Modulation of Electronic Structure and Thermoelectric Properties of Orthorhombic and Cubic SnSe by AgBiSe$_2$ Alloyming

Sushmita Chandra$^{1,4}$, Raagya Arora$^{2,3}$, Umesh V. Waghmare$^{3,4}$ and Kanishka Biswas$^{*,1,4}$

$^1$New Chemistry Unit, $^2$Chemistry and Physics of Materials Unit and $^3$Theoretical Sciences Unit, $^4$School of Advanced Materials and International Centre for Materials, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Jakkur P.O., Bangalore 560064, India

$^*$Email: kanishka@jncasr.ac.in

METHODS

Reagents. The high purity elements utilized for the synthesis of (SnSe)$_{1-x}$(AgBiSe$_2$)$_x$ (0.00 ≤ x ≤ 1.00) samples are tin (Alfa Aesar 99.99+ %), silver (Ag, Aldrich 99.999%), bismuth (Alfa Aesar 99.9999%), and selenium (Se, Alfa Aesar 99.9999%).

Synthesis. Polycrystalline (SnSe)$_{1-x}$(AgBiSe$_2$)$_x$ (0.00 ≤ x ≤ 1.00) samples were synthesized by combining stoichiometric ratios of elemental Ag, Bi, Sn and Se in high quality quartz tubes. The quartz tubes were maintained at a pressure of 10$^{-5}$ Torr and sealed under vacuum. The seal tubes were initially heated to 773 K over a period of 12 hrs, then heated again to 1223 K in next 5 hrs followed by annealing for 10 hrs and subsequently cooled to room temperature for a period of 15 hrs. The resulted ingots were crushed by using a mortar and pestle and sieved to fine powder. After that, ball-milling has been carried out at a speed of 250 rpm for 4 hrs at N$_2$ atmosphere in stainless-steel containers using a planetary Ball Mill (FRITSCH PULVERISETTE 7, Germany).

Spark plasma sintering (SPS). SPS was done using a SPS211-LX (Dr. Sinter Lab) instrument. The finely powdered samples were sintered to prepare a cylinder (10 mm × 8 mm) using graphite dies at 40 MPa pressure and 450 °C temperature. The samples were cut and polished.
in different directions to measure the anisotropic electrical and thermal transport properties of (SnSe)_{1-x}(AgBiSe_2)_x (0.00 ≤ x ≤ 0.80).

**Powder X-ray diffraction.** Room temperature powder X-ray diffraction for all the samples were recorded using a Cu Kα (λ = 1.5406 Å) radiation on a Bruker D8 Diffractometer. Rietveld refinement of the PXRD pattern was performed using FULLPROF software.

**Field emission scanning electron microscopy (FESEM) in back-scattered electron (BSE) mode.** FESEM-BSE images were taken using ZEISS Gemini SEM – Field Emission Scanning Electron Microscope.

**Band gap measurement.** To estimate optical band gap of the as-synthesized specimens of (SnSe)_{1-x}(AgBiSe_2)_x (0.00 ≤ x ≤ 1.00), diffuse reflectance measurements were carried out with finely grounded powder at room temperature using a Perkin-Elmer Lambda 900 UV/Vis/near-IR spectrometer in reflectance mode (λ = 2500-250 nm) and FT-IR Bruker IFS 66V/S spectrometer (λ = 4000-400 cm\(^{-1}\)), respectively. Absorption (α/Λ) data were calculated from the reflectance data using Kubelka-Munk equation: \(\alpha/\Lambda = (1-R)^2/(2R)\), where \(R\) is the reflectance, \(\alpha\) and \(\Lambda\) are respectively the absorption and scattering coefficients. The energy band gap was then determined from \(\alpha/\Lambda\) vs. E (eV) plot.

**Electrical transport.** Electrical conductivity and Seebeck coefficients were measured simultaneously under helium atmosphere from room temperature to 850 K on a ULVAC-RIKO ZEM-3 instrument system. The SPS processed sample were cut and polished in a rectangular shape with the dimensions of ~ 2 × 2 × 8 mm\(^3\) to carry out the measurements. Electrical and thermal transport were measured in same direction.

