APPENDIX A

Computational Details

A.1 Bulk Materials

LiMgBi

We performed density functional theory based *first-principles* calculations to investigate topological phase transitions under the application of pressure. For this purpose, we obtained crystallographic information for LiMgBi in F$\overline{4}$3m[216] space group from MaterialsProject repository. Optimization of lattice constant (a) was performed following the convergence test for total energy with respect to, wave function cut off and **k**-mesh. We used norm-conserving pseudopotentials under generalized gradient approximation which considers 1s^1, 3s^2 and 6s^{2}6p^3 orbitals of Li, Mg and Bi respectively for calculations without considering spin-orbit interactions. The pseudopotential method is based on martins-troullier with exchange correlation of perdew-burke-ernzerhof functional type.[2,4] For calculations under spin-orbit interactions we used, projector augmented wave sets with perdew-burke-ernzerhof exchange correlation which considers the contribution from core electrons giving rise to relativistic effects in our calculations.[3] The optimization was performed by, finding a global minima in terms of the total energy of the system and then narrowing down (using bisection method) to a local minima with a constrain that, the total pressure on the atoms is 0.00 kbar. The converged value of plane wave kinetic energy cut-off for norm-conserving (projector augmented wave) pseudopotential and charge density for norm-conserving (projector augmented wave) pseudopotential are 50 Ry (90 Ry) and 200 Ry (360 Ry) respectively. A uniform monkhorst-pack grid for **k**-points of 7 × 7 × 7 was used in the self-consistent calculations for both norm-conserving and projector augmented wave pseudopotentials.[7] For better prediction of energy band gap and in order to verify our generalized gradient approximation results, we have repeated some of our calculations with state-of-the-art screened coulomb hybrid functional calculations based on Heyd-Scuseria-Ernzerhof functional in Vienna *ab initio* simulation package.[5,6] The cut-off for the plane-wave basis expansion was taken as 500 eV. To sample the brillioun zone we have used a monkhorst-pack-grid of 6 × 6 × 6 *k*-points. The convergence criterion of 0.01 eV/Å for hellmann-feynman forces and 10^{-6} eV for total energy were considered. Phonon calculations were performed using density functional perturbation theory.[11] For phonon calculations, we used 10 × 10 × 10 **q**-mesh which was followed by plotting the dynamical matrices in the entire brillouin zone.

LiMgSb

We employed *first-principles* calculation using plane wave self consistent formulation implemented in Quantum ESPRESSO code.[1] We employed norm conserving generalized gradient approximation pseudopotentials (which utilize the, $1s^1$, $3s^2$ and $5s^2 5p^3$ orbital contributions from of Li, Mg and Sb respectively) with martins-troullier method.[2,4] The plane wave basis set was optimized by convergence method, the resulting kinetic energy cutoff was 90 Ry. The optimized k-mesh i.e., monkhorst-pack grid of 8 × 8 × 8 was used.[7] The optimization was confirmed by the threshold for total force on atoms of the order of 10^{-4} eV/Å with total stress on atoms 0.00 kbar.

LiMgAs

We performed electronic studies using, density functional theory based *first-principles* calculations in Quantum ESPRESSO code which implements plane wave self consistent formulation. We employed norm conserving generalized gradient approximation pseudopotentials which utilize the, $1s^1$, $3s^2$ and $4s^2 4p^3$ orbital contributions from of Li, Mg and As respectively. Martins-troullier pseudopotential method is used with exchange correlation of perdew-burke-ernzerhof functional type.[2,4] Projector augmented wave sets with perdew-burke-ernzerhof exchange correlation were used for spin-orbit interaction calculations since, it considers the relativistic effects arising from the core electrons.[3] Lattice constant, wave function kinetic energy cut-off and *k*-mesh were optimized by performing convergence test with, the test condition of total pressure on atoms as 0.00 kbar. The wave function kinetic energy cut-off was obtained to be 90 Ry (90 Ry for projector augmented wave). Uniform momentum monkhorst-pack grid was used in the calculations with, 8 × 8 × 8 (8 × 8 × 8 for projector augmented wave).[7] Structural stability was verified by calculating phonon dispersion curves using density functional perturbation theory.[11] A q-mesh of $6 \times 6 \times 6$ was used.

