Modulation of Electronic Structure and Thermoelectric Properties of Orthorhombic and Cubic SnSe by $AgBiSe_2$ Alloying

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Introduction to Thermoelectrics

- Approximately 65 % of the utilized energy being lost as waste heat.
- ~10-20% conversion to the useful form ⟶ significant impact on overall energy utilization.

Thermoelectric Figure of Merit, *ZT*

$$ZT = \frac{S^2\sigma}{\kappa_{total}}T$$

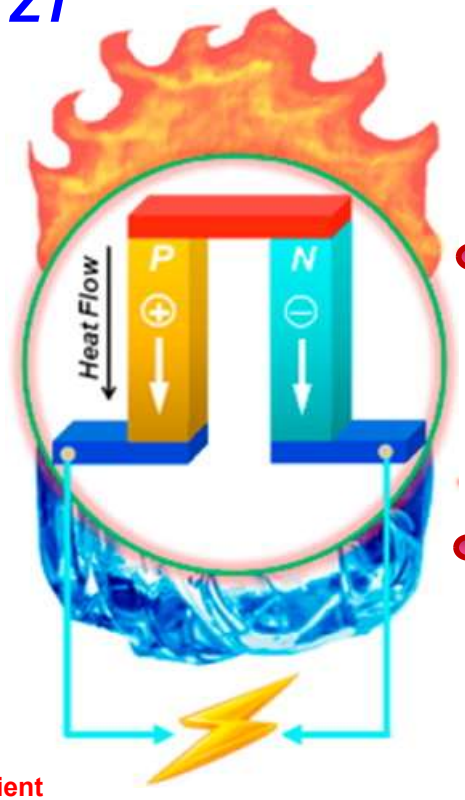
Glass
Low thermal conductivity

+

Metal
High electrical conductivity

+

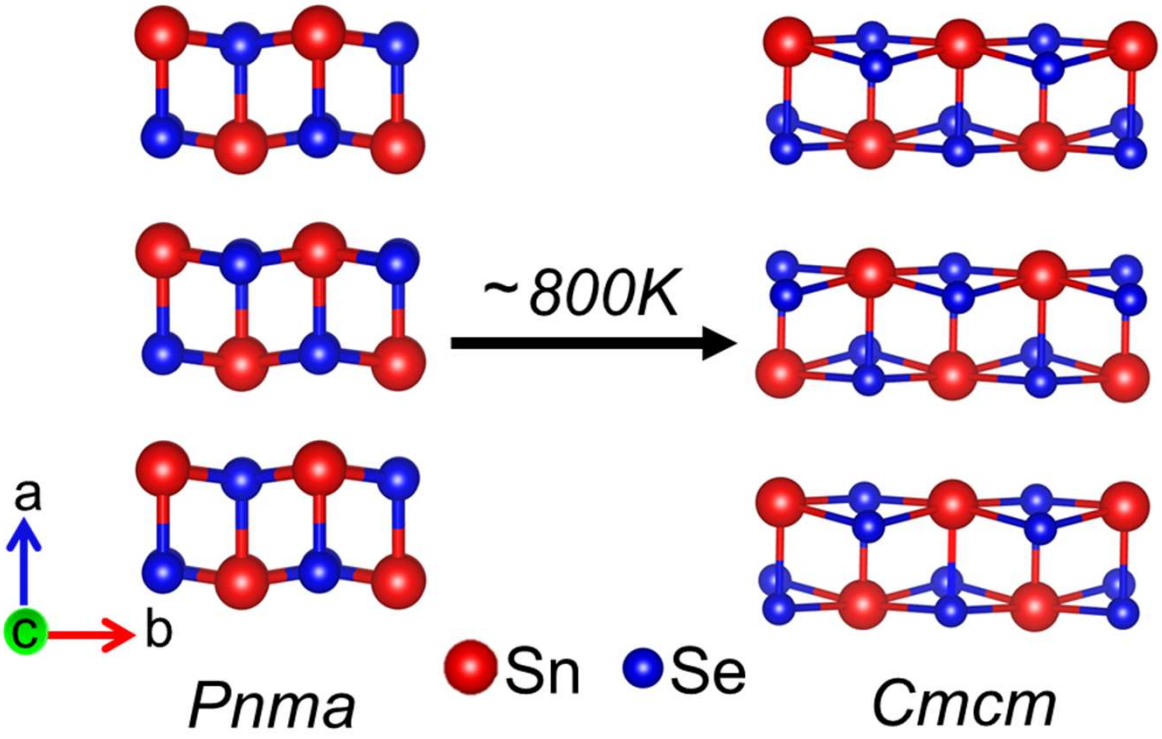
Semiconductor
High Seebeck Coefficient

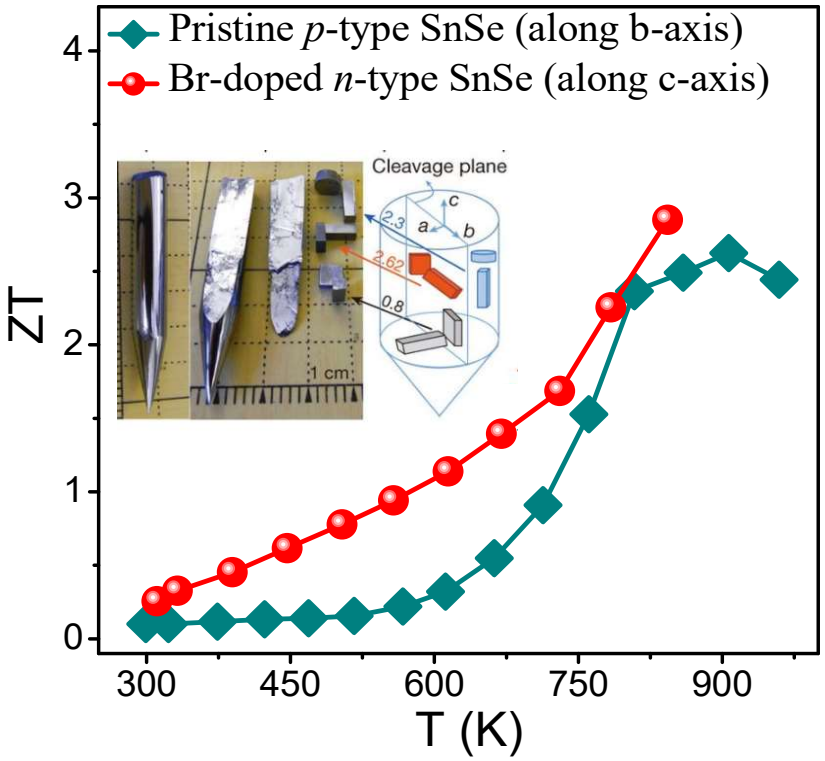


- Optimizing Carrier Concentration
- Improving Carrier Mobility
- Enhancing Effective Mass
- Reducing Thermal Conductivity
- Decoupling Electron and Phonon Transport
- Low Lattice Thermal Conductivity

Chem. Rev., 2016, *116*, 12123; ***Science***, 2017, *357*, 1369

SnSe: An Overview





- SnSe crystallizes in orthorhombic unit cell (*Pnma*) at ambient conditions.
- At 800 K, SnSe undergoes a displacive phase transition from *Pnma* to *Cmcm*.
- *p*-type single crystals of SnSe show an unprecedented *ZT* of 2.6 at 923 K along the crystallographic *b*-axis, whereas, *n*-type SnSe single crystals exhibit a record-high *ZT* of 2.8 at 773 K along *a*-axis.