**Hall measurement.** For determining the carrier concentrations, Hall measurements were carried out on the same rectangular specimens used for electrical transport measurement in four-contact geometry up to a magnetic field of 0.57 T at room-temperature using custom-built equipment developed by Excel Instruments.
**Thermal transport.** Temperature dependent thermal diffusivity ($D$) was evaluated using a laser flash diffusivity technique in a Netzsch LFA-457 instrument. In addition, temperature dependent heat capacity was also measured in the same instrument by using a standard pyroceram (Fig. S12). Next, the total thermal conductivity ($\kappa$) was derived using the formula, $\kappa = D C_p \rho$, where $\rho$ is density of the sample and the experimentally determined density was found to be ~97% of the theoretical density. Further, the electrical thermal conductivity, $\kappa_{ele}$ were derived using Wiedemann-Franz Law, $\kappa_{ele} = L \sigma T$, where $L$ denotes the Lorenz number which was estimated by fitting the temperature dependent Seebeck data$^{1-3}$ and provided in Fig. S13.

**Computational details.** Our first-principles calculations within density functional theory (DFT) were performed with QUANTUM ESPRESSO Package (QE) and projector augmented wave (PAW) potentials.$^4$ Electronic exchange and correlation energy was treated within a generalized gradient approximated (GGA)$^5$ functional with Perdew, Burke, and Ernzerhof (PBE) parametrization.$^6$

Electronic wave functions and charge density were represented using plane wave basis sets truncated at cut-off energies of 45 Ry and 360 Ry respectively. The discontinuity in occupation numbers of electronic states was smeared with broadening temperature of $k_B T = 0.003$ Ry in a Fermi-Dirac distribution function. We determined electronic structure of (SnSe)$_{1-x}$(AgBiSe$_2$)$_x$ in crystal structures with optimized (minimum energy) lattice parameters. At ambient conditions, SnSe stabilizes in the orthorhombic $Pnma$ phase containing eight atoms in the periodic unit cell. Integrations over its Brillouin Zone (BZ) were sampled on a uniform $8 \times 8 \times 8$ mesh of k-points. Electronic spectrum was determined at Bloch vectors along high symmetry lines ($X - \Gamma - Y - P - \Gamma - A - Z - \Gamma - T$) in the BZS. Our optimized lattice parameters for pristine SnSe in the orthorhombic structure ($Pnma$) are $a = 11.77$ Å, $b = 4.22$ Å, $c = 4.53$ Å, which are within the typical GGA errors of experimental lattice parameters ($a = 11.57$ Å, $b$
= 4.19 Å, c = 4.46 Å). The cubic phase of (SnSe)$_{0.67}$(AgBiSe$_2$)$_{0.33}$ was simulated using a \(\sqrt{2}\times\sqrt{2}\times1\) supercell of conventional \(Fm\bar{3}m\) structure containing 16 atoms. Our estimates of lattice parameters of (SnSe)$_{0.67}$(AgBiSe$_2$)$_{0.33}$ in this structure (\(\sqrt{2}\times\sqrt{2}\times1\) supercell) are \(a = 8.43\) Å, \(b = 8.43\) Å, \(c = 5.96\) Å, which are within the typical GGA errors of experimental values of \(a = 8.36\) Å, \(b = 8.36\) Å, \(c = 5.91\) Å. Electronic spectrum was determined at Bloch vectors along high symmetry lines (\(\Gamma - X - M - \Gamma - Z - R - A - Z - X - R - M - A\)) in the BZ of its tetragonal unit by including the spin-orbit coupling (SOC) in calculations with fully relativistic potentials.\(^7\)

The special quasirandom structures (SQS) of (SnSe)$_{0.67}$(AgBiSe$_2$)$_{0.33}$ in the cubic phase and of (SnSe)$_{0.8}$(AgBiSe$_2$)$_{0.2}$ in the orthorhombic phase were generated using the Monte Carlo SQS tool in the Alloy Theoretical Automated Toolkit (ATAT).\(^8\) Our estimates of lattice parameters of the cubic structure of (SnSe)$_{0.67}$(AgBiSe$_2$)$_{0.33}$ are \(a = b = c = 5.98\) Å, and of orthorhombic (SnSe)$_{0.8}$(AgBiSe$_2$)$_{0.2}$ are \(a = 12.05\) Å, \(b = 4.26\) Å and \(c = 4.52\) Å. To determine the bulk electronic topology of cubic SnSe, we used Z2PACK code\(^9\) to calculate the \(Z_2\) topological invariants and mirror Chern number (\(n_M\)). This code uses hybrid Wannier functions\(^{10,11}\) and employs the ideas of time-reversal polarization in determination of the \(Z_2\) invariants.
**Fig. S1.** PXRD patterns of polycrystalline \((\text{SnSe})_{1-x}(\text{AgBiSe}_2)_x\) samples where the composition ranging in between \(0.00 \leq x < 0.28\) are orthorhombic, \(0.30 \leq x \leq 0.80\) are cubic and \(0.80 < x \leq 1.00\) are hexagonal.

