Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Anomalies in the bulk and surface electronic properties in SnS: Effect of native defects

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S1. SnS supercell

Here, SnS bulk supercell with lattice parameter *a*= 11.41 Å, *b*= 4.026 Å and *c*= 4.427 Å as shown in Figure S1 was considered for calculation of the electronic structure. Moreover, SnS surface supercell (*i.e.,* 1×1×1) was constructed with SnS (111) slab (*i.e.,* bulk SnS slab with (111) surface orientation) and the vacuum on top of it as shown in Figure S2 for the surface study of SnS. Furthermore, a bigger SnS (111) surface supercell (*i.e.,* 1×2×1) was constructed for the multi defect to avoid the defect-defect interaction (see Figure S2 (c)).

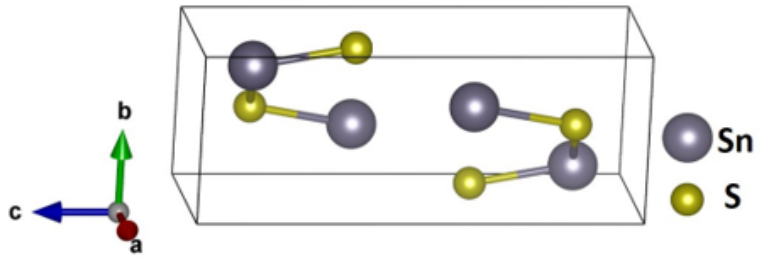

Figure S1. Schematic of the bulk SnS supercell showing the atomic positions.

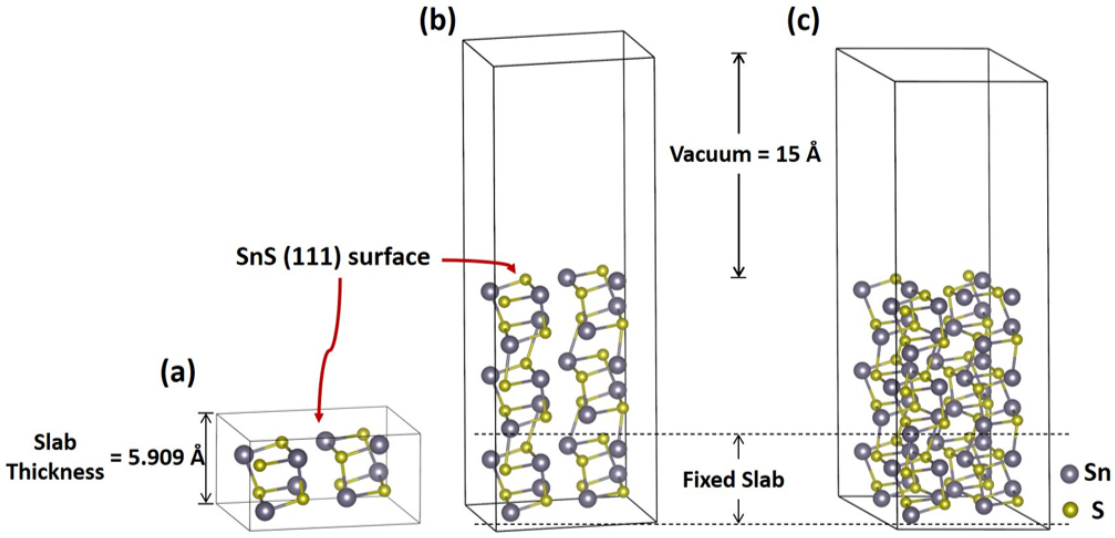

Figure S2. Schematic of **(a)** the bulk SnS (111) slab **(b)** SnS (111) surface supercell **(c)** A (1×2×1) SnS (111) surface supercell.