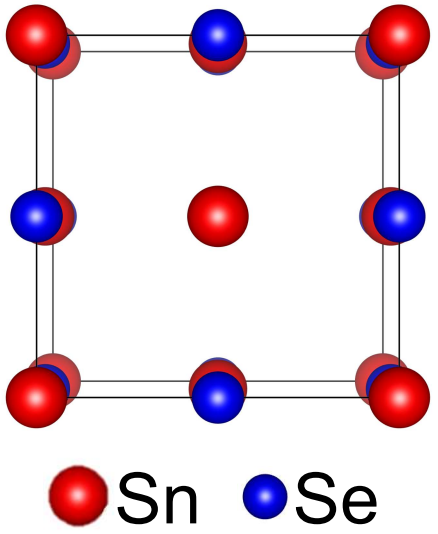
Nature **2014**, *508*, 373; *Science* **2018**, *360*, 778

Motivation

- Phase transition at elevated temperature results in extended defects and enhancement in the lattice strain which degrades the mechanical properties of SnSe and limits its long-term power generation applications at high temperature.
- Furthermore, it has been theoretically predicted that the high symmetric cubic phase can only be stabilized at very high pressures or by inducing strain.

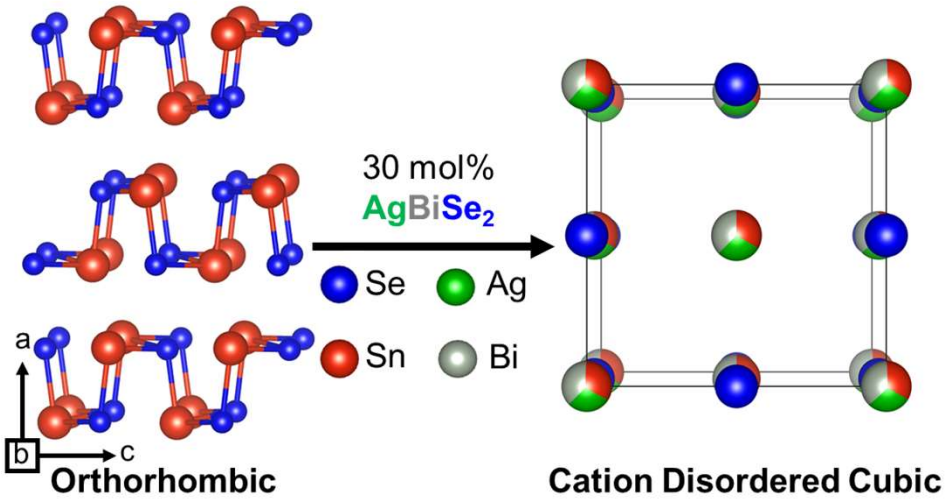
SnSe (Orthorhombic, *Pnma*) → 13-15 GPa, Pressure (P) → SnSe (Orthorhombic, *Cmcm*) → P> 50 GPa, DFT → SnSe (Cubic, $Fm\bar{3}m$)

Cubic SnSe has been theoretically predicted to show large anharmonicity, high Seebeck coefficient and intrinsically low lattice thermal conductivity.