**Fig. S2.** FESEM-BSE images for ball milled and SPS processed orthorhombic \((\text{SnSe})_{0.78}(\text{AgBiSe}_2)_{0.22}\) polycrystal with different resolution. The line like features present in (a) are due to polishing of sample.
Fig. S3. FESEM-BSE images for ball milled and SPS processed cubic (SnSe)_{0.70}(AgBiSe_2)_{0.30} polycrystal with different resolution. The line like features present in (a) & (b) are due to polishing of sample.

Fig. S4. (a) Backscattered electron images taken during FESEM for ball milled and SPS processed orthorhombic (SnSe)_{0.78}(AgBiSe_2)_{0.22} polycrystal with corresponding EDAX spectra in (b). (c) EDAX elemental color mapping for Sn, Ag, Bi and Se for the area in (a).
**Fig. S5.** (a) Backscattered electron images taken during FESEM for ball milled and SPS processed cubic (SnSe)$_{0.70}$ (AgBiSe$_2$)$_{0.30}$ polycrystal with corresponding EDAX spectra in (b). (c) EDAX elemental color mapping for Sn, Ag, Bi and Se for the area in (a).

**Fig. S6.** (a) Crystal structure of SnSe in the orthorhombic unit cell with space group $Pnma$ (Sn Red, Se blue). (b) Electronic structures of the orthorhombic ($Pnma$) SnSe with the inclusion of the effect of spin-orbit coupling.
Fig. S7. (a) Crystal structure of disordered cubic (SnSe)$_{0.67}$(AgBiSe$_2$)$_{0.33}$ (Sn Red, Se blue, Ag green, Bi grey). (b) Electronic structures of the $\sqrt{2} \times \sqrt{2} \times 1$ tetragonal supercell of the cubic phase of (SnSe)$_{0.67}$(AgBiSe$_2$)$_{0.33}$ with the inclusion of the effect of spin-orbit coupling. (c) Electronic density of states (DOS) and projected density of states (PDOS) of cubic (SnSe)$_{0.67}$(AgBiSe$_2$)$_{0.33}$.

Fig. S8. (a) Crystal structure of lower-symmetric disordered cubic (SnSe)$_{0.67}$(AgBiSe$_2$)$_{0.33}$ (Sn Red, Se blue, Ag green, Bi grey) obtained by interchanging a pair of Sn and Ag atoms in Fig. S3a. (b) Electronic structure of the second configuration of $\sqrt{2} \times \sqrt{2} \times 1$ tetragonal supercell of cubic structure of (SnSe)$_{0.67}$(AgBiSe$_2$)$_{0.33}$ with the inclusion of the effect of spin-orbit coupling.
**Fig. S9.** Temperature dependent (a) electrical conductivity ($\sigma$), (b) Seebeck coefficient ($S$), (c) power factor ($S^2\sigma$), (d) total thermal conductivity ($\kappa$), and (e) thermoelectric figure of merit ($zT$) of ball milled and SPS processed orthorhombic (SnSe)$_{0.78}$(AgBiSe$_2$)$_{0.22}$ sample measured along both parallel and perpendicular to SPS pressing directions.

**Fig. S10.** Temperature dependent electrical thermal conductivity ($\kappa_{el}$) of ball-milled polycrystalline (SnSe)$_{1-x}$(AgBiSe$_2$)$_x$ (where, $x = 0, 0.22$ are orthorhombic and $x = 0.30$ is cubic in nature) measured along parallel to the SPS pressing direction.
**Fig. S11.** The reversibility and reproducibility of the thermoelectric figure of merit of the SPS processed ball milled orthorhombic (SnSe)_{0.78}(AgBiSe_{2})_{0.22} sample measured for different batches (synthesized separately) with the heating cooling cycles. The $zT$ is measured along the parallel to SPS pressing direction.

**Fig. S12.** Typical heat capacity ($C_p$) of polycrystalline (SnSe)$_{1-x}$(AgBiSe$_2$)$_x$ samples along with the Dulong-Petit $C_p$ value of SnSe.
Fig. S13. Temperature dependent Lorenz number of ball-milled polycrystalline (SnSe)$_{1-x}$ (AgBiSe$_2$)$_x$ (where, $x = 0, 0.22$ are orthorhombic and $x = 0.30$ is cubic in nature) along parallel to the SPS pressing direction.

