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1 Tunable valleytronics with symmetry-retaining high polarization degree in $\text{SnS}_x\text{Se}_{1-x}$ model
2 system

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22 **Abstract**

23 SnS has recently been shown to possess unique valleytronic capability with large polarization
24 degree, where non-degenerate valleys can be accessed using linearly polarized light, bestowed
25 upon by the unique anisotropy and wavefunction symmetry. It is thus of utmost importance to
26 demonstrate the extension of such effects for the IV-VI system in general, thereby elucidating the
27 generality and tunability of such valleytronics. We show the highly tunable valleytronics via gradual
28 compositional control of the Tin(II) Sulfo-Selenide ($\text{SnS}_x\text{Se}_{1-x}$) alloy system with excellent
29 retainment of symmetry-determined selection rules. We show the presence of both Γ_Y and Γ_X
30 valleys in all alloy compositions via selectivity in absorption and emission of linearly polarized light
31 by optical reflection (R)/transmission (T) and photoluminescence (PL) measurements, and tuned
32 the bandgaps of the valleys within a range of 1.28eV to 1.05eV and 1.48eV to 1.24eV respectively.
33 This simultaneous tuning of non-degenerate valleys agrees well with theoretical calculations. We
34 then fitted the bandgap values in compositional space, obtaining the bowing parameters as a
35 useful database. We further demonstrated the feasibility of using IV-VI valleytronics systems in
36 general by elucidating the retainment of strong polarization degrees of as high as 91% across all
37 compositions. The generalization of such purely symmetry-dependent valleytronics also opens up
38 opportunities for discovery of more multi-functional materials.

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40 The field of valleytronics presents great opportunities in providing an additional valley degree of
41 freedom in the control of electronic systems [1] [2]; much promise in utilizing this unique material's
42 or system's properties hinges upon the ability to access and hence control each valley selectively.
43 Earlier work on valleytronics demonstrated the selective population of degenerate conduction band
44 minima, using strong biases, in systems such as Si [3] [4], AlAs [5] [6], and diamond [7]. More
45 recently, theoretical work on graphene valleytronics [8] has led to the exploration of valleytronics in
46 two-dimensional (2D) systems.

47 One of the most effective and well-exploited way to explore the valleys of a material is to leverage
48 the light-matter interaction; in essence, certain polarization of light is used to selectively populate
49 each valley, which can then form different population states where on-off information can be
50 subsequently utilized. Previous reports of valleytronic behavior on 2D transition metal
51 dichalcogenides (TMDCs) have demonstrated selective optical valley excitation with varying
52 degrees of success [9] [10] [11] [12]. These reports have generated renewed interest in the
53 valleytronics field, one of which being the actual manipulation of valley population under ambient
54 and bias-free conditions with a high polarization degree, which was only recently reported [13],
55 where we demonstrated a form of valleytronics in Tin(II) Sulfide (SnS).

56 Such valleytronics has a two-fold manifestation. First, the two sets of valleys in SnS reside along
57 the ΓY and ΓX directions in reciprocal space respectively, and, by the selection rules, are
58 exclusively selected by y and x polarized light respectively (Supplementary Text S1, adapted from
59 [13]). Second, the anisotropic nature of the material bestows upon the valleys the non-degeneracy
60 in bandgap values. As such, both incident light polarization and energy can potentially be used to
61 independently access each valley, granting the material system more flexibility in terms of
62 excitation conditions.

63 An important extension to such flexibility is then to expand such valleytronics to the rest of the IV-
64 VI family, which will not only allow a wider wavelength range for excitation/emission but, more
65 importantly, prove that such valleytronics is a general behavior within the material system.

66 Herein, we report a model system in $\text{SnS}_x\text{Se}_{1-x}$, $0 \leq x \leq 1$, demonstrating both the retainment of valley
67 selectivity and the gradual tuning of bandgaps at both valleys across all alloy compositions. The

68 retainment of PL intensity and polarization degrees across the whole compositional range proves
69 that members of the $\text{SnS}_x\text{Se}_{1-x}$ family are suitable for such valleytronics in general.

70 We also demonstrate the continuous tuning of bandgaps for both valleys across the whole
71 compositional range; the range of bandgaps (1.28eV to 1.05eV and 1.48eV to 1.24eV for the two
72 valleys respectively) is much larger than that of 2D semiconductor alloys [14] [15] [16] [17],
73 especially when considering the combined effects of both valleys under different polarizations.
74 Furthermore, typical advantages of semiconductor alloys over pure semiconductors, including the
75 flexibility in choice of synthesis methods [16] and the additional parameter of lattice matching [18],
76 can be utilized on top of bandgap tunability.