For all the compounds, with thorough qualitative analysis, we quantified our results by calculating the surface states and $\mathbb{Z}_2$ invariants using WannierTools which used the tight-binding model generated by Wannier90.[8,9]

AuI

The electronic properties (electronic band structure, density of state and orbital projected density of states) were calculated using state-of-the-art density functional theory based *first-principles* method as implemented in the Quantum ESPRESSO code.[1] The scalar relativistic norm-conserving pseudopotentials are employed for the calculations with martins-troullier method to replace the core ionic potential and consider the electronic effect only due to the valence electrons.[2] In order to consider the spin-orbit interaction effects, full relativistic projector augmented wave sets were used to account for the effect of core electrons.[3] These pseudopotentials were used with exchange-correlation functional of perdew-burke-ernzerhof type under the generalized gradient approximation.[4] The system was optimized with proper convergence test using the bisection method to obtain the ground state of the system. Converged values of the plane wave kinetic energy cut-off of 80 Ry with a uniform monkhorst-pack grid for k-vectors of $9 \times 9 \times 9$ were used in the self-consistent calculations with convergence threshold of $<10^{-6}$ Ry.[7] We generated the tight-binding model for AuI using the maximally localised wannier functions which was obtained by proper minimization of the spread function $\widetilde{\Omega}$ using the Wannier90.[8] The tight-binding model was then passed through the WannierTools code to characterize and further investigate the topological states.[9] WannierTools was used to calculate the surface states and $\mathbb{Z}_2$ invariants with the help of iterative Green's function and wilson Loop calculations respectively.

For validating the mechanical stability of AuI, the second-order elastic stiffness tensor was computed within Lagrangian theory of elasticity as implemented in the ElaStic code.[10] For calculating the elastic constants of the system, a set of deformations were imposed on the optimized ground-state crystal structure and all deformed structures were relaxed keeping tight convergence criteria. Followed by this, the second ordered partial derivative of the total energy (U) with respect to the Lagrangian strain were computed using equation A.1 below. Where, V_0 is the volume of ground state reference structure with U being the total energy of the deformed structures, and η_α and η_β being the Lagrangian strains in Voigt notation.

$$C_{\alpha\beta} = \frac{1}{V_0}\frac{\partial^2 U}{\partial\eta_\alpha\partial\eta_\beta} \tag{A.1}$$

The dynamic stability was investigated by calculating the phonon dispersion curves and the phonon density of states. Density functional perturbation theory was used with q-mesh of $8 \times 8 \times 8$ and self-consistency threshold of $<10^{-14}$ Ry.[11] This was followed by plotting the dynamical matrices in the entire brillouin zone. Followed by this, the thermoelectric efficiency zT of the material was evaluated using equation A.2. Where, the symbols S, σ and T represent the Seebeck co-efficient, electrical conductivity and temperature, respectively, and the terms κ_e and κ_l are the electronic and lattice (phonon) contributions to the thermal conductivity.

$$zT = \left(\frac{S^2\sigma}{\kappa_e + \kappa_l}\right)T \tag{A.2}$$

The Boltzmann transport theory as implemented in BoltzTraP package which has been utilized for computing the electronic contribution to the thermoelectric transport properties of AuI.[12] The thermoelectric parameters like S, σ, κ_e, power factor (PF = $S^2\sigma$) and zT were computed as a function of the chemical potential, carrier concentration and temperature for assessing their effect on the thermoelectric performance of AuI. It is a known fact that, the solution obtained under semi-classical Boltzmann transport treatment yields relaxation time (τ) dependent σ and κ_e. Hence, for obtaining τ independent thermoelectric parameters, we have employed deformation potential theory that has been widely utilized for computing mobility (μ) and relaxation time (τ) of bulk as well as low dimensional materials. The deformation potential based mobility was calculated using equation A.3. Where, apart from the standard constants, the terms C^{3D}, m^* and E_1 represent the elastic constant, the carrier effective mass and the deformation potential respectively.

$$\mu = \frac{(8\pi)^{1/2} e\hbar^4 C^{3D}}{3(k_B T)^{3/2}(m^*)^{5/2}E_1^2} \tag{A.3}$$

Besides computing the electronic thermoelectric parameters, the lattice thermal conductivity of the material plays a crucial role in determination of the overall zT. For accurate predictions of the lattice contribution to thermal conductivity requires the inclusion of anharmonicity. This can be done by incorporating third or higher order interatomic force constants.

