Supporting Information

Computational Approach to Enhance Thermoelectric Performance in Ag$_2$Se by S and Te Substitutions

Raju K Biswas*[a] and Swapan K Pati*[b]

[a]*Department of Physics, Faculty of Physical and Mathematical Sciences (FMPS)*
M S Ramaiah University of Applied Sciences (MSRUAS), Bangalore 560058, India

[b]*Theoretical Sciences Unit, School of Advanced Materials*
Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR)
Jakkur P.O., Bangalore 560064, India.

E-mail: raju.pi.mp@msruas.ac.in & E-mail: pati@jncasr.ac.in

STABILITY STUDY:

To discuss the structural, thermodynamical, and chemical stability of the pseudobinary and pseudo ternary phases of Ag$_2$Se, we use ab-initio-based density functional perturbation theory (DFPT) methods. It has become a well-established technique for investigating the structural stability of various materials.[1,2] In this regard, our lattice dynamics study using phonon dispersion calculation reveals that pristine and doped Ag$_2$Se are dynamically stable. In phonon dispersion curves shown in **Fig. S2**, supplementary material, we observe that all vibrational modes are positive in magnitude, which implies the mechanical stability of both pristine and doped Ag$_2$Se crystal structures. Furthermore, thermodynamic stability is also examined by performing formation energy and binding energy calculations for doped Ag$_2$Se. The estimated formation energies for S-doped, Te-doped and Te & S co-doped A2Se are -0.81 eV, -0.27 eV and -0.40 eV, respectively (Tabulated in **Table S1**, supplementary material). Moreover, binding energies are also calculated, which are -6.12 eV, -5.02 eV and -10.47 eV, respectively (Tabulated in **Table S1**, supplementary material). Interestingly, formation energy in combination with binding energy determines the chemical stability of these pseudobinary and pseudo ternary phases of Ag$_2$Se.

Formation energy: $F.E = E(M@Ag_2Se) + E(Se) - E(Ag_2Se) - E(M)$ (S1)

Binding energy: $B.E = E(Ag_2Se_{1-x}M_x) - E(Ag_2Se_{1-x}) - E(M)$ (S2)

Here, M= Te and S atoms. $E(M@Ag_2Se), E(Se), E(Ag_2Se), E(M),$ are the total energies of the unit cell where M atom substituted one Se atom, single Se atom in the unit cell, Ag_2Se unit cell, and single M atom in the unit cell, respectively. On the other hand, $E(Ag_2Se_{1-x}M_x), E(Ag_2Se_{1-x}), E(M),$ are total energy of unit cell where one M atom substituted Se atom, one Se atom absent Ag_2Se unit cell, and single M atom unit cell, respectively.

Table S1 Tabulated formation and binding energy per atom for pristine and doped Ag$_2$Se. Formation energy and binding energies for pristine Ag$_2$Se are considered as reference. The negative values of formation and binding energy imply that doped Ag$_2$Se crystal structures are stable.

Energy (eV)	Ag$_8$Se$_4$	Ag$_8$Se$_3$S	Ag$_8$Se$_3$Te	Ag$_8$Se$_2$TeS
Formation Energy (F.E)	0.0	-0.81	-0.27	-0.40
Binding Energy (B.E)	0.0	-0.51	-0.41	-0.87

Table S2 List of k-points to plot electronic band structure for pristine and doped Ag$_2$Se:

Γ	0.0	0.0	0.0
M	0.5	0.0	0.0
K	0.5	0.5	0.0

Γ	0.0	0.0	0.0
Z	0.0	0.0	0.5
R	0.5	0.0	0.5
X	0.5	0.5	0.5
Z	0.0	0.0	0.5

Table S3 Band gap estimated using HSE06 functional for pristine and doped Ag_2Se.

Materials	Ag_8Se_4	Ag_8Se_3S	Ag_8Se_3Te	Ag_8Se_2TeS
$E_g(eV)$	0.64	0.78	0.41	0.66

Table S4 E^c and C_{3D} obtained for holes under acoustics phonon approximation.