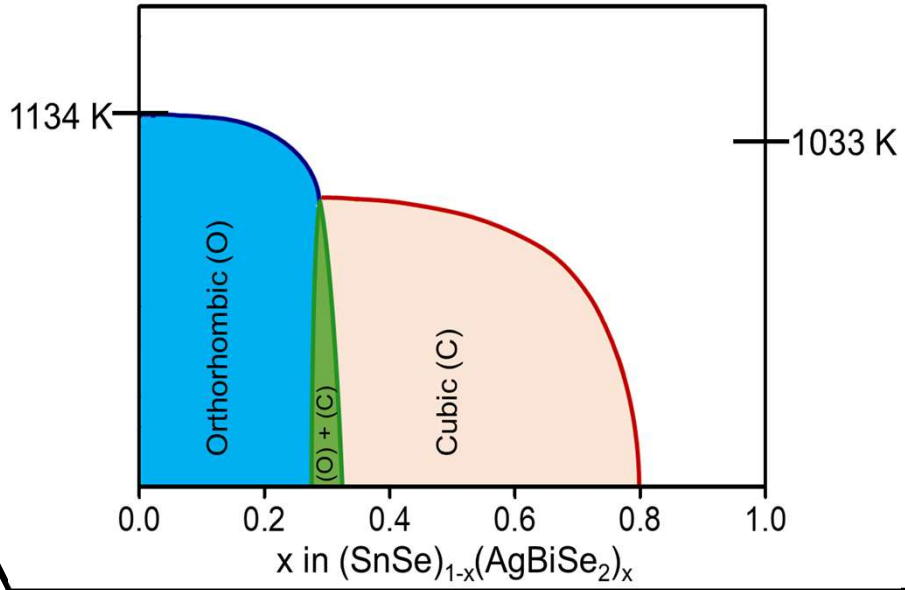


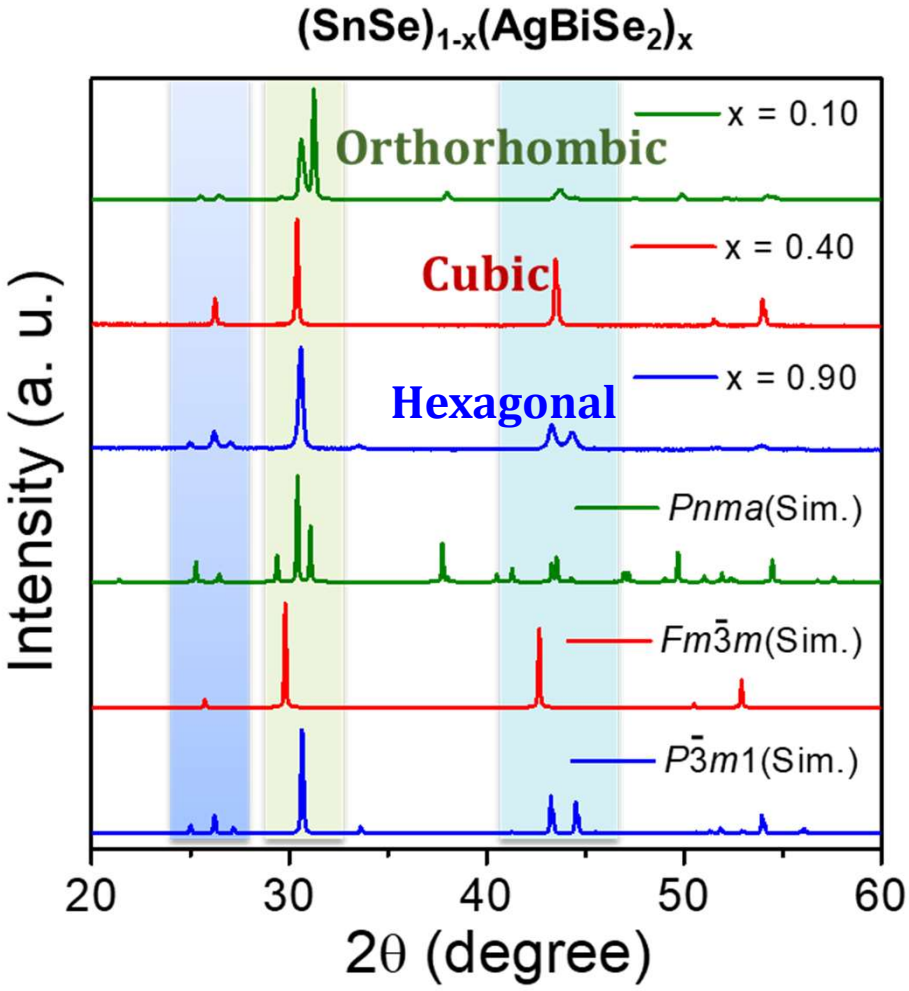
Adv. Mater., **2015**, *27*, 4150; *Phys. Rev. B*, **2013**, *88*, 235122

Chemical Approach to Stabilize Cubic SnSe



Successful stabilization of the high-pressure cubic rock-salt phase of SnSe by alloying it with $AgBiSe_2$ ($0.30 \leq x \leq 0.80$) at ambient temperature and pressure.





Solid solution mixing of $AgBiSe_2$ with SnSe increases the configurational entropy by introducing atomic disorder into the system.

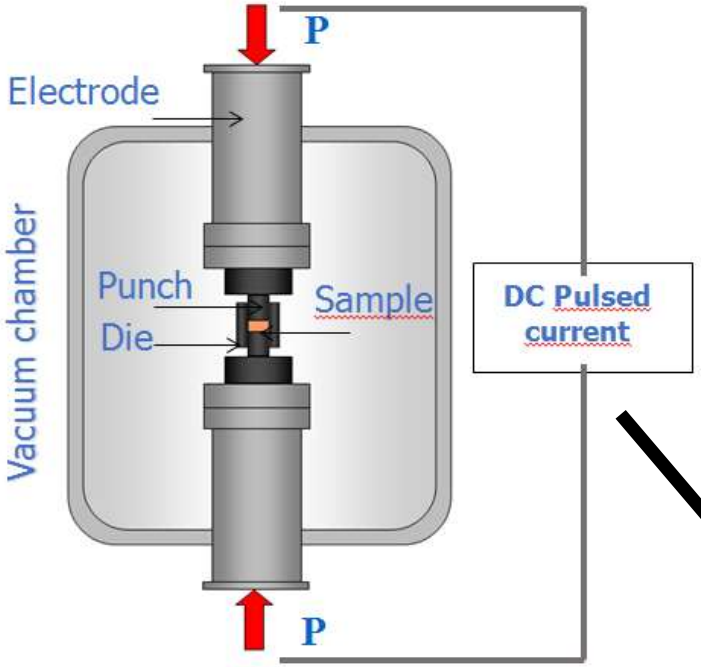
Chandra, S.; Arora, R.; Waghmare, U. V.; Biswas, K. ***Chem. Sci.***, 2021, *12*, 13074