S2. Surface defect site

Here, to obtain the suitable site for V_{Sn}, V_S, Sn_i, S_i, Sn_S and S_{Sn} defects in SnS (111) surface supercell, formation energy was calculated for different surface configurations. In this regard, the different surface supercell was created by considering the defects on each possible site of the top surface atom. Moreover, the possible defect site for each defect was shown in Figure S3. In addition, the interstitial positions for the Sn_i and S_i were selected based upon the centre point between the surrounding atom (*i.e.*, the coordination of P1 was selected as a centre point of the Sn2, Sn3, S1 and S4 atomic site). Next, the formation energy for each possible site was calculated as shown in Table S1. Moreover, the defect site with the least formation energy was selected because this is a more stable surface structure of SnS (111) surface supercell with a defect. Therefore, the defect site of Sn3, S4, P3, P2, S1, Sn3 were selected for V_{Sn}, V_S, Sn_i, S_i, Sn_S and S_{Sn} defects in SnS (111) surface supercell, respectively.

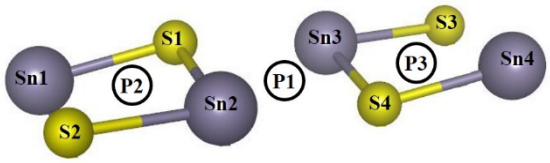

Figure S3. Defect sites on the top surface of SnS (111) supercell

Table S1. Defect formation energy

Defect	Position	Formation Energy	
		Sn-rich	S-rich
V_{Sn}	Sn1	1.414118	0.507184578
	Sn2	1.426418	0.519484578
	Sn3	1.412368	0.505434578
	Sn4	1.703178	0.796244578
V_S	S1	0.619553	1.526487421
	S2	0.652363	1.559297421
	S3	0.641173	1.548107421
	S4	0.545613	1.452547421
Sn_i	P1	1.220812	2.127745422
	P2	13.689512	14.59644542
	P3	0.884732	1.791665422
S_i	P1	1.557237	0.650302579
	P2	1.427327	0.520392579
	P3	1.450647	0.543712579
Sn_S	S1	0.952005	2.765872843
	S2	0.961045	2.774912843
	S3	1.102425	2.916292843
	S4	1.299475	3.113342843
S_{Sn}	Sn1	2.237175	0.423307157
	Sn2	2.424795	0.610927157
	Sn3	2.055125	0.241257157
	Sn4	2.541525	0.727657157

S3. Surface relaxation

The summary of the ionic displacements of the atoms in the top slabs for the SnS (111) surface supercell and the SnS surface supercell with various defects were reported in Table S2-S11. Note that, the positive displacements along the *c*-direction denoted the relaxations towards the vacuum side. Moreover, the magnitude of these displacements (*Δa, Δb* and *Δc*) was measured based on the differences between the atomic positions of the initial unrelaxed surface model and that of the relaxed surface model.

Table S2. Displacement of the top surface atoms on SnS (111) surface supercell.

Atom	***Δa***	***Δb***	***Δc***
Sn1	0.186074	0.401023	0.536532
Sn2	-0.125552	0.105623	0.149653
Sn3	0.054756	0.104376	-0.043838
Sn4	-0.295991	-0.14545	-0.329943
Sn5	0.491389	0.358348	0.745885
Sn6	1.03629	0.413483	0.149544
Sn7	0.698894	-0.137314	-0.19324
Sn8	0.248013	-0.163412	0.196939
S1	0.0240848	0.252566	-0.093423
S2	-0.166825	0.182622	0.218039
S3	0.173419	0.0596606	-0.024471
S4	-0.046764	-0.017541	0.224098
S5	0.943742	-0.024071	0.328458
S6	0.167473	-0.165422	0.111134
S7	0.944353	-0.010694	0.308461
S8	0.269846	-0.180528	0.22128

Table S3. Displacement of the top surface atoms on SnS (111) surface supercell with V_{Sn}.