Materials	Ag_8Se_4	Ag_8Se_3S	Ag_8Se_3Te	Ag_8Se_2TeS
E^c(eV)	3.2	1.68	2.09	1.32
C_{3D}(J/m³)	4.2×10^{11}	2.74×10^{11}	3.57×10^{11}	1.47×10^{11}
m^*	0.78	0.96	0.81	0.51

Table S5 E^c and C_{3D} obtained for electrons under acoustics phonon approximation.

Materials	Ag_8Se_4	Ag_8Se_3S	Ag_8Se_3Te	Ag_8Se_2TeS
E^c(eV)	2.57	2.24	1.14	2.4
C_{3D}(J/m³)	4.2×10^{11}	2.74×10^{11}	3.57×10^{11}	1.47×10^{11}

m^*	0.28	0.36	0.21	0.14

Table S6. E^c and C_{3D} obtained for phonon under acoustics phonon approximation.

Materials	Ag_8Se_4	Ag_8Se_3S	Ag_8Se_3Te	Ag_8Se_2TeS
E^c**(eV)**	0.017	0.002	0.0029	0.0033
C_{3D}**(J/m³)**	119×10^{11}	2.74×10^{11}	3.57×10^{11}	1.47×10^{11}
$\omega_{q_p LO}$**(cm⁻¹)**	34.40	34.73	32.75	29.35
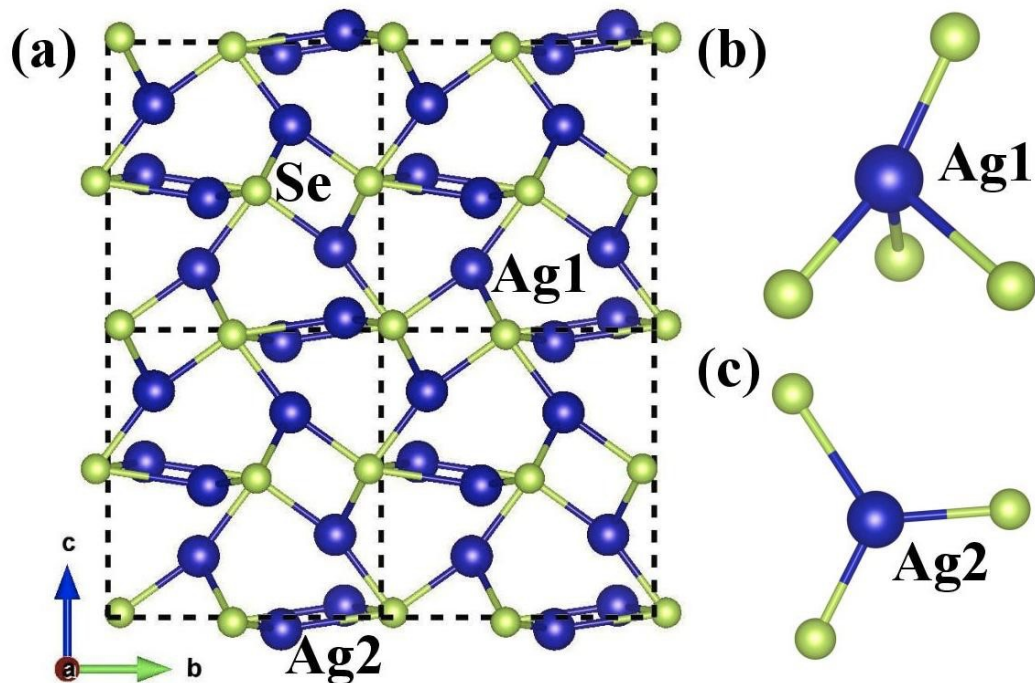
Fig. S1 Crystal structure of Ag_2Se at room temperature. Silver atoms are shown as blue balls, selenium atoms as larger light green balls. (a) Ag_2Se crystal structure viewed from a-axis. Local atomic coordination of Ag atoms in the crystal structure