Synthesis

Powdered SnSe

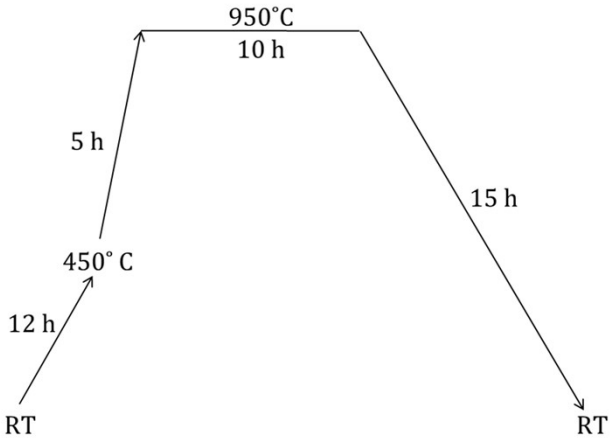
SPS Profile

Variables	Magnitude	Time (min.)
Pressure	50 MPa	13
Temperature	450 °C	8

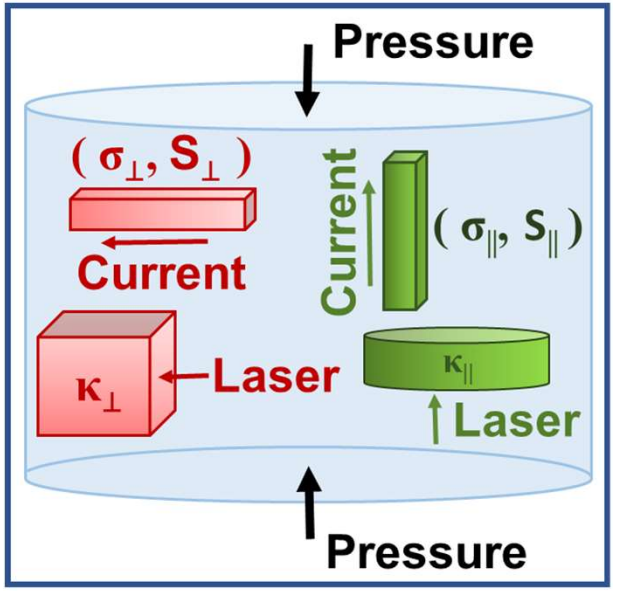


Spark Plasma Sintering
To prepare dense pellet

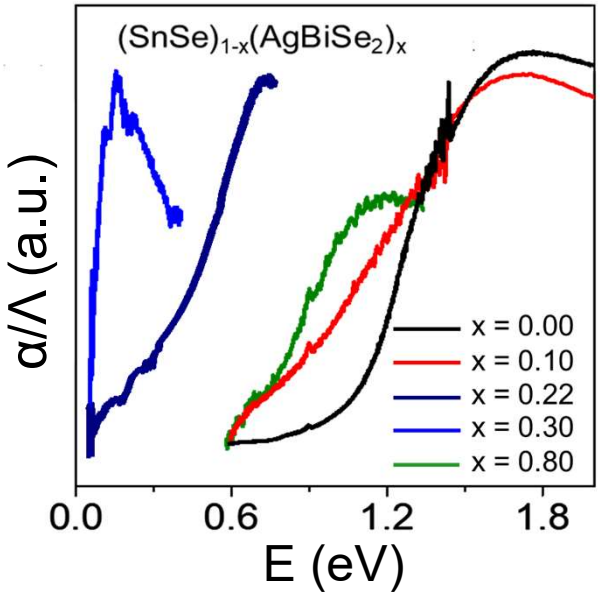
Scheme for Solid State Melting Reaction

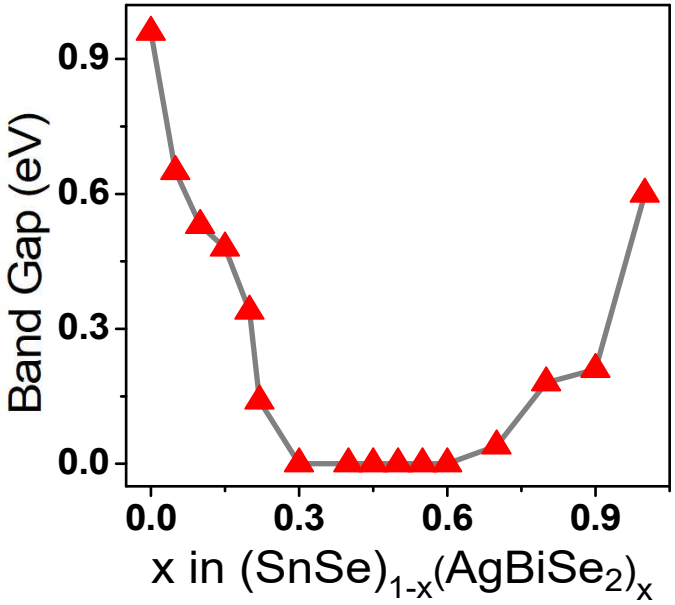


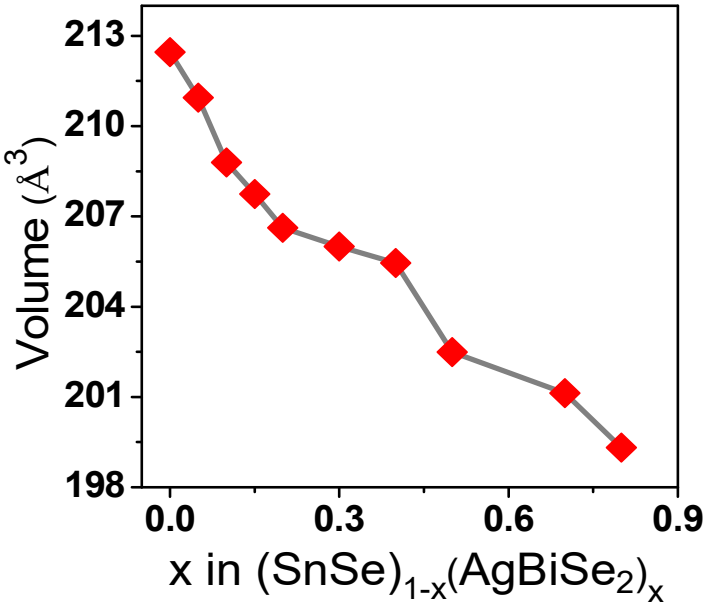
Polishing the pellets in desired shape



Band-gap Evolution of $(SnSe)_{1-x}(AgBiSe_2)_x$



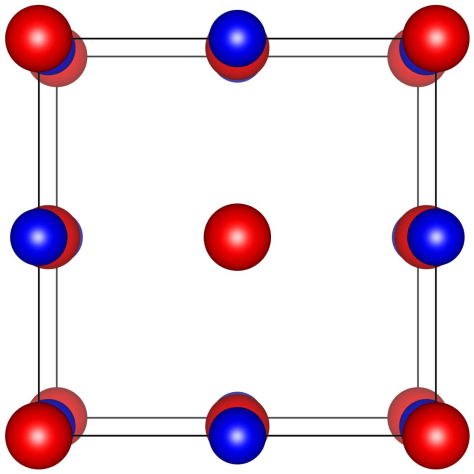


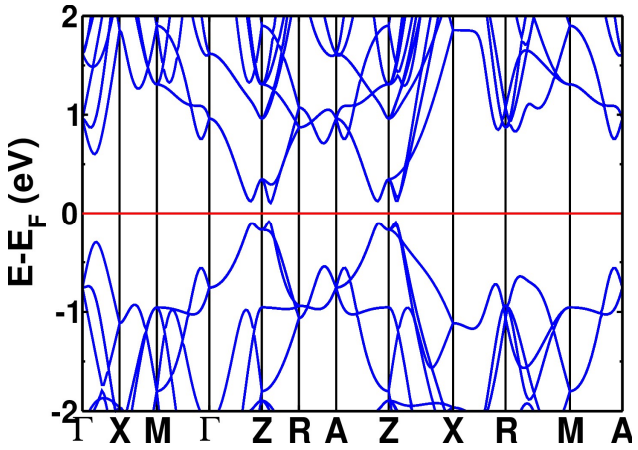


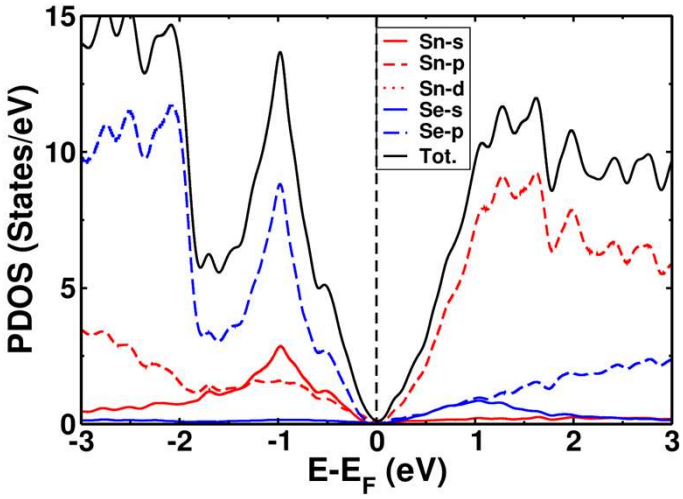
- The band gap of the pristine orthorhombic SnSe is measured at room temperature and found to be about 0.90 eV.
- SnSe, when alloyed with $AgBiSe_2$, band gap closes rapidly near to zero at x = 0.30 due to increase in chemical pressure originating from a sharp decrease in unit cell volume.
- The band gap in the cubic structure at higher $AgBiSe_2$ concentration is strongly influenced by the chemical disorder in occupation of Bi, Ag, and Sn at the cationic site.

