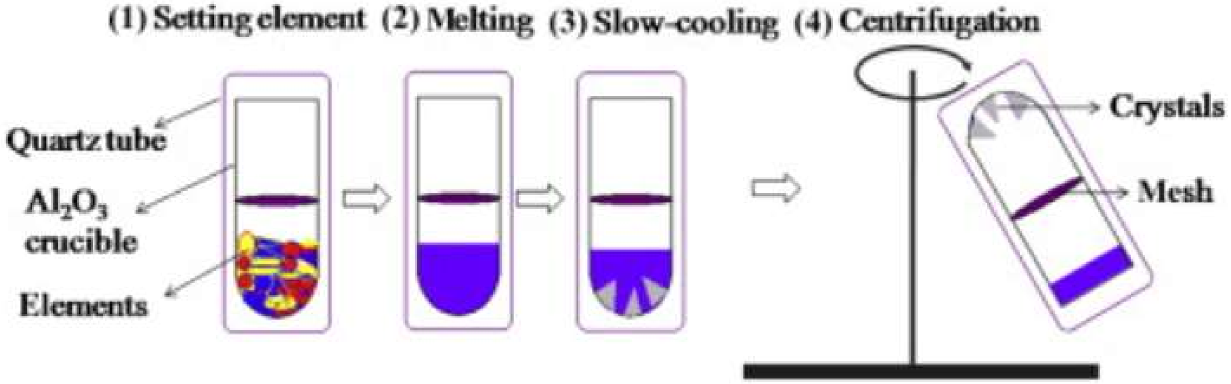
(Fig. 2: Seebeck & Peltier effect diagram[3])

The Peltier effect is where two materials will transfer heat energy between themselves when a current passes through them[2]. This effect is a different manifestation of the phenomenon that governs the Seebeck effect, and thus is governed by the same equation. The last phenomenon is known as the Thomson effect. This is where a conductor evolves or absorbs heat when electric current passes through a circuit composed of a single material that has a temperature difference along its length[4]. A good thermoelectric material needs to have a high zT, which means it has low lattice thermal conductivity and chemically tunable electronic properties[5]. This helps to inform what I should test for when materials show up.

Zintl phase materials have many different subfamilies that can all exhibit vastly different properties. I will be focusing primarily on one family that exhibits thermoelectricity: the 14-1-11 family (which can be analyzed within the framework of a $Ca_{14}AlSb_{11}$ as the archetype of the family). We are choosing the 14-1-11 phase due to evidence of the electron numbers being more flexible that other conventional Zintl phases, which allows for tunable electronic properties[6].