77 $\text{SnS}_x\text{Se}_{1-x}$ was chosen because of the similarity in band structures for SnS and SnSe, with the
78 presence of two valleys along the ΓY and ΓX axes and the band separation at the Γ point having a
79 larger value than the two valleys [19]. Since both materials' band structures arise from
80 combinations of the same constituent wavefunctions [20], which satisfies the same symmetry
81 considerations [21], valley selection rules in SnS have to also apply to SnSe, along with all
82 $\text{SnS}_x\text{Se}_{1-x}$ compositions.

83 Both SnS and SnSe have the Pmcn crystal structure with an orthorhombic unit cell comprising of
84 puckered layers [22], and the lattice parameters of $\text{SnS}_x\text{Se}_{1-x}$ has been experimentally shown to
85 vary gradually across the alloy compositions [23]. The 2x2 supercells of SnS, SnSe, and a
86 representative $\text{SnS}_{0.5}\text{Se}_{0.5}$ alloy are presented in Fig. 1a. Using the fitted lattice parameters from
87 [23] and adopting the simplest case of homogeneous alloying [16], our density functional theory
88 (DFT) calculations yield band structures with two local band gaps along the ΓY and ΓX axes,
89 denoted by $E_{g,\Gamma Y}$ and $E_{g,\Gamma X}$ respectively, across the whole compositional range (Fig. 2 and Fig. S1).

90 We synthesized $\text{SnS}_x\text{Se}_{1-x}$ microplates, $0 \leq x \leq 1$ in nominal increments of $\Delta x = 0.125$ via Physical
91 Vapor Deposition (PVD) and observed their flat morphology via SEM. Fig. 1b shows the optical
92 microscope image, SEM image and SEM-EDX mappings of Sn, S, and Se of a representative
93 nominally $\text{SnS}_{0.875}\text{Se}_{0.125}$ alloy (The peak intensities for S and Se in the SEM-EDX spectra as well
94 as images and mapping results of other alloys are presented in Fig. S2 and Fig. S3 respectively).

95 The exact S:Se ratios obtained from SEM-EDX follow a gradual trend and were used for
96 quantitative analysis.

97 From the plot of actual composition versus nominal (design) composition (Fig. 1c), we can see that
98 the Se content of all compositions is consistently higher than the design amount. This can be
99 attributed to the lower equilibrium vapor pressure of SnSe as compared with SnS [24] [25], which is
100 commonly reflected in the higher required PVD growth temperature of SnSe as compared with SnS
101 [26] [27]. Our SEM-EDX results reflects the compositional tunability using our growth method.
102 Further tuning, especially for large S content, is beyond the scope of this work, but should also be
103 achievable using S compensation [28] or multi-sourced CVD methods [29] [30].

104 Raman spectra of SnS [26] and SnSe [27] under -z excitation (perpendicular to the layers) contain
105 characteristic peaks that correspond to three A_g modes and one B_{3g} mode. We observed that these
106 modes follow gradual shifts for the alloys (Fig. 1d and Fig. 1e). Note that the composition values
107 are nominal, not actual. The larger change of actual composition from SnS to $\text{SnS}_{0.875}\text{Se}_{0.125}$ leads
108 to the rapid change of B_{3g} modes. We used the relative peak intensities [27] to determine the
109 armchair (y) and zigzag (x) directions of each alloy composition, and presented the respective
110 spectra under 532nm excitation when the incident polarization is aligned along the x and y axes for
111 parallel (Fig. 1d) and cross (Fig. 1e) polarization configurations. Note that the peak for the $A_{1g}^{(1)}$
112 mode of SnSe cannot be observed due to the wavenumber being lower than the Raman filter
113 edge. Also, for clarity, Raman spectra aligned along the y axis under parallel excitation is repeated
114 using 785nm excitation to clearly distinguish and reveal the trends for the $A_{1g}^{(3)}$ modes of the alloys
115 (Fig. S4).

116 We observed a clear two-mode behavior for all Raman peaks, where the alloys can exhibit two
117 peaks (SnS-like and SnSe-like) that belong to the same Raman mode. This alloy behavior can be
118 explained using the modified random element isodisplacement (MREI) model [17] [31], where
119 strong S-Se interactions gives two eigenvalues, one SnS-like and one SnSe-like, as the solutions
120 to the quadratic equation of the model. This observation agrees with the common understanding
121 that SnS and SnSe possess comparable interlayer and intralayer forces, as evidenced by the
122 relatively small difference in interlayer and intralayer atomic distances [19]. Since all of the Raman

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123 modes of concern here are related to relative interlayer motions [27], S-Se interactions should be
124 significant, which explains the two-mode behavior.