where (b) Ag1 atoms are arranged tetrahedrally. (c) The coordination sphere of Ag2 is triangular.
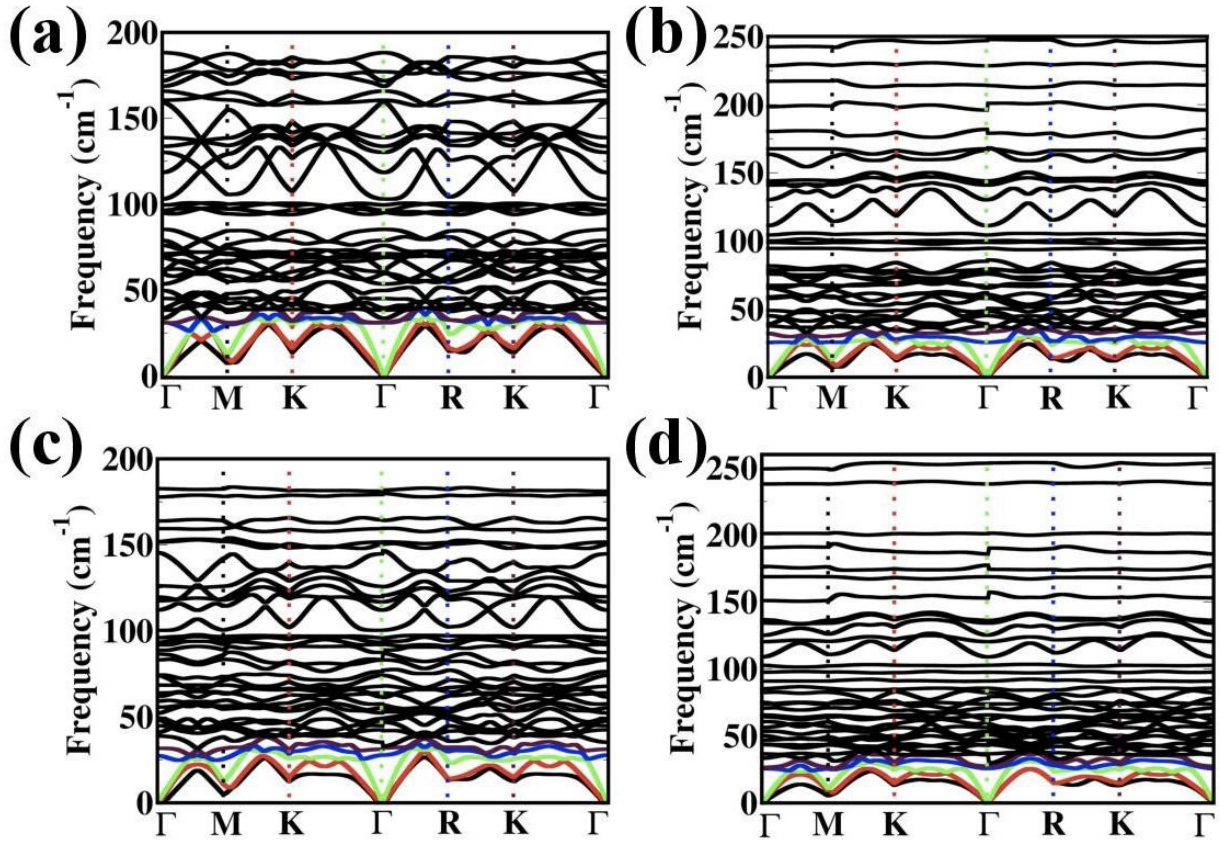