Electronic Structure of Cubic SnSe

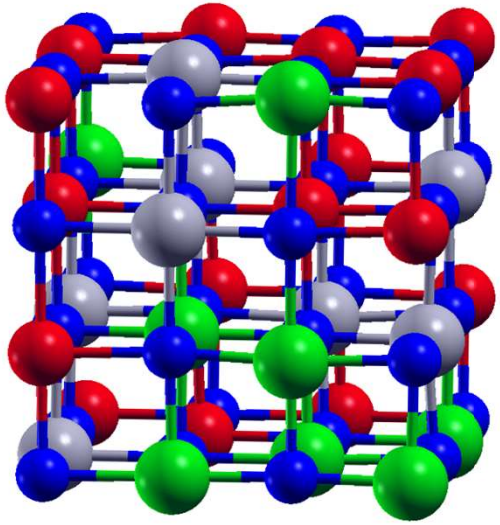
Cubic SnSe: Bang gap 0.121 eV (Theoretical)



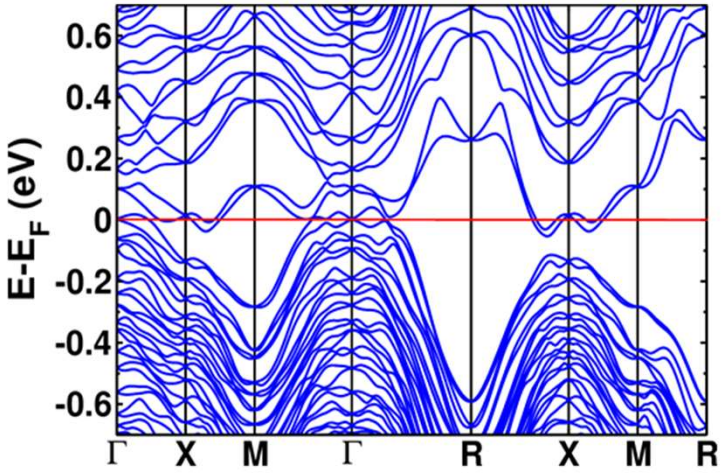


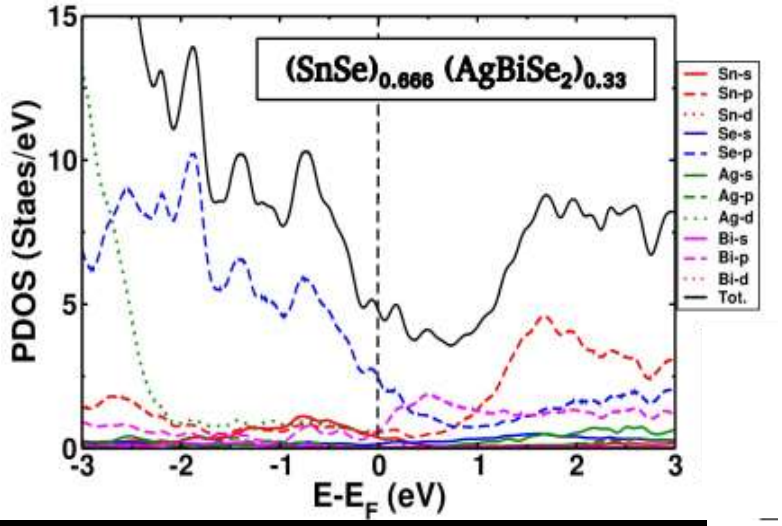


Cubic $(SnSe)_{0.67}(AgBiSe_2)_{0.33}$: Not well-defined gap



Sn Ag Bi Se

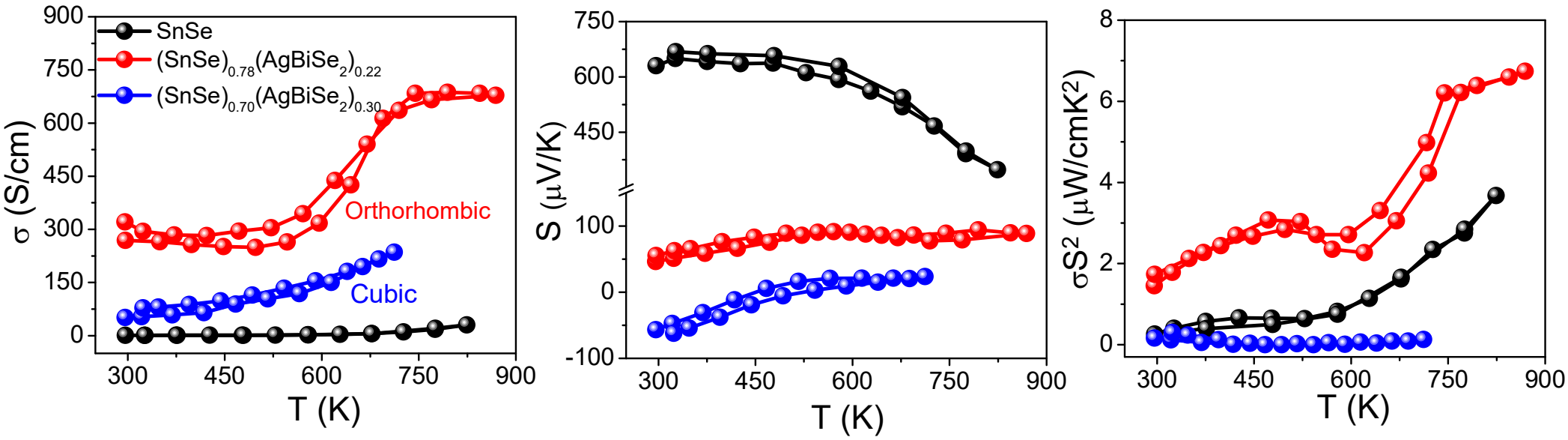




Cubic phase of SnSe is a topological crystalline insulator (TCI) whereas, cubic $(SnSe)_{0.67}(AgBiSe_2)_{0.33}$ shows semi metallic band structure.