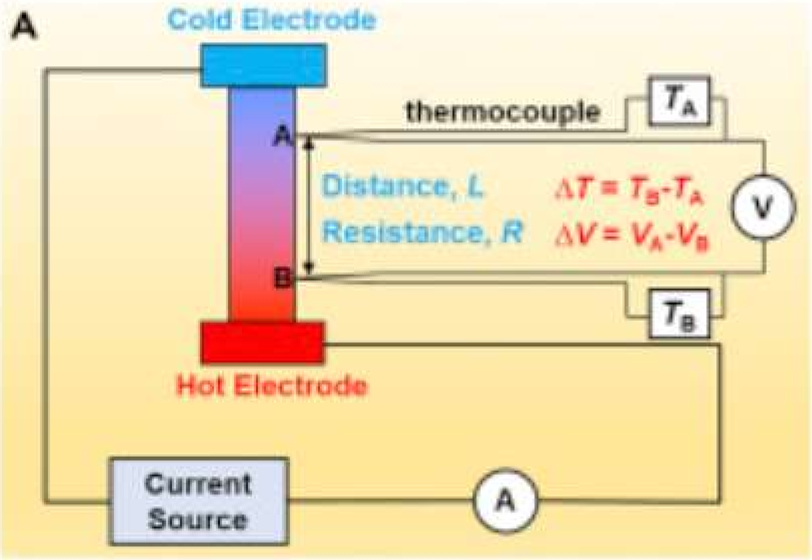
Experimental Procedure

For the experimental procedure, a flux growth method was used in order to grow single crystals. This required careful weighing of reactants in precise millimoles and ratios. Two reactants were placed at the bottom, and the third reactant, which was the flux, was measured in excess of the others and layered on top. The order is important because our self-flux needs to be able to melt and fully encase the other reactants. The weight ratio is selected based on the desired unit crystal stoichiometry. For this family, the ratios are generally 14 mmol, 1 mmol, and 11 mmol, with the 1 mmol element as the flux. After the reactants are put into the tube, quartz wool is put above them in the tube, which acts as a sieve later in the process. Once the quartz wool is in the tube, the tube is put under vacuum and sealed off using a hydrogen-oxygen torch. After it is sealed, the ampoule is placed into a furnace and heated up beyond the melting temperature of the self-flux element. This batch of reactions were heated 100°C/hr for 10 hours, to a temperature of 1000°C. The solution was held at 1000°C for 65 hrs. The solution was then cooled gradually at 3°C/hr to 650°C. This is to reach some lower temperature so as to keep the flux liquid but allow any crystals to be solid. The tube was taken out of the furnace and flipped to allow the flux to drain past the quartz wool, but catch the crystals. The ampoules were put into a centrifuge to spin off any excess flux on the products.



(Fig. 3: Flux growth method[7])

The ampoules were smashed and the debris was sifted through. Any crystals that were found in the debris are put into sample vials and kept for analysis. Analysis for these crystals required preparation in order to put them into a Scanning Electron Microscope (SEM), an Electron Diffraction Spectroscope (EDS), and an X-Ray Diffractometer (XRD). This consisted of dividing the crystal into a small enough piece with a flat face, which is then placed on double-sided copper tape with the flat facet facing up so that the SEM and EDS can acquire accurate data. The XRD solely requires a small enough crystal (between 30-300 microns) to acquire accurate data. In the future, testing for thermoelectricity will be required, which requires Ulvac-Riko ZEM system and Linseis LSR systems in order to measure Seebeck coefficients (S) and the electrical conductivity (**σ**)[8].



(Fig. 4: Process of measuring Seebeck coefficient and electrical conductivity for a material with a temperature gradient[8])

Preliminary Results & Discussion

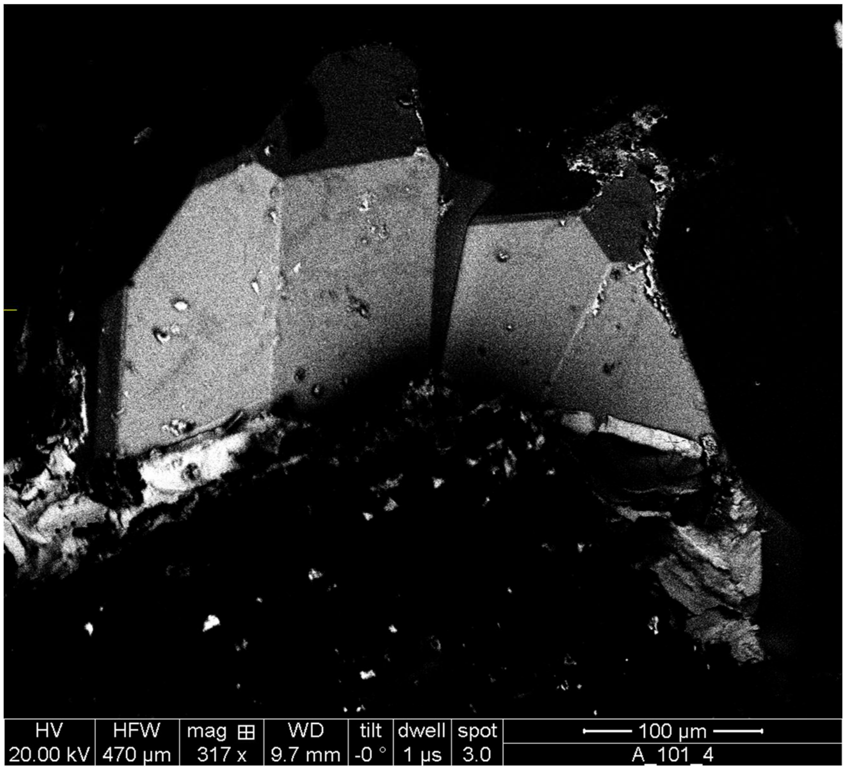
The initial sample set explored the 14-1-11 family of Thermoelectric Zintl phases using an indium flux. 5 reactions were weighed out and experimented on. Three of the five produced results that were deemed worth investigating. Instead of using the full 14-1-11 mmol, the weights were cut in half for the 14 mmol element and 11 mmol, and 20 mmol of flux were used for the 1 mmol element. The final weights for the elements were 7 mmol - 20 mmol - 6.5 mmol. The last element also had excess millimoles weighed out to account for transfer loss.