Atom	*Δa*	*Δb*	*Δc*
Sn1	0.0368511	0.302927	0.674156
Sn2	-0.405514	0.0442624	6.08E-02
Sn4	-0.0681798	0.0382604	-0.442527
Sn5	0.486951	0.114873	0.861625
Sn6	1.01147	0.0796944	0.272774
Sn7	0.865924	-0.220414	-0.135453
Sn8	0.401895	0.00660636	0.381825
S1	-0.249264	0.141394	-0.155441
S2	-0.323439	0.0725091	0.259799
S3	-0.390887	0.0955486	-0.0496516
S4	0.122781	0.431529	0.264002
S5	1.00806	0.0145086	0.47716
S6	0.142397	-0.112439	0.0156808
S7	1.10757	0.178667	0.333508
S8	0.316365	0.0537424	0.141042

Table S4. Displacement of the top surface atoms on SnS (111) surface supercell with V_S.

Atom	*Δa*	*Δb*	*Δc*
Sn1	0.0194238	0.379012	0.529805
Sn2	-0.266853	0.0959902	0.0686376
Sn3	-0.0590339	-0.264233	-0.255198
Sn4	0.325474	-0.131724	-0.297726
Sn5	0.413934	0.34359	0.736753
Sn6	0.886035	0.389389	0.0989082
Sn7	0.571935	-0.130539	-0.0484753
Sn8	0.183282	-0.0844914	0.452899
S1	-0.152927	0.22913	-0.13136
S2	-0.351242	0.177294	0.22916
S3	0.129799	-0.0142155	0.0632616
S5	0.786963	-0.056834	0.322459
S6	0.0964384	-0.197975	0.0182502
S7	0.753441	-0.0685762	0.211393
S8	0.251026	-0.230298	0.457926

Table S5. Displacement of the top surface atoms on SnS (111) surface supercell with Sn_i.

Atom	*Δa*	*Δb*	*Δc*
Sn_i	0.250544	-0.384544	1.39408
Sn1	0.172037	0.354971	0.713301
Sn2	-0.119671	0.0102817	0.222476
Sn3	1.4043	0.338035	-0.210805
Sn4	-0.853124	-0.0243497	0.0186075
Sn5	0.513904	0.279421	0.819269
Sn6	0.918205	0.329454	-0.285457
Sn7	0.606386	-0.146016	0.0196792
Sn8	0.0642315	-0.16258	0.355658
S1	0.186298	0.332637	0.767603
S2	-0.130356	0.136587	0.325583
S3	-0.0672118	0.0402081	0.165413
S4	0.253006	0.045178	0.240931
S5	0.741084	-0.174592	0.562457
S6	0.187191	-0.457852	0.186068
S7	0.774083	-0.0689931	0.476235
S8	0.181462	-0.214696	0.615165

Table S6. Displacement of the top surface atoms on SnS (111) surface supercell with S_i.

Atom	*Δa*	*Δb*	*Δc*
S_i	0.844178	1.07646	0.947628
Sn1	-0.0966828	0.160098	0.507056
Sn2	-0.653325	0.114159	0.334612
Sn3	-0.302327	0.192188	0.104814
Sn4	-0.604897	-0.0888939	-0.369042
Sn5	0.204459	-0.199112	0.412874
Sn6	0.833151	0.00380155	0.114105
Sn7	0.59883	-0.0387785	-0.234171
Sn8	0.151237	-0.0811003	0.285549
S1	-0.372148	-0.382201	-0.226152
S2	0.441598	-0.245522	-0.364272
S3	-0.220793	0.190261	-0.0466484
S4	-0.310784	0.0644986	0.278483
S5	0.751687	-0.28121	0.27265
S6	0.108251	-0.602247	0.354525
S7	0.886445	0.069348	0.439274
S8	0.181458	-0.0822316	0.150177

Table S7. Displacement of the top surface atoms on SnS (111) surface supercell with Sn_S.