Table S1. Structural parameters of Rietveld refinement for orthorhombic (SnSe)$_{0.78}$(AgBiSe$_2$)$_{0.22}$ sample.

Space group: $Pnma$; $a = 11.50$ Å, $b = 4.15$ Å, $c = 4.44$ Å, $\alpha = \beta = \gamma = 90^\circ$

| Constituent Elements | x/a   | y/b   | z/c    | $U_{iso}$ (Å$^2$) | Occupancy | $\chi^2$ |
|----------------------|-------|-------|--------|-------------------|-----------|----------|
| 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        |          |

R-factors: $R_{wp}: 12.61$; $R_{exp}: 8.19$
Table S2. Structural parameters of Rietveld refinement for cubic (SnSe)_{0.70}(AgBiSe_{2})_{0.30} sample.

Space group: \(Fm\overline{3}m\); \(a = b = c = 5.8819 \text{ Å}, \alpha = \beta = \gamma = 90^\circ\)

| Constituent Elements | \(x/a\) | \(y/b\) | \(z/c\) | \(U_{iso} (\text{Å}^2)\) | Occupancy | \(\chi^2\) |
|----------------------|---------|---------|---------|--------------------------|-----------|---------|
| 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         |         |

R-factors: \(R_{wp}\): 11.93; \(R_{exp}\): 5.6

Table S3. Charge carrier concentration and mobility of the ball milled and SPS processed polycrystalline (SnSe)\(_{1-x}(AgBiSe_{2})_{x}\) (\(x = 0, 0.22, 0.30\)) samples.

| Composition | Carrier concentration \(n (\text{cm}^{-3})\) | Carrier Mobility \(\mu (\text{cm}^2\text{V}^{-1}\text{S}^{-1})\) |
|-------------|---------------------------------------------|----------------------------------------------------|
| SnSe        | \(8.9 \times 10^{17}\) (\(p\)-type)        | 8.3                                                |
| (SnSe)\(_{0.78}(AgBiSe_{2})_{0.22}\) (Orthorhombic) | \(8.2 \times 10^{19}\) (\(p\)-type) | 20.8                                              |
| (SnSe)\(_{0.70}(AgBiSe_{2})_{0.30}\) (Cubic) | \(6.17 \times 10^{18}\) (\(n\)-type) | 54.6                                              |

Table S4. Densities of the ball milled and SPS processed polycrystalline (SnSe)\(_{1-x}(AgBiSe_{2})_{x}\) (\(x = 0, 0.22, 0.30\)) samples.

| Composition | Density (\(\text{gm cm}^{-3}\)) |
|-------------|---------------------------------|
| SnSe        | 5.99                            |
| (SnSe)\(_{0.78}(AgBiSe_{2})_{0.22}\) (Orthorhombic) | 6.01                                |
| (SnSe)\(_{0.70}(AgBiSe_{2})_{0.30}\) (Cubic) | 5.93                                |
Table S5. Comparison of κ_{lat} of various high performance SnSe based polycrystals.

| Product                                | κ_{lat} (W m⁻¹ K⁻¹) | T (K) | Reference |
|----------------------------------------|----------------------|-------|-----------|
| (SnSe)₀.₇₈(AgBiSe₂)₀.₂₂                | 0.19                 | 773   | (This Work) |
| AgSnSbSe₁.₅Te₁.₅                     | 0.32                 | 723   | 12        |
| Sn₀.₅₀(AgBi)₀.₂₅Se₀.₅₀Te₀.₅₀         | 0.24                 | 820   | 13        |
| (Na₀.₀₁Sn₀.₉₉Se)-5%(PbSe)             | 0.11                 | 773   | 14        |
| Sn₀.₄₀(AgBi)₀.₃₀Se                    | 0.45                 | 842   | 15        |
| K₀.₀₁Sn₀.₉₉Se                         | 0.20                 | 773   | 16        |
| Ag₀.₀₁Sn₀.₉₉Se₀.₈₅Se₀.₁₅             | 0.11                 | 825   | 17        |
| Sn₀.₉₅Se                              | 0.23                 | 873   | 18        |
| SnSe + 1mol% PbSe                     | 0.15                 | 873   | 19        |
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