Reactants (in 7-20-6.5 mmol ratio as listed from left to right)	**Results**
Mg - In - Sb	Produced crystals. When tested with SEM and EDS, verified as pure Silicon

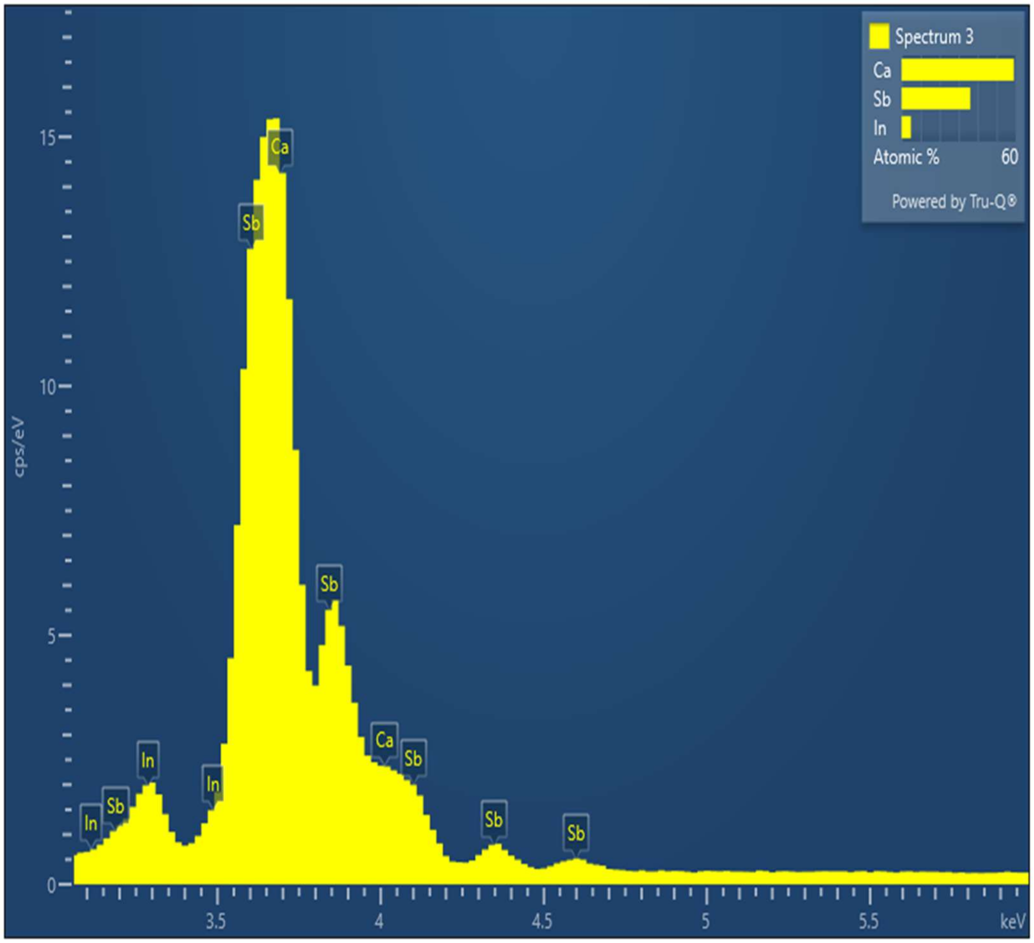
Mg - In - P	Produced mostly oxidized material. Untested
Ca - In - Sb	Produced crystals. When tested with SEM and EDS, results suggest a new material is present with $Ca_{14}In_1Sb_{11}$ structure
Ca - In - Bi	Produced crystals. When tested with SEM and EDS, results suggest a new material is present with $Ca_{14}In_1Bi_{11}$ structure
Ca - In - P	Produced mostly oxidized material. Untested