In collaboration with Prof. Waghmare's group, JNCASR

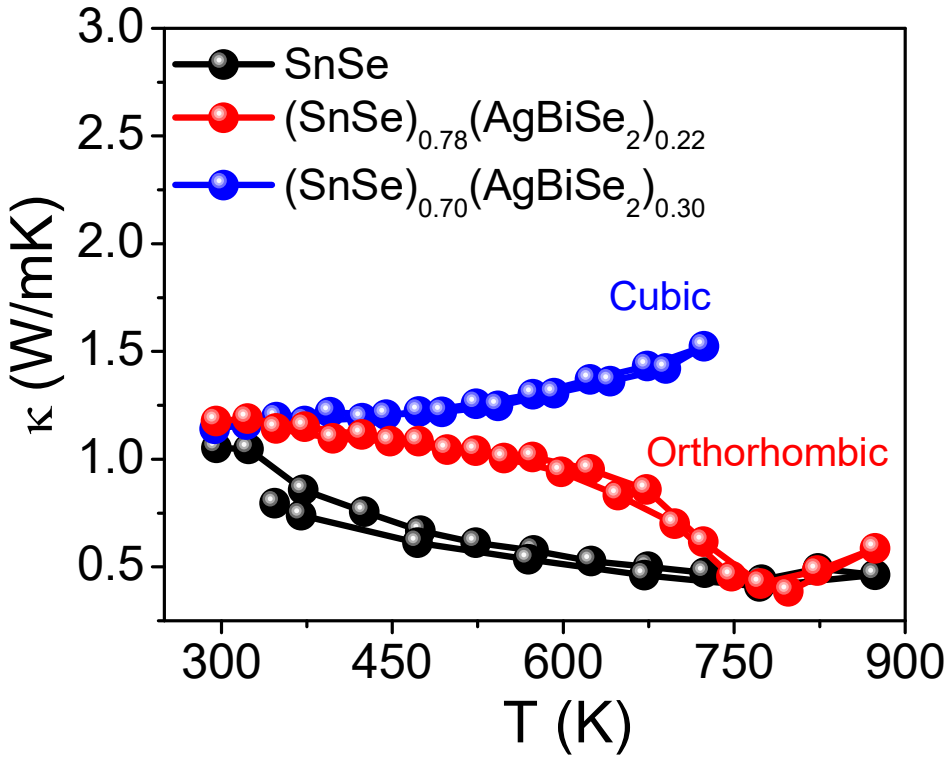
Electrical Transport of $(SnSe)_{1-x}(AgBiSe_2)_x$



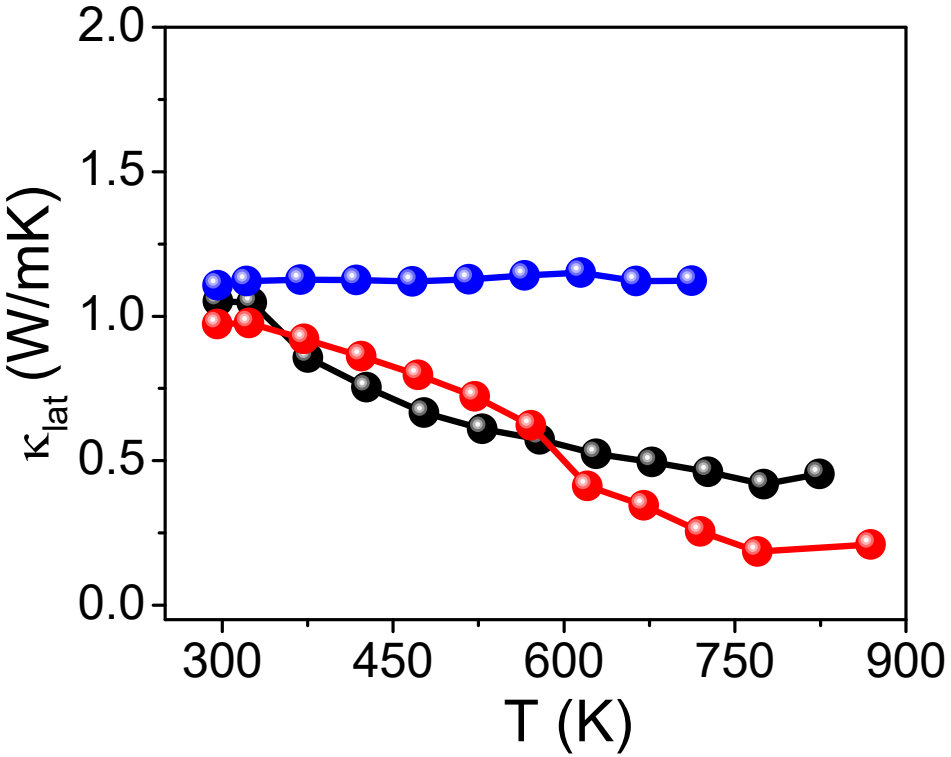
- For the orthorhombic $(SnSe)_{0.78}(AgBiSe_2)_{0.22}$, electrical conductivity increases with increasing temperature which indicates the semiconducting transport.
- Cubic $(SnSe)_{0.70}(AgBiSe_2)_{0.30}$ shows semi metallic *n*-type conduction at room temperature.

Composition	Carrier Concentration (n) cm^{-3}
SnSe	8.9×10^{17}
$(SnSe)_{0.78}(AgBiSe_2)_{0.22}$ (Orthorhombic)	8.2×10^{19}
$(SnSe)_{0.70}(AgBiSe_2)_{0.30}$ (Cubic)	6.17×10^{18}

