

## Topic for a Master's Thesis

# Thermoelectric SnSe for near room-temperature applications tailored by metavalent bonding

**INTRODUCTION** Thermoelectric solid energy conversion technology provides a reliable way to use waste heat for power generation. Tin selenide (SnSe) as a new promising thermoelectric material exhibits one of the lowest lattice thermal conductivities ( $\kappa_l$ ), and **cubic SnSe with high symmetry has a larger valley degeneracy than orthorhombic SnSe, which favors a high Seebeck coefficient ( $S$ )**. Our previous work shows that **the phase transition from orthorhombic to cubic can be realized in Ag-V-VI<sub>2</sub> doped SnSe**. Among all these samples, SnSe-AgBiTe<sub>2</sub> has a particularly good low-temperature performance, but the  $zT$  value decreases quickly above 400 K (Fig. 1) because of the thermal excitation of minority carriers (bipolar effect). This bipolar effect can be inhibited by enlarging the bandgap ( $E_g$ ), which improves  $zT$  over a broad temperature ranges. The main goal of this project is to optimize the bandgap and thus the TE properties by tailoring chemical bonds.

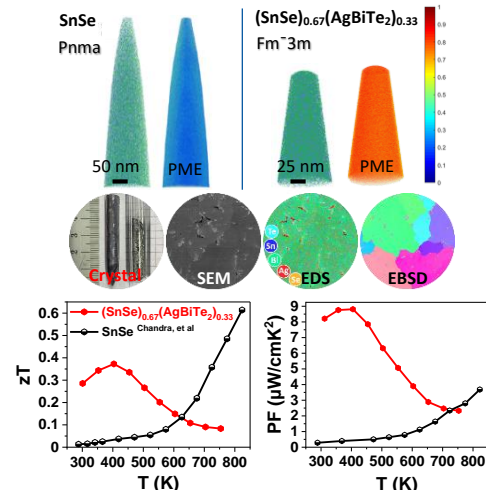


Fig. 1: Experimental data for pure and AgBiTe<sub>2</sub>-doped SnSe. APT reconstructed the 3D distribution of atoms and the PME comparison.  $zT$  value and power factors (PF).

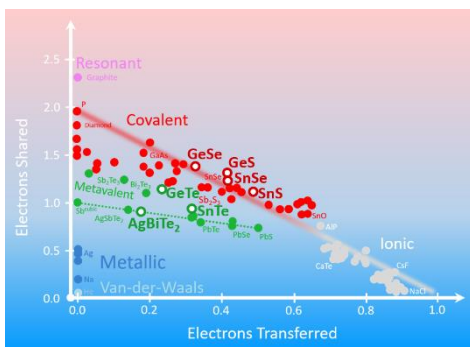


Fig. 2: A map using the number of electrons transferred (ET) and the number of electrons shared (ES) between adjacent atoms, which indicates the metavalent bonding mechanism.

As shown in Fig. 2, different chemical bonding mechanisms can be described by two variables, i.e., the electrons transferred (ET) and electrons shared (ES). The larger the ET or ES, the larger the bandgap. We confirmed the cubic structure of the SnSe-AgBiTe<sub>2</sub> alloy by EBSD and XRD, and its metavalent bonding mechanism by atom probe tomography (Fig. 1). To open the bandgap, we can first slightly decrease the content of AgBiTe<sub>2</sub> to increase the ES value. Yet, the content of AgBiTe<sub>2</sub> cannot be too low. Otherwise, we might not stabilize the cubic SnSe phase. The next step to further enlarge the  $E_g$  can be realized by substituting Sn with Ge since the map shows that Ge chalcogenides such as GeTe and GeSe have larger ES values than their Sn chalcogenides counterparts (SnTe and SnSe). Therefore, **Sn will be progressively substituted by Ge** to reduce the p-orbital overlap of neighboring atoms and then to widen  $E_g$  and reduce the bipolar thermal conductivity.

**THESIS DETAILS** We will prepare Sn<sub>1-y</sub>Ge<sub>y</sub>Se(AgBiTe<sub>2</sub>)<sub>x</sub> ( $x = 29\% \sim 25\%$ ;  $y = 1\% \sim 5\%$ ) crystals through the vertical Muffle furnace and Bridgman oven (Fig. 3) which can accurately control the temperature and automatically grow crystals through the set program, and then characterize the microstructures by XRD and EDX, measure the optical properties by Ellipsometry and FTIR-Spectrometer, and investigate the bonding mechanism by APT. All the techniques necessary to obtain a successful Master's thesis are available at I. Institute of Physics, RWTH Aachen University.

Fig. 3: Bridgman oven.



## References:

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