(Table 1: Trials Conducted and the results)

Sample 1: $Ca_{14}In_1Sb_{11}$



(Fig. 5: An SEM picture analyzing the suspected $Ca_{14}In_1Sb_{11}$ sample)

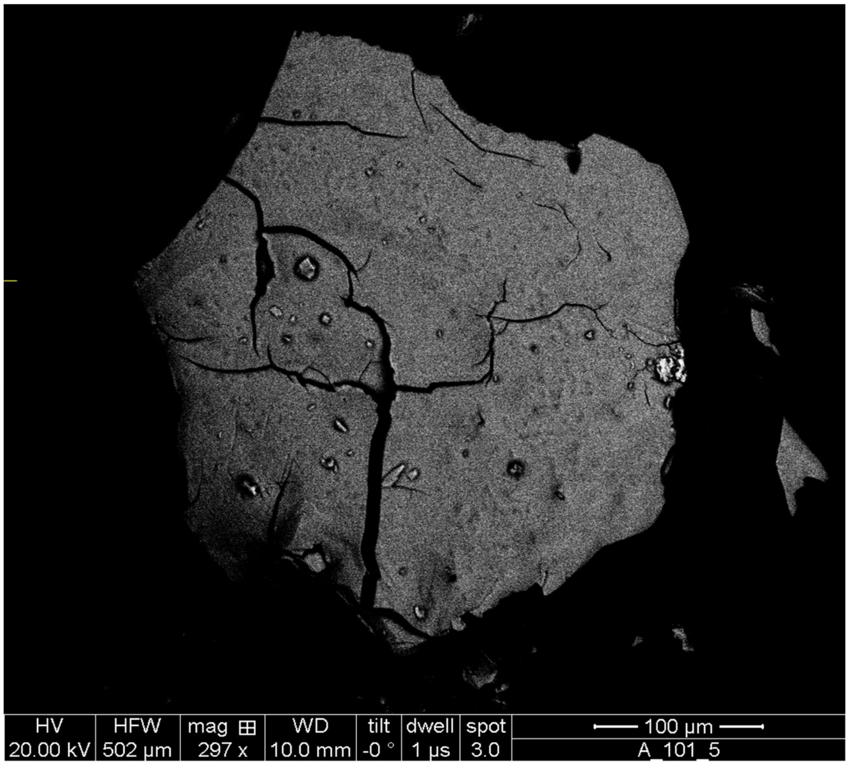


(Fig. 6: EDS analysis and output of the suspected $Ca_{14}In_{1}Sb_{11}$)