Atom	*Δa*	*Δb*	*Δc*
Sn_S	-0.458758	-0.121395	0.618401
Sn1	0.135369	0.0577321	0.57503
Sn2	-0.0788663	-0.00490903	-0.109197
Sn3	-0.0379768	0.377371	0.0635762
Sn4	-0.439693	0.0709681	-0.326768
Sn5	0.560552	0.136186	0.586769
Sn6	1.06855	-0.0463574	0.387656
Sn7	0.722493	-0.000945317	-0.178782
Sn8	0.229272	0.0390694	0.295458
S2	-0.166073	-0.1235	0.0904835
S3	-0.00223445	0.281518	-0.00746236
S4	-0.168345	0.257149	0.338295
S5	0.986883	-0.251647	0.428684
S6	0.214917	-0.324696	-0.0955159
S7	1.06148	0.205695	0.434858
S8	0.22339	0.0339096	0.224152

Table S8. Displacement of the top surface atoms on SnS (111) surface supercell with S_{Sn}.

Atom	*Δa*	*Δb*	*Δc*
S_{Sn}	-0.629782	-0.386453	0.922144
Sn1	0.412602	0.380373	0.493959
Sn2	0.144867	0.088969	0.196778
Sn4	-0.579033	-0.285359	-0.382607
Sn5	0.642146	0.363561	0.657274
Sn6	1.17785	0.321638	0.25863
Sn7	0.869223	-0.00601978	-0.450263
Sn8	0.429611	0.195519	0.324246
S1	0.243723	0.209402	-0.0585952
S2	0.118031	0.175758	0.181901
S3	0.126893	0.160579	-0.0368568
S4	-0.122591	0.726387	0.442874
S5	1.10119	-0.0517087	0.32985
S6	0.335493	-0.175257	0.196021
S7	1.09318	0.211933	0.248508
S8	0.379844	-0.0447495	0.212098

Table S9. Displacement of the top surface atoms on SnS (111) surface supercell with V_{Sn} + 2 V_S.

Atom	*Δa*	*Δb*	*Δc*
Sn1	0.02897934	0.292111902	0.281373859
Sn2	-0.071254179	0.053831394	-0.05963109
Sn3	-0.105168218	-0.265348406	0.238743157
Sn4	-0.175142228	-0.011521945	0.058948557
Sn5	-0.188270547	-0.105476842	-0.118685174
Sn6	-0.234279623	0.084347113	-0.362413239
Sn7	0.074521923	0.080631282	-0.173462052
Sn8	0.801339049	0.133820331	0.066511601
Sn9	0.024952237	0.172306562	0.674460408
Sn10	0.817472537	0.236633637	-0.002340942
Sn11	0.278889641	0.113429971	0.608290558
Sn12	0.496178173	-0.13264771	-0.043555267
Sn13	0.10358942	-0.289926885	0.367339092
Sn14	0.392638617	-0.128162959	-0.018996676
Sn15	0.201480656	0.018163671	0.229158656
S1	-0.132963064	0.159796181	-0.239738396
S2	-0.06979036	0.119085048	-0.192190555
S3	-0.290298935	0.107634059	0.075340959
S4	0.156321946	-0.000604731	-0.060772516
S5	0.051390785	0.575662878	0.293039842
S6	-0.02139751	0.05797735	0.029270487
S7	0.674836346	-0.139710796	0.143770428
S8	-0.215406113	-0.186199211	0.037636111
S9	0.671831765	-0.142065051	0.159394133
S10	-0.045318065	-0.256557792	0.031963829
S11	0.696602032	-0.105157229	-0.036628286
S12	0.137818578	-0.247274939	0.540692714
S13	0.565705432	-0.209153146	0.063400994
S14	0.302647851	-0.249327803	0.554493428

Table S10. Displacement of the top surface atoms on SnS (111) surface supercell with V_{Sn} + 2 Sn_i.