Fig. S2 Phonon dispersion curve of (a) Ag_8Se_4, (b) Ag_8Se_3S, (c) Ag_8Se_3Te, (d) Ag_8Se_2TeS, have been calculated using DFPT and plotted as a function of q-point. The lattice dynamics curves signify both pristine and doped Ag_2Se are dynamically stable. The green and red colour phonon bands represent longitudinal and transverse acoustics modes, respectively. On the other hand, the blue colour phonon band signifies low energetic optical phonon mode.
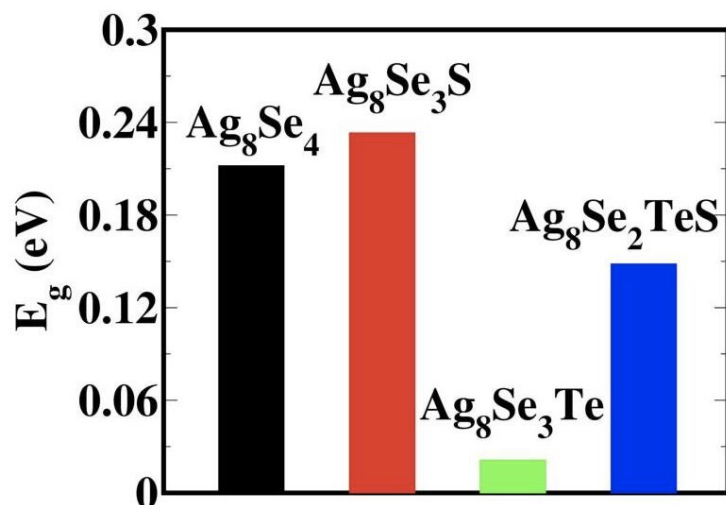
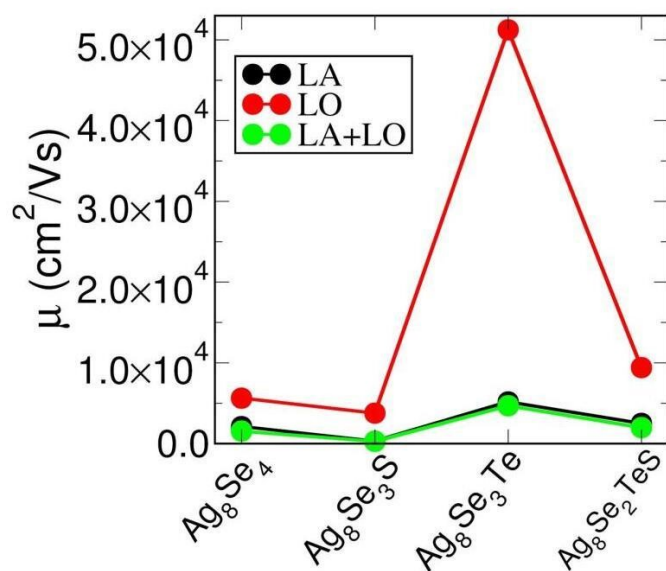**Fig. S3** PBE-SOC bandgap for pristine and doped Ag_2Se.

