Supplementary material

Stretchable and Dynamically Stable Promising Two-Dimensional Thermoelectric Materials: ScP and ScAs

Kulwinder Kaur¹, Devaraj Murali^{1,2} and Birabar Ranjit Kumar Nanda¹

¹Condensed Matter Theory and Computational Lab, Department of Physics

IIT Madras (Chennai)-600036

²Department of Physics, Indian Institute of Information Technology Design and Manufacturing, Kurnool (Andhra Pradesh)-518002

email id: <u>nandab@iitm.ac.in</u>

(I) Phonon dispersion for buckled and planar structure of ScP

Most of the two dimensional materials crystallize either in puckered, planar or buckled structure. The optimized structural parameters of buckled, planar and puckered structure are listed in Table 1 of main text.



Fig. S1: Optimized structure and phonon dispersion of (a) buckled (b) planar structure of ScP. These structures are not dynamically stable due to the presence of imaginary phonon frequencies.

The puckered structure of ScP and ScAs have lower ground state enegy as compared to buckled and planar. The phonon studies show that the planar and buckled structure are unstable due to the presence of imaginary phonon frequency. Fig. S1, shows the phonon dispersion curve for buckled and puckered structure of ScP. Similar trends observed in ScAs.

(II) Total and projected density of states of ScP

The total electronic density of states (DOS) and projected density of states (PDOS) of ScP are shown in Fig. S2. The figure shows that the valence and conduction bands are dominated by the P-p and Sc-d characters respectively. As the orbital projected band structures of Fig. S3 suggest, the band-I is formed by p_x and p_y states where as the band-II is formed by the p_z state. The band-III and IV are formed by $d_x^2 - y^2$ and $d_z^2 - 1$ states respectively (Fig 5 in main text). Similar trends are observed for ScAs as well.



Fig. S2: The calculated (a) total electronic density of states (b) projected density of states of ScP (unstrained case). The valence band edge is composed of p_x and p_y of P and conduction band edge is made up of $d_x^2-_y^2$ and d_{xy} .



Fig. S3: P-p and Sc-*d* projected GGA band structure of (a) unstrained (b) 9% strained ScP.

Band structure with spin orbit coupling (SOC):

The band structure with SOC is shown in Fig. S4. For the unstrained system, the SOC splits the pbands (band-I) with the upper one pushes above to cross band-III. As a consequence, p-d band inversion occurs which gives rise to a very weak band gap (~ 0.2 meV). With tensile strain, the separation between the band-I and III increases and therefore, the overlap between these two bands become less leading to reduction in the strength of the band inversion. Beyond a critical strain (\sim 9%) the p-d band inversion vanishes and the hybridized band gap determines the band topology of the ScX.



Fig. S4: Calculated electronic band structure of ScP (upper panel) and ScAs (lower panel) with spin orbit coupling (SOC) under biaxial strain.

(III) Electronic thermal conductivity (k_e)

The electronic thermal conductivity as a function of chemical potential, strain and temperature are plotted in Fig. S5. As, we discussed in main text, k_e strongly depends upon the mobility and temperature. As the mobility decreases with temperature, the electronic part of the thermal conductivity also decreases with temperature.



Fig. S5: The electronic thermal conductivity along armchair and zigzag direction as function of chemical potential at different temperatures in ScX.

(IV) Mode Grüneisen parameter

The mode Grüneisen parameter which characterise the lattice anharmonicity is response of phonon frequency for volumetric change:

$$\gamma_j(q) = \frac{-\partial ln(\omega_j(q))}{\partial ln^{i}(V)}$$

Where, V is crystal volume and $\omega_j(\mathbf{q})$ is phonon frequency corresponding to wavevector \mathbf{q} and phonon branch j. Using cubic Inter-atomic Force Constants (IFC), we calculated mode Grüneisen parameters for ScP and ScAs along high symmetry directions and these are shown in Fig. S6. It is quite clear from figure that both ScAs and ScP show frequency shifts along phonon q vector. Moreover, these frequency shifts are anisotropic indicating anharmonic effects arising from large displacement of lighter masses in the compound. For both ScAs and ScP the maximum frequency change is observed for LA mode near Γ point.



Fig. S6: The calculated mode-Grüneisen parameters for (a) ScP and (b) ScAs using cubic IFC's along high symmetry directions. Green and Blue symbol correspond to shifts in phonon frequencies corresponding to longitudinal and optical phonons respectively. Frequency shifts are highly anisotropic indicating large degree of anharmonicity.

(V) Band structure of ScP within HSE06



Fig. S7: (Left) Comparison between the GGA and HSE obtained band structure of unstrained ScP. (Right) The comparison of HSE band structure of unstrained ScP with the GGA band structure of 6% strained ScP.

In order to have a preliminary idea on the role of exchange-correlation functional on the electronic structure of ScX, we have calculated the band structure of unstrained ScP (See Fig. S7), as a test case, using HSE06 as exchange correlation functional[1] with standard screening parameter of 0.25. It yields a band gap 0.54 eV as compared to the PBE-GGA band gap of 0.18 eV. However,

we find that the effective HSE obtained effective mass for the bottom conduction band to be $0.017m_e$ and for the top valence band to be $0.016m_e$. The respective PBE-GGA calculated values are 0.020 and $0.017m_e$. Therefore, negligible change in the effective masses ensures that the mobility does not change.

As expected, the lattice thermal conductivity is not affected with HSE. However, due to change in the band gap, the chemical potential at which the ZT maximizes will now change.

Interestingly, the unstrained HSE band structure has great resemblance with 6% strain GGA band structure (see Fig. 4(right side)). This suggests that the transport and thermoelectric properties that we calculate with GGA in higher strained condition may be obtained with HSE in lower strained condition.

In general, we believe that even though GGA underestimates the band gap, the thermoelectric phenomenon of these stretchable of s, p electron materials ScX can be predicted with reasonable accuracy with GGA. Most importantly the qualitative trend is not going to change.

References

1. J. Heyd, G. E. Scuseria, M. Ernzerhof, J. Chem. Phys. 2003, 118, 8207.