125 Tunability of bandgap values at each valley is demonstrated using reflection (R) and transmission
126 (T) as well as PL measurements, following the same protocol in our previous work on SnS [13].
127 White light R and T measurements were conducted with the incident excitation polarized along the
128 y or x direction, hence demonstrating valley selectivity for absorption. Normalized Tauc plots are
129 presented in Fig. 3a, clearly showing the decrease in optical bandgap values as Se content
130 increases. Using Tauc plot analyses, we show that the bandgaps can be gradually tuned within a
131 range of 1.28eV to 1.05eV and 1.48eV to 1.24eV for the ΓX and ΓY valleys respectively.

132 PL measurements were conducted under parallel or cross polarization, with a second polarizer
133 serving as an analyser placed before the detector, to further demonstrate selectivity for emission.
134 Fig. 3b shows the PL spectra under parallel polarized 532nm excitation that is aligned to the y and
135 x axes for all alloy compositions, which elucidates the presence of a single PL peak in each
136 spectrum that corresponds to the ΓY and ΓX valleys respectively. (Due to the limit of the Silicon
137 visible range detector, the PL peaks from the ΓX valleys cannot be detected for alloys with Se
138 content $\text{SnS}_{0.25}\text{Se}_{0.75}$ (nominal) and above. We subsequently conducted PL measurements using
139 785nm excitation and an InGaAs infrared detector (Fig. S5) to obtain the PL peak positions of
140 those alloys.) It can be observed that the PL peak positions red-shifts with more Se for a range of
141 1.29eV to 1.20eV and 1.64eV to 1.45eV respectively. This agrees with the decrease in optical
142 bandgap values obtained from R and T spectra.

143 The trends in bandgaps values for the valleys can be explained using the difference in
144 contributions of elemental atomic orbitals to the sub-bands that make up the conduction band
145 minimum (CBM) and valence band maximum (VBM). Orbital projected band structures in Fig. 2
146 show that the CBMs are predominantly made up of 5p orbitals from Sn, while the VBMs are mainly
147 composed of p orbitals of chalcogenide atoms. The contribution by Se is from the 4p orbitals,
148 which is higher in energy as compared with the 3p orbitals of S. Therefore, with a greater Se
149 content, the hybridised orbitals that make up the VBM of alloys will have more Se character, hence

150 leading to a smaller bandgap. This is clearly shown in Fig. 2b, where the VBM of $\text{SnS}_{0.5}\text{Se}_{0.5}$ is
151 contributed mostly by Se orbitals.

152 The trends in bandgap values agree with the calculated band structure (Fig. 2 and Fig. S1),
153 ascertaining the validity of the optical measurement results. More importantly, our DFT calculations
154 show that the CBM and VBM along ΓX (ΓY) is contributed almost entirely by p_x (p_y) orbitals. This
155 confirms that the symmetry of the wavefunctions that make up the CB and VB along ΓX and ΓY for
156 all alloy compositions remain the same as that of SnS ; the irreducible representations of orbitals
157 that make up the CBM and VBM remain the same across all compositions.

158 Hence, using our previously discussed selection rules (Supplementary Text S1, adapted from [13]),
159 CB to VB transitions at the valleys can only occur for light polarized along the x and y directions
160 respectively; valley selectivity is retained across all $\text{SnS}_x\text{Se}_{1-x}$ alloy compositions, in agreement
161 with the experimental results shown above.

162 We further quantify such retainment of valley selectivity with the figures of merit, the intervalley
163 ($P_{\text{intervalley},\Gamma Y/\Gamma X}$) and intravalley ($P_{\text{intervalley},\Gamma Y/\Gamma X}$) polarization degrees, as defined in our previous work
164 [13] as:

$$165 \quad P_{\text{intervalley},\Gamma X} = \frac{I_{\Gamma X\parallel}(\theta=90^\circ) - I_{\Gamma Y\parallel}(\theta=90^\circ)}{I_{\Gamma X\parallel}(\theta=90^\circ) + I_{\Gamma Y\parallel}(\theta=90^\circ)} \text{ and } P_{\text{intervalley},\Gamma Y} = \frac{I_{\Gamma Y\parallel}(\theta=0^\circ) - I_{\Gamma X\parallel}(\theta=0^\circ)}{I_{\Gamma Y\parallel}(\theta=0^\circ) + I_{\Gamma X\parallel}(\theta=0^\circ)}$$