Fig. S4 Mode resolved mobility for pristine as well as doped Ag_2Se. Black line represents mobility limited by the longitudinal acoustics (LA) phonon; Red line represents mobility limited by the longitudinal optical (LO) phonon; Green line represents mobility limited by both LA as well as LO phonons.
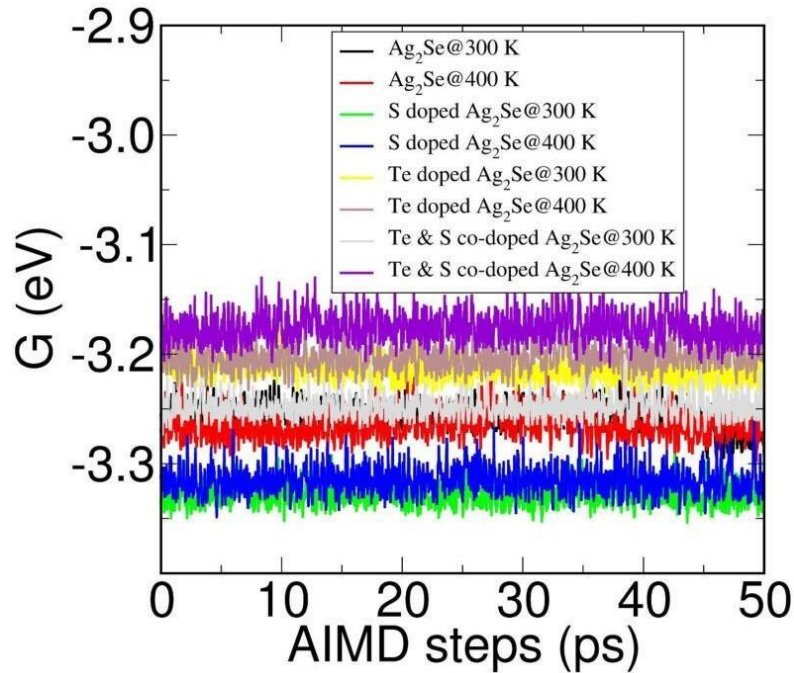
Fig. S5 Gibbs free energy as a function of AIMD steps is plotted for pristine and doped Ag_2Se at 300 K and 400 K.
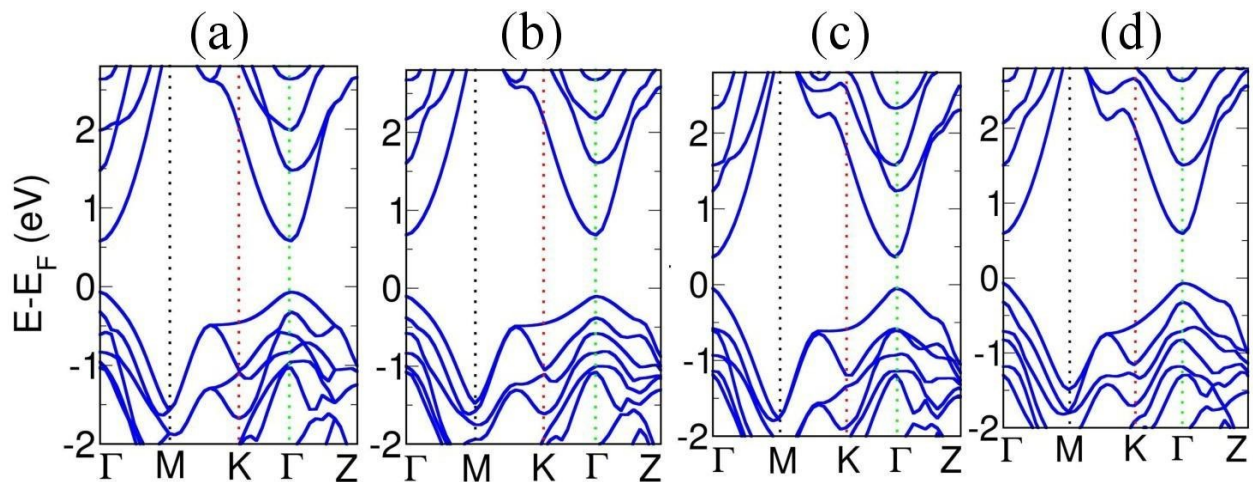

Fig. S6 Electronic band structure at the HSE06 of (a) Pristine, (b) S doped, (c) Te doped, (d) Te & S co-doped, Ag_2Se, along the high symmetry k-points. The Fermi level is considered as a reference for each figure.

ESTIMATION OF CARRIER DENSITY: Intrinsic carrier density (n) of semiconductor with parabolic energy band dispersion can be calculated using the expression **[3]**,

$$n = 2\left(\frac{2\pi k_B T}{h^2}\right)^{\frac{3}{2}} (m_e^* m_h^*)^{\frac{3}{4}} \exp\left(-\frac{E_g}{2k_B T}\right) \tag{S3}$$

where k_B, h, T are Boltzmann constant, Planck constant and room temperature in Kelvin (300 K), respectively. E_g, m_e^*, and m_h^* are electronic band gap, electron and hole effective masses, respectively.

REFERENCES

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