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

2 **system**

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1

22   **<u>Abstract</u>**

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 (SnS_xSe_{1-x}) alloy system with excellent

29   retainment of symmetry-determined selection rules. We show the presence of both ΓY and ΓX

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.

39

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 SnS_xSe_{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

3

68   retainment of PL intensity and polarization degrees across the whole compositional range proves

69   that members of the SnS_xSe_{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   SnS_xSe_{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   SnS_xSe_{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 SnS_xSe_{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 $SnS_{0.5}Se_{0.5}$ 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 SnS_xSe_{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 $SnS_{0.875}Se_{0.125}$ 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 $SnS_{0.875}Se_{0.125}$ 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

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 $SnS_{0.25}Se_{0.75}$ (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

6

150   leading to a smaller bandgap. This is clearly shown in Fig. 2b, where the VBM of $SnS_{0.5}Se_{0.5}$ 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 SnS_xSe_{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 ($P_{\text{intravalley},\Gamma Y/\Gamma X}$) polarization degrees, as defined in our previous work

164   [13] as:

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

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

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    $P_{\text{intravalley},\Gamma Y/\Gamma X}$, which are also presented in Fig. 4a. The strong polarization degrees of, for example,

170   up to 91% and an average of 75% for $P_{\text{intravalley},\Gamma X}$, 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 SnS_xSe_{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

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
$$E_{g,SnS_xSe_{1-x}} = xE_{g,SnS} + (1-x)E_{g,SnSe} + bx(1-x)$$

178 we obtained $b_{,\Gamma Y(\text{white light})}$=-0.11185eV, $b_{,\Gamma X(\text{white light})}$=-0.0331eV, $b_{,\Gamma Y(\text{PL})}$=-0.06843eV, and $b_{,\Gamma X(\text{PL})}$=-

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, $I_{PL} \propto I_{excitation}{}^{k}$, 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 SnS$_x$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 SnS$_x$Se$_{1-x}$ as a model system to be conducted.

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10

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**

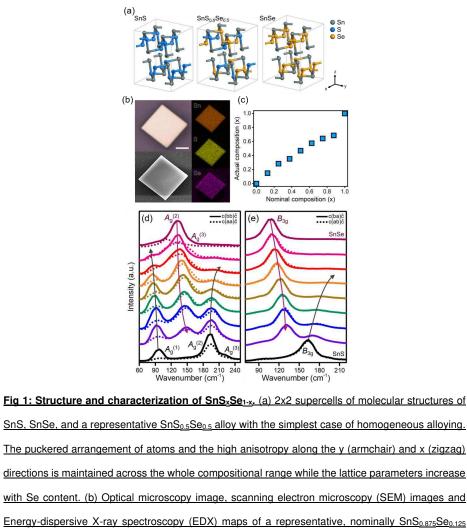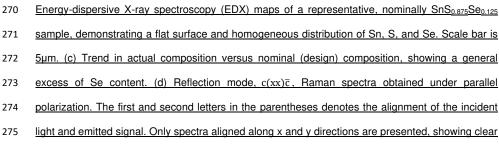262 Correspondence and material requests should be addressed to Jie Yao.

11

263   **Figures**

264

265   **Fig 1: Structure and characterization of SnS$_x$Se$_{1-x}$.** (a) 2x2 supercells of molecular structures of

266   SnS, SnSe, and a representative SnS$_{0.5}$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 SnS$_{0.875}$Se$_{0.125}$

271   sample, demonstrating a flat surface and homogeneous distribution of Sn, S, and Se. Scale bar is

272   5µm. (c) Trend in actual composition versus nominal (design) composition, showing a general

273   excess of Se content. (d) Reflection mode, $c(xx)\bar{c}$, 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

277   samples. (e) Raman spectra obtained under cross polarization, showing clear trends in intensities

278   for the B_{3g} modes.

279

280

Fig 2: Calculated band structures for selected SnS$_x$Se$_{1-x}$. Orbital projected band structures along

Y-Γ-X and DOS of representative alloy compositions of (a) SnSe, (b) SnS$_{0.5}$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,

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.

289

290

Fig 3: Optical measurements of SnS$_x$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.
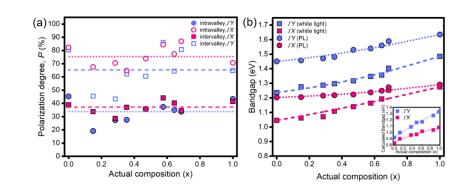
Fig 4: Valley selectivity in SnS$_x$Se$_{1-x}$. (a) Trends in polarization degrees with compositional variation, showing the retainment of high valley selectivity across all alloy compositions in SnS$_x$Se$_{1-x}$. Intervalley (intravalley) polarization degrees are presented as squares (circles), with dashed (dotted) lines demarcating the respective average values. Solid and open data points denotes the polarization degrees that depends predominantly on PL signals of the ΓY and ΓX valleys respectively. (b) Optical bandgaps obtained by white light R and T as well as PL measurements, plotted with fitting functions using Vegard's law. Cal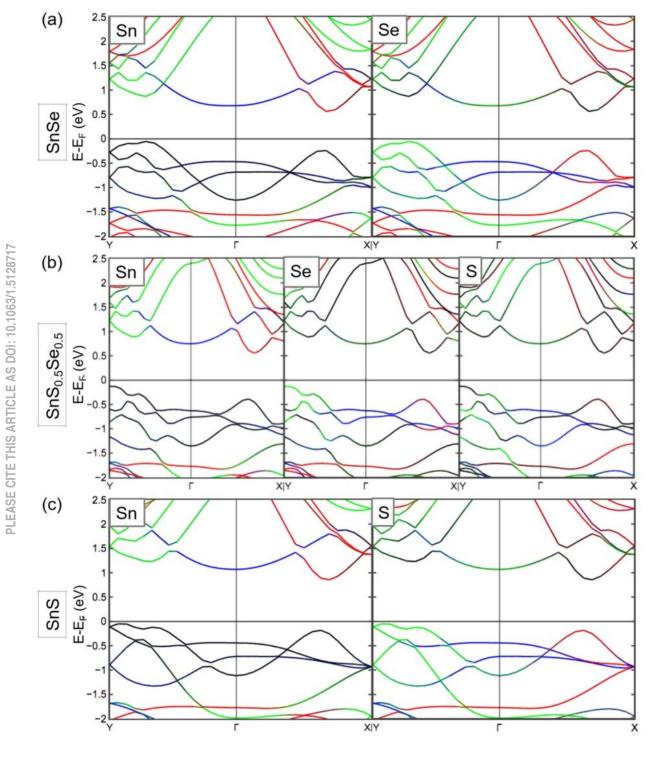culated bandgap values are presented in the inset, showing a smooth variation and similar trends for both ΓY and ΓX valleys respectively.