The first step towards this requires the computation of the second order harmonic interatomic force constants, which in present case are calculated under density functional perturbation theory. Following this, we have utilized a complementary python script provided together with the ShengBTE package for creating supercell structures of size $3 \times 3 \times 3$ considering the fifth nearest neighbour atoms.[13] In total 260 supercell structures were constructed and were considered for self-consistent relaxation. The outputs of these 260 structures together with the second order interatomic force constants were fed to the same python utility tool for generating third order anharmonic interatomic force constants. At the end, the third order interatomic force constants with appropriate input script were utilized to iteratively solve the Boltzmann transport equation for phonons to calculate the temperature dependent thermal conductivity and related transport properties as implemented in ShengBTE package.[13]

A.2 Low Dimensional Materials

LiMgAs Monolayer

We performed electronic studies using, density functional theory based *first-principles* calculations in Quantum ESPRESSO code which implements plane wave self consistent formulation.[1] We employed norm conserving generalized gradient approximation pseudopotentials which utilizes the, $1s^1$, $3s^2$ and $4s^2 4p^3$ orbital contributions from of Li, Mg and As respectively. Martins-troullier pseudopotential method is used with exchange correlation of perdew-burke-ernzerhof functional type.[2,4] Projector augmented wave sets with perdew-burke-ernzerhof exchange correlation are used for spin-orbit interaction calculations since, it considers the relativistic effects arising from the core electrons.[3] Lattice constant, wave function kinetic energy cut-off and k-mesh were optimized by performing convergence test with, the test condition of total pressure on atoms as 0.00 kbar. The wave function kinetic energy cut-off was obtained to be 50 Ry (80 Ry for projector augmented wave). Uniform momentum grid of monkhorst-pack type was used in the calculations with, $6 \times 6 \times 1$ ($8 \times 8 \times 1$ for projector augmented wave).[7] Structural stability was verified by calculating phonon dispersion curves using density functional perturbation theory.[11] A q-mesh of $5 \times 5 \times 1$ was used. With thorough qualitative analysis, we quantified our results by calculating the $\mathbb{Z}_2$ invariant using Wannier90 around the wilson charge loops this was followed by the plotting edge state spectra in WannierTools.[8,9]

Functionalized Tellurene and Selenene

We implemented *first-principles* based density functional theory in Quantum ESPRESSO package to obtain the ground state energy of the system (with a vacuum of $c = 25.00$ Å along the [001] crystal direction to isolate the interactions between periodic images) under plane wave self consistent formulation and calculate the electronic band structures, density of states and orbital/elemental projected density of states.[1] We used, scalar-relativistic and norm conserving martins-troullier pseudopotentials for calculations without spin-orbit interactions and fully-relativistic projector augmented wave pseudopotentials (for calculations with spin-orbit interactions) under generalized gradient approximation with perdew-burke-ernzerhof type of exchange-correlation functional in our calculations.[2–4] The converged value of kinetic energy cutoff was 80 Ry and the corresponding uniform momentum monkhorst-pack grid was of $8 \times 8 \times 1$.[7] The structures were fully relaxed with force convergence criteria of $< 10^{-6}$ a.u. The dynamic stability of the system was investigated in terms of phonon dispersion curves and phonon density of states under the density functional perturbation theory regime with a q-mesh of $5 \times 5 \times 1$.[11] We then projected the plane wave functions onto the maximally localized wannier functions (with convergence of the spread function) by using Wannier90 code to compute the quantum transport properties and create the tight-binding hamiltonian as an input for the WannierTools code.[8,9] The spin Hall conductivity (SHC) ($\sigma_{xy}^{spinz}(\omega)$) was computed using the kubo-greenwood formula within the independent-particle approximation, and the *Berry* curvature ($\Omega_z(k)$) and k-resolved spin *Berry* curvature ($\Omega_{xy}^{spinz}(k)$) to understand the topological properties and the quantum transport phenomena. For this purpose, a dense k-mesh of $100 \times 100 \times 1$ was used; since large contributions of spin Berry curvatures occur in minute regions of k space which leads to slow convergence. We finally compute the $\mathbb{Z}_2$ invariant, Chern number (C) and edge states using the WannierTools code.[9]