Atom	*Δa*	*Δb*	*Δc*
Sn_i1	-0.136343218	0.365761977	-0.034390249
Sn_i2	-0.309332682	-0.411884798	1.206697062
Sn1	0.17784362	0.296587325	-0.022986345
Sn2	-1.192040649	-0.874760035	0.029168833
Sn3	-10.63965205	2.285614575	-0.420553406
Sn4	-0.548434966	0.000023496	-0.046378338
Sn5	-0.694399262	-0.420307953	0.122706791
Sn6	0.662887476	-0.355177083	-0.426374781
Sn7	-0.933628644	0.846457441	0.678751166
Sn8	0.467998436	0.074608846	-0.15505884
Sn9	0.11574603	-0.01168153	0.559218878
Sn10	0.637289394	0.085961775	-0.151777843
Sn11	0.120839254	-0.229679196	0.113895827
Sn12	0.271910301	-0.281355233	-0.185253893
Sn13	0.113277962	-0.371720744	-0.009782968
Sn14	0.061274533	-0.744985172	-0.248043028
Sn15	0.388973443	0.15472361	0.035618525
S1	-0.026807545	-0.320043239	0.266588555
S2	0.103557899	-0.366995358	-0.14969152
S3	-0.560387688	-0.056229884	-0.079399366
S4	-0.125821062	0.249061036	0.728447291
S5	0.210779255	0.082428951	-0.215389889
S6	-0.127638245	-0.291660043	-0.056663767
S7	-1.021633179	-0.254643074	-0.288776191
S8	0.315002353	0.690479033	0.051689507
S9	0.314254197	0.09604938	0.035222559
S10	-0.104116415	-0.136455067	0.076503685
S11	0.492856065	0.057796634	0.212525188
S12	-0.022570414	-0.127279568	-0.144566232
S13	0.775756973	0.074955862	-0.316566405
S14	0.392837439	-0.439198563	0.471526497
S15	0.690532324	-0.048748656	0.195852029
S16	0.249684782	0.103490736	0.25131144

Table S11. Displacement of the top surface atoms on SnS (111) surface supercell with V_{Sn} + Sn_S.

Atom	*Δa*	*Δb*	*Δc*
Sn_S	-0.965281168	0.000145585	0.601217389
Sn1	0.040473763	0.173750598	0.351085133
Sn2	-0.191314189	-0.081789325	-0.149403017
Sn3	-0.346819394	0.13567432	0.385883651
Sn4	-0.299958204	0.290050475	-0.072712482
Sn5	-0.149071634	-0.443382194	-0.138634491
Sn6	-0.041686131	-0.118650662	-0.258970328
Sn7	-0.064802567	0.066334554	-0.154616405
Sn8	0.764367298	0.0829722	-0.002054375
Sn9	0.329940824	-0.104426627	0.44380018
Sn10	0.833346541	0.048359696	0.074094006
Sn11	0.276875312	0.09046234	0.553358778
Sn12	0.635055204	-0.07704286	-0.083509084
Sn13	0.13168639	-0.345665887	0.284365385
Sn14	0.645665689	-0.024264798	0.0646828
Sn15	0.202553071	-0.044696547	0.269584921
S1	-0.209814192	0.019953195	-0.161242296
S2	-0.274792156	-0.059781728	-0.083954425
S3	-0.382693219	-0.019098308	0.001029124
S4	0.201335546	0.227332013	-0.057784863
S5	0.152766757	0.312790258	0.215752939
S6	0.322920384	0.14018838	0.134426992
S7	0.157858413	0.095497554	0.168770487
S8	0.704765046	-0.160446889	0.213352941
S9	0.018963936	-0.223885637	-0.110452183
S10	0.72172537	-0.120130669	0.308437005
S11	-0.080788507	-0.187593246	-0.034639744
S12	0.81718175	0.071529873	-0.07898791
S13	0.191047741	-0.144603988	0.45905406
S14	0.779810212	-0.008288481	0.224941475
S15	0.191657368	-0.078555538	0.459925378