$$166 \quad P_{\text{intervalley},\Gamma X} = \frac{I_{\Gamma X\parallel}(\theta=90^\circ) - I_{\Gamma X\perp}(\theta=90^\circ)}{I_{\Gamma X\parallel}(\theta=90^\circ) + I_{\Gamma X\perp}(\theta=90^\circ)} \text{ and } P_{\text{intervalley},\Gamma Y} = \frac{I_{\Gamma Y\parallel}(\theta=0^\circ) - I_{\Gamma Y\perp}(\theta=0^\circ)}{I_{\Gamma Y\parallel}(\theta=0^\circ) + I_{\Gamma Y\perp}(\theta=0^\circ)}$$

167 It is clear from Fig. 3b, that $P_{\text{intervalley},\Gamma Y/\Gamma X}$ (Fig. 4a) remains significant across all compositions.
168 Results from PL measurements conducted under cross polarization were then used to calculate
169 $P_{\text{intervalley},\Gamma Y/\Gamma X}$, which are also presented in Fig. 4a. The strong polarization degrees of, for example,
170 up to 91% and an average of 75% for $P_{\text{intervalley},\Gamma X}$, proves that the alloys still rival results obtained
171 using monolayer TMDCs from experiments conducted at cryogenic temperatures [9] [12] [32].

172 Our PL, white light R and T and theoretical results clearly show tunable, wavelength-dependent,
173 non-degenerate valleytronics in $\text{SnS}_x\text{Se}_{1-x}$. For practical purposes, it is thus important to apply
174 Vegard's law [33] to generate a database for the bandgap values and the bowing parameter, b

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175 [34]. Fig. 4b shows the optical bandgap values obtained via white light R and T as well as PL for
176 both valleys, plotted in compositional space. Using

$$177 \quad E_{g,\text{SnS}_x\text{Se}_{1-x}} = xE_{g,\text{SnS}} + (1-x)E_{g,\text{SnSe}} + bx(1-x)$$

178 we obtained $b_{\Gamma\text{Y}(\text{white light})} = -0.11185\text{eV}$, $b_{\Gamma\text{X}(\text{white light})} = -0.0331\text{eV}$, $b_{\Gamma\text{Y}(\text{PL})} = -0.06843\text{eV}$, and $b_{\Gamma\text{X}(\text{PL})} = -$
179 0.0521eV , respectively. The fitted functions are also overlaid in Fig. 4b. We note that the bowing
180 parameters obtained for the valleys using both absorption and PL methods are close to each other
181 and very small [35], which gives a rather linear relationship that simplifies the tunability. Calculated
182 bandgaps (obtained from Fig.S1) values are also presented in the inset of Fig. 4b.

183 While beyond the scope of this work, we also observe from Fig. 3b and Fig. S5 that the full-width at
184 half-maximum (FWHM) of the PL peaks (Fig. S6a and Fig. S6b) increases with greater Se content,
185 along with a decrease in PL intensity (Fig. S6c). We further conducted power-dependent PL
186 measurements, fitted, and analysed the PL peak intensity using a power law, $I_{\text{PL}} \propto I_{\text{excitation}}^k$, as
187 presented in Supplementary Text S2 and Fig. S6d, to understand the effect on the nature of the
188 bandgap transitions with alloying.

189 In conclusion, we have conducted reflection/ transmission and PL measurements that show the
190 tunability of the two bandgaps from 1.28eV to 1.05eV and 1.48eV to 1.24eV in bulk $\text{SnS}_x\text{Se}_{1-x}$ for
191 the valleys residing along ΓX and ΓY respectively. These valleys retained the selection rules as
192 previously reported in bulk SnS, under ambient conditions and without additional biases. The
193 valleys are strongly and solely excited by y- and x-polarized light and also mostly emit y- and x-
194 polarized light respectively, effectively serving as a demonstration of tunability of non-degenerate
195 valleys. Our model system also has, nominally, the advantage of superior polarization degrees of
196 up to 91%. We also elucidate the bandgap bowing parameters for the alloy system and revealed
197 some insights of the transitions, including quantitative analyses that revealed recombination
198 mechanisms to be dominantly independent of dopants levels. Such discovery may allow future
199 work on practical applications with $\text{SnS}_x\text{Se}_{1-x}$ as a model system to be conducted.