AuI Monolayer

We performed state-of-the-art density functional theory based *first-principles* computations as implemented in Quantum ESPRESSO code under the plane wave self consistent formalism.[1] We used scalar relativistic norm conserving martins-troullier pseudopotentials under generalized gradient approximation with exchange correlation functional of perdew-burke-ernzerhof type.[2,4] For spin-orbit interaction calculations, full relativistic projector augmented wave sets with perdew-burke-ernzerhof exchange correlation functional were used to account for the relativistic effects arising from the core electrons.[3] The optimized kinetic energy cut-off and uniform monkhorst-pack momentum grid (k-mesh for brillouin zone sampling) used for unit cell calculations were 90 Ry and $10 \times 10 \times 1$ respectively.[7] The dynamic stability of the system was confirmed by calculating the phonon dispersion curves using density functional perturbation theory with a q-mesh of $5 \times 5 \times 1$.[11] A vacuum of 25Å was introduced along the [001] crystal direction in order to eliminate the interactions with the neighbouring periodic images. Ab-initio molecular dynamics simulations were performed for 3 picoseconds (3000 femtoseconds) at 300 K thermostat temperature to verify the structural stability. To investigate the catalytic properties a $3 \times 3 \times 1$ supercell was designed with kinetic energy cut off and k-mesh of 60 Ry and $5 \times 5 \times 1$ respectively. In order to consider the van der Waals effect, Grimme correlations were incorporated in our computations.[14] These were followed by; computing $\mathbb{Z}_2$ invariant around the wilson loops, edge state spectrum and slab band structures using WannierTools (WT) which employs the tight binding model generated by Wannier90.[8,9]

Topological Quantum Catalyst LiMgAs

We performed density functional theory based *first-principles* calculations using Quantum ESPRESSO.[1] For calculations without spin-orbit interactions, we used scalar-relativistic and norm-conserving martins-troullier pseudopotentials and for calculations with spin-orbit interactions, we used fully-relativistic projector augemented wave pseudopotentials.[2,3] The generalized gradient approximation was implemented with perdew-burke-ernzerhof type of exchange-correlation functional.[4] The hexagonal unit cell was transformed into an orthorhombic unit cell using the rotation matrix ($\mathcal{R}$) which transforms the hexagonal basis vector into orthorhombic basis vector. This orthorhombic unit cell was then transformed into nanoribbons (with ribbon width N = 15 to avoid edge-edge interactions) which are periodic along, (a) [100] and (b) [010] crystal directions with zig-zag and planar like edge terminations respectively. The corresponding uniform momentum monkhorst-pack grid (k-mesh) for brillouin zone sampling was set to be $1 \times 6 \times 1$ and $6 \times 1 \times 1$ respectively.[7] A vacuum of 25 Å along the [001] direction and 17 Å along the aperiodic directions in the nanoribbon configurations were imposed to avoid interactions due to periodic images. We also performed the calculations with $3 \times 3 \times 1$ supercell of two dimensional LiMgAs (with

25 Å vacuum along the [001] crystal direction) with k-mesh for brillouin zone sampling as $6 \times 6 \times 1$. The optimized kinetic energy cutoff used in all the calculations was set to 60 Ry and the systems were relaxed with force convergence criteria of $< 10^{-6}$ a.u. Throughout the calculations, Grimme correlations were incorporated to address the van der Waals effects.[14] From the perspective of stability and room temperature viability, we performed ab-initio molecular dynamics simulations for 3 picoseconds (3000 femtoseconds) with thermostat set at 300 K. We calculated the slab band structures using WannierTools wherein the exact tight-binding Hamiltonian generated by Wannier90 was implemented.[8,9]

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