Thermal Transport of $(SnSe)_{1-x}(AgBiSe_2)_x$

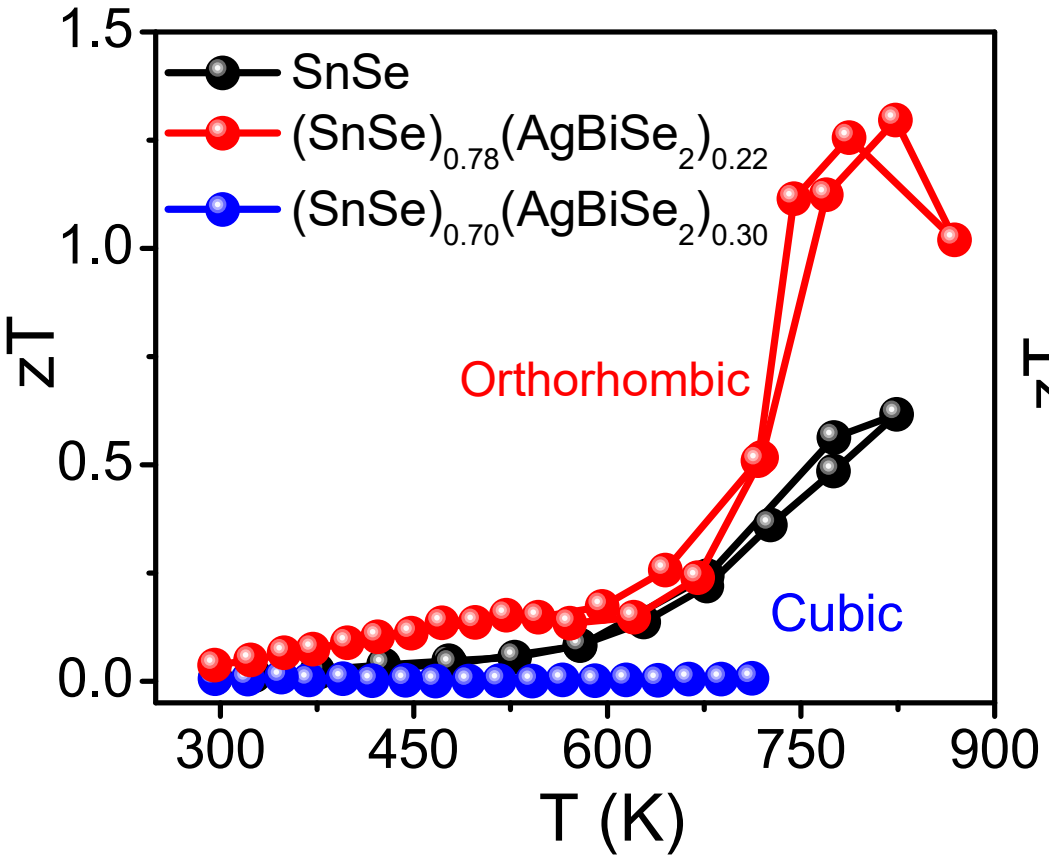


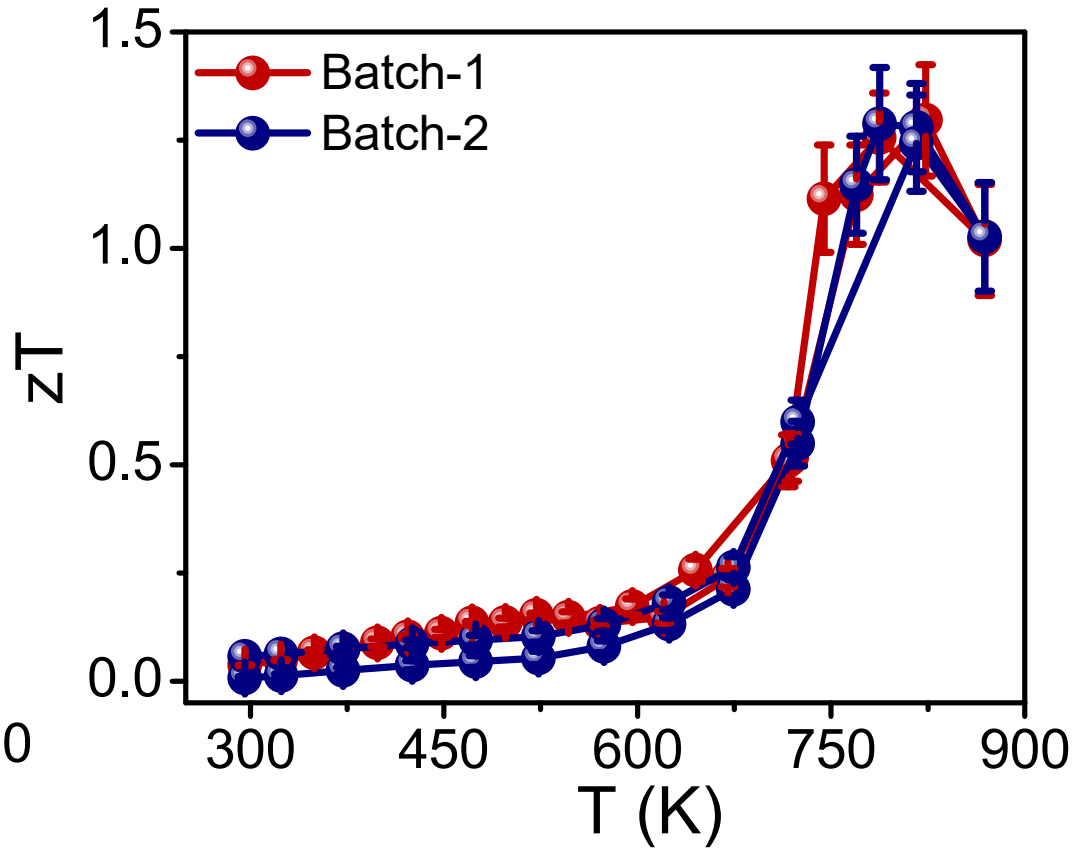
Orthorhombic $(SnSe)_{0.78}(AgBiSe_2)_{0.22}$ shows an ultra-low lattice thermal conductivity of ~0.19 $Wm^{-1}K^{-1}$ at 773 K due to the enhanced phonon scattering induced by the point defects owing to entropy-driven solid solution in SnSe-$AgBiSe_2$ system in addition to lattice anharmonicity.



The higher lattice thermal conductivity of cubic $(SnSe)_{0.70}(AgBiSe_2)_{0.30}$, can be attributed to the destruction of the layered orthorhombic crystal structure of SnSe.

Thermoelectric Performance of $(SnSe)_{1-x}(AgBiSe_2)_x$





A highest *zT* value of ~ 1.3 at 823 K was observed for *p*-type polycrystalline orthorhombic $(SnSe)_{0.78}(AgBiSe_2)_{0.22}$ sample at 823 K when measured along parallel to SPS pressing direction which is reversible and reproducible for different batches of samples as well as for heating-cooling cycles.

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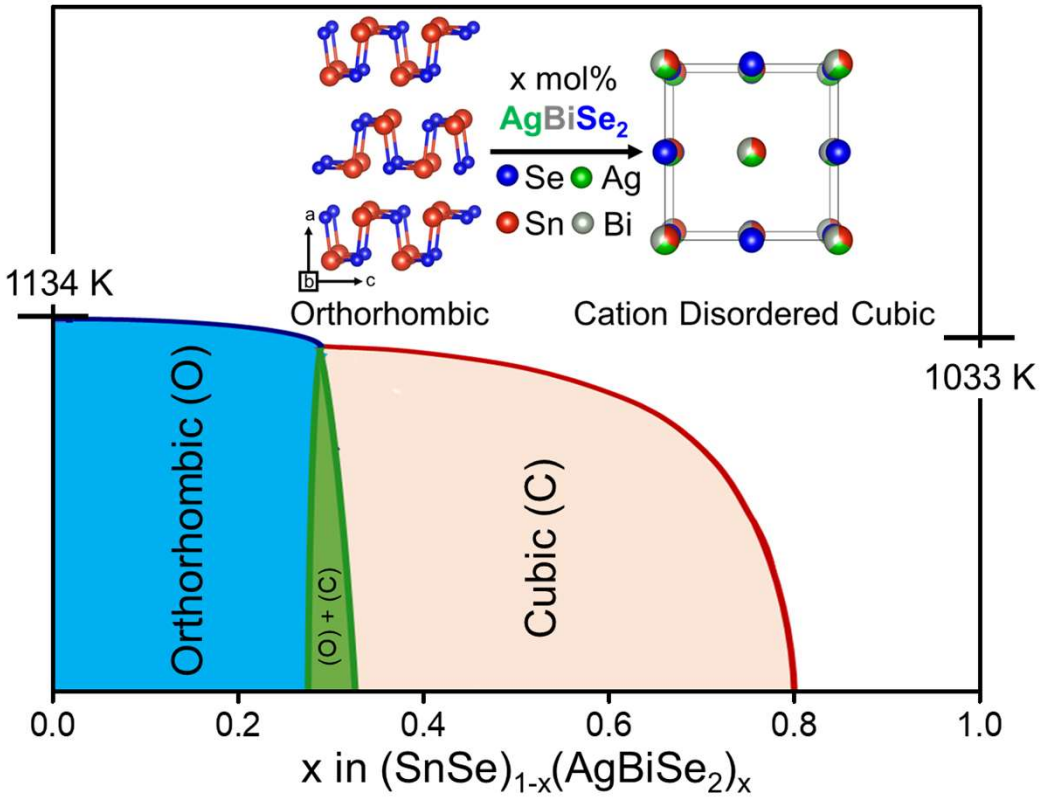
Conclusions



- Solid solution mixing of $AgBiSe_2$ with SnSe increases the configurational entropy by introducing atomic disorder into the system and consequently stabilizes the cubic phase at ambient condition.