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246 **Supplementary material**

247 See supplementary material for power law analyses of CB to VB transitions, which further explains
248 bandgap transitions, as well as supporting SEM, Raman, and DFT evidences.

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253 **Author contributions**

254 J.Y. coordinated the work. S.L and J.Y designed the experiments. S.L. conducted the optical
255 measurements and analysed the data. T.W.H. and E.M.C. conducted the optical measurements.
256 T.H. and K.P. carried out the DFT calculations and electric dipole analysis. Z.F., C.H.S., C.Y., R.L,
257 and Y.L. synthesized and characterized the materials. S.L and J.Y wrote the manuscript with the
258 help from all authors.

259 **Competing financial interests**

260 The authors declare no competing financial interests.

261 **Materials & Correspondence**

262 Correspondence and material requests should be addressed to Jie Yao.

263 **Figures**

264

265 **Fig 1: Structure and characterization of $\text{SnS}_x\text{Se}_{1-x}$.** (a) 2x2 supercells of molecular structures of
 266 SnS, SnSe, and a representative $\text{SnS}_{0.5}\text{Se}_{0.5}$ alloy with the simplest case of homogeneous alloying.
 267 The puckered arrangement of atoms and the high anisotropy along the y (armchair) and x (zigzag)
 268 directions is maintained across the whole compositional range while the lattice parameters increase
 269 with Se content. (b) Optical microscopy image, scanning electron microscopy (SEM) images and
 270 Energy-dispersive X-ray spectroscopy (EDX) maps of a representative, nominally $\text{SnS}_{0.875}\text{Se}_{0.125}$
 271 sample, demonstrating a flat surface and homogeneous distribution of Sn, S, and Se. Scale bar is
 272 5 μm . (c) Trend in actual composition versus nominal (design) composition, showing a general
 273 excess of Se content. (d) Reflection mode, $c(\bar{x}x)\bar{c}$, Raman spectra obtained under parallel
 274 polarization. The first and second letters in the parentheses denotes the alignment of the incident
 275 light and emitted signal. Only spectra aligned along x and y directions are presented, showing clear
 276 trends in intensities for the A_g modes, thus ascertaining the identity and orientation of the measured

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277 samples. (e) Raman spectra obtained under cross polarization, showing clear trends in intensities
 278 for the B_{3g} modes.

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Fig 2: Calculated band structures for selected $\text{SnS}_x\text{Se}_{1-x}$. Orbital projected band structures along $Y-\Gamma-X$ and DOS of representative alloy compositions of (a) SnSe, (b) $\text{SnS}_{0.5}\text{Se}_{0.5}$, and (c) SnS are presented. Band structures are projected on elements of Sn, S and Se, and p_x , p_y and p_z orbitals. Our elemental and orbital specific band structures denote that for all alloy compositions, p orbitals from Sn and the chalcogenides make up predominantly the conduction and valence bands.

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286 respectively. Red, green, and blue shades correspond to contributions of each subband by p_x , p_y ,
287 and p_z orbitals respectively; this demonstrates that ΓX and ΓY valleys are predominantly made up of
288 p_x and p_y orbitals respectively for all alloy compositions.

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Fig 3: Optical measurements of $\text{SnS}_x\text{Se}_{1-x}$. (a) Normalized Tauc plots of both directions for different alloy compositions obtained from white light R and T measurements, showing a distinct decrease in bandgap value with increasing Se content. (b) PL peaks under parallel polarization. Only spectra aligned along x and y directions are presented, showing that for all alloy compositions, the high (low) energy peak has the strongest intensity when the excitation light is polarized along the y (x) direction, showing the retainment of valley selectivity across all alloy compositions. There is also a clear trend of decrease in bandgap value with increasing Se content.

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299 **Fig 4: Valley selectivity in $\text{SnS}_x\text{Se}_{1-x}$.** (a) Trends in polarization degrees with compositional
300 variation, showing the retainment of high valley selectivity across all alloy compositions in $\text{SnS}_x\text{Se}_{1-x}$.
301 Intervalley (intravalley) polarization degrees are presented as squares (circles), with dashed
302 (dotted) lines demarcating the respective average values. Solid and open data points denotes the
303 polarization degrees that depends predominantly on PL signals of the Γ Y and Γ X valleys respectively.
304 (b) Optical bandgaps obtained by white light R and T as well as PL measurements, plotted with fitting
305 functions using Vegard's law. Calculated bandgap values are presented in the inset, showing a
306 smooth variation and similar trends for both Γ Y and Γ X valleys respectively.

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