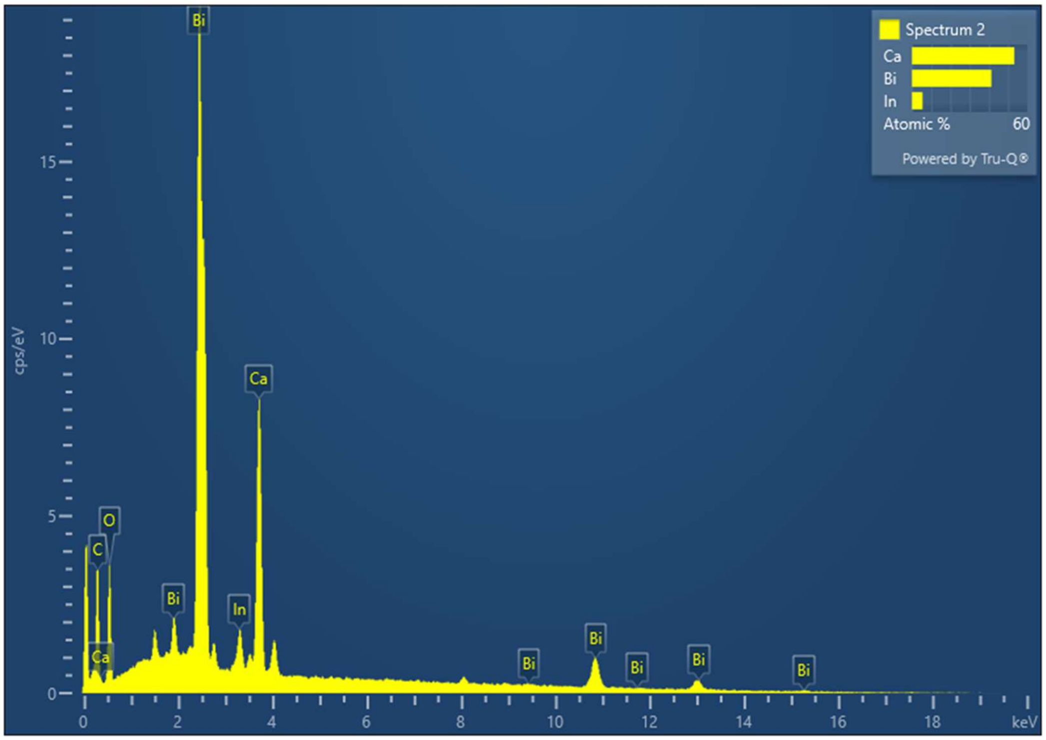
Elements	**Atomic %**	**Expected Atomic %**
Calcium (Ca)	59.02%	53.85%
Indium (In)	4.86%	3.85%
Antimony (Sb)	36.12%	42.30%
Total	100%	100%

(Table 2: EDS-measured atomic percentages vs. stoichiometrically-expected atomic percentages of suspected $Ca_{14}In_{1}Sb_{11}$)

Sample 2: $Ca_{14}In_1Bi_{11}$



(Fig. 7: An SEM picture analyzing the suspected $Ca_{14}In_1Bi_{11}$ sample)



(Fig. 8: EDS analysis and output of the suspected $Ca_{14}In_1Bi_{11}$)

Elements	**Atomic %**	**Expected Atomic %**
Calcium (Ca)	53.20%	53.85%
Indium (In)	5.50%	3.85%
Bismuth (Bi)	41.30%	42.30%
Total	100%	100%

(Table 3: EDS-measured atomic percentages vs. stoichiometrically-expected atomic percentages of suspected $Ca_{14}In_1Bi_1$)

Research Efforts in Progress

In order to verify whether the materials are new, XRD will be used to confirm that the unit cell has not been reported in any databases. Afterwards, the samples will be tested for thermoelectric capabilities.

Acknowledgements

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Biography

Jared Shortt is a senior Physics/Astrophysics and Film Studies Major at Missouri State University in the Physics and Material Science department. After graduating, he plans on getting a masters of Material Science at Missouri State University.