- Cubic $(SnSe)_{0.70}(AgBiSe_2)_{0.30}$ shows semi metallic *n*-type conduction at room temperature.

- We have obtained a peak *zT* value of ~ 1.3 at 823 K for *p*-type polycrystalline orthorhombic $(SnSe)_{0.78}(AgBiSe_2)_{0.22}$ sample.

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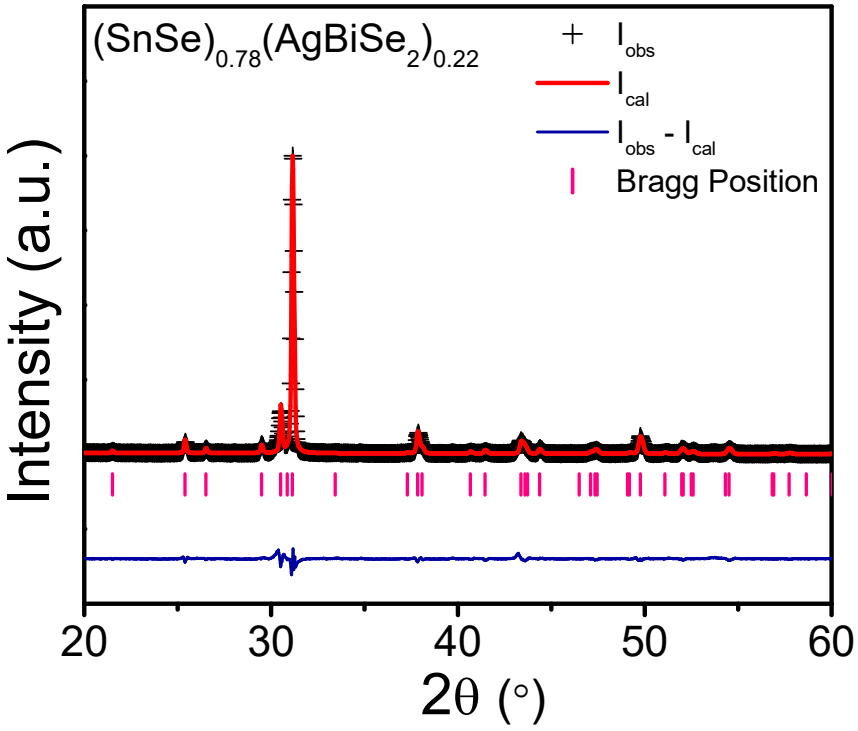
- My lab mates @Solid State Chemistry lab and friends at JNCASR.

Acknowledgments

Thank You !!!

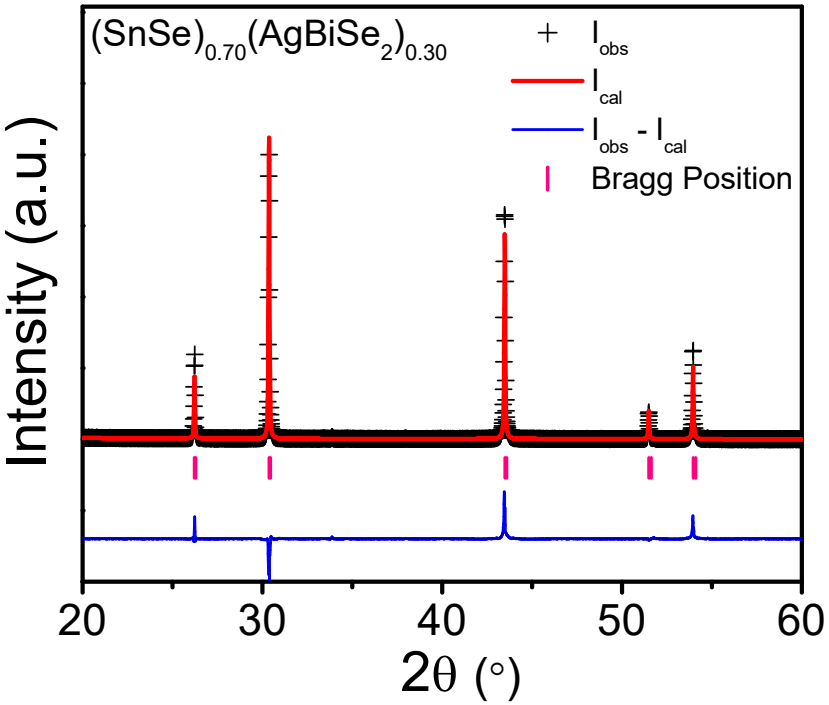
Reitveld Refinement of $(SnSe)_{0.78}(AgBiSe_2)_{0.22}$



Space group: *Pnma*; a = 11.50 Å, b = 4.15 Å, c = 4.44 Å, α = β = γ= 90°
R-factors: R_{wp}: 12.61; R_{exp}: 8.19

Constituent Elements	x/a	y/b	z/c	U_{iso} (Å^2)	Occupancy	χ^2
Sn	0.8564(5)	0.25	0.4755(4)	0.1148(4)	0.63(2)	2.37
Ag	0.8564(5)	0.25	0.4755(4)	0.1148(4)	0.21(2)	
Bi	0.8564(5)	0.25	0.4755(4)	0.1148(4)	0.16(2)	
Se	0.1181(4)	0.25	0.1091(5)	0.0380(5)	1	

Reitveld Refinement of $(SnSe)_{0.70}(AgBiSe_2)_{0.30}$



Space group: *Fm*-3*m*; a = b = c = 5.8819 Å, α = β = γ= 90°
R-factors: R_{wp}: 11.93; R_{exp}: 5.6

Constituent Elements	x/a	y/b	z/c	U_{iso} (Å^2)	Occupancy	χ^2
Sn	0.0	0.0	0.0	0.1558(3)	0.54(2)	4.43
Ag	0.0	0.0	0.0	0.1558(3)	0.27(2)	
Bi	0.0	0.0	0.0	0.1558(3)	0.19(2)	
Se	0.5	0.5	0.5	0.0815(4)	1	

Anisotropic Thermoelectric Properties of $(SnSe)_{0.78}(AgBiSe_2)_{0.22}$