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Supplementary Information for "Structural design principles for low hole effective mass s-orbital-based p-type oxides"

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I. COMPUTATIONAL DETAILS

To clarify how the local environment of Sn−O impacts on hole effective mass (m_h), we perform analyses for a series of known Sn-based oxides available in Inorganic Crystal Structure Database (ICSD)[1] by utilizing database from Material Project (MP)[2]. It is worth of noting that characterizing electronic band structure can help to explore various properties of materials such as transport, optical absorption, chemistry of bonding, etc... Here, we also compute and investigate band structures within density functional theory (DFT) using VASP package[3, 4], with general-gradient approximation (GGA) exchange correlation functional, Perdew, Burke, and Ernzerhof (PBE). The quality of transport for each compound is assessed through average effective mass, particularly for hole, computed by BoltzTrap. code[5] (more details for this recipe have shown in previous publications[6, 7]). The qualitative analyses of chemical bondings are implemented through projected band structure and projected Crystal Crystal Orbital Hamilton Population (COHP) using Lobster package[8, 9]. The creation of input-files and processing of outputs are performed by utilizing Pymatgen code[10].

The m_h, in fact, is direction-dependent quantity and represented by a second-rank tensor in reciprocal space.

$$\mathbf{m_h^T} = \begin{pmatrix} m_{11} & m_{12} & m_{13} \\ m_{12} & m_{22} & m_{23} \\ m_{13} & m_{23} & m_{33} \end{pmatrix} \tag{S1}$$

Nonetheless, for linking transport property to geometric configuration of Sn−O networks we need to compute m_h in a given direction $\vec{d}$ (m_h^d). We used representation quadric and calculate m_h^d as the formula below:

$$m_h^d = m_1 a_1^2 + m_2 a_2^2 + m_3 a_3^2 \tag{S2}$$

where, m_1, m_2, m_3 are three principal values of m_h^T in (S1); a_1, a_2, a_3 are three cosine values of angles between $\vec{d}$ and three corresponding eigenvectors of m_h^T in (S1). More details on (S2) can be found in the textbook[11].

II. RESULTS

Table SI shows information about materials unfitted with our model including formula, space group (SG), inorganic crystal structure data base[1] identification number (icsd-id), average m_h ($m_h^a = \sum_{i=1}^{3} m_h^T(ii)/3$), average Sn−O−Sn angle ($\measuredangle_a$) and average $O - Sn$ distance (d_a). These compounds are eliminated because they have isolated clusters of Sn−O instead of continuous network or their VBMs have very few contribution of Sn-s and O-p. More details are in remarks column of Table SI.

In the same way, Table SII shows information for selected materials. For each compound, we investigate all directions of geometric structure in which the Sn−O networks spread out. We compute the average bonding Sn−O−Sn and m_h^d along these directions. The projected band structure (PBS) computed with standard Density Functional Theory (DFT) on two sites Sn (red color) and O (blue color) and the projected Crystal Orbital Overlap Populations (COOP) (calculated by Lobster package[8, 9]) for SnO, $K_2Sn_2O_3$-$R\bar{3}m$ and $K_2Sn_2O_3$-$I2_13$ are shown in Fig. S1, Fig. S2 and Fig. S3, respectively.

In general, PBSs indicate that valence bands of these Sn-based materials (in an energy range of 9 (eV)) are composed of Sn-O chemical interactions. However, COOPs show that the complexity of interactions differs from SnO to $K_2Sn_2O_3$-$I2_13$. For SnO and $K_2Sn_2O_3$-$R\bar{3}m$, these materials have Sn−O networks growing as two-dimensional stacking layers. Therefore, beside intra-layer Sn-O interactions (Sn-5s/O-2p and Sn-5p/O-2p) there are many other inter-layer interactions between Sn atoms (Sn-5s/Sn-5p and Sn-5s/Sn-5s). On the other hand, with three-dimensional Sn-O networks, $K_2Sn_2O_3$-$I2_13$ exhibits significantly weak Sn-Sn interactions.

[1] "Inorganic Crystal Structure Database," https://www.fiz-karlsruhe.de/de/leistungen/kristallographie/icsd.html (2013), [FIZ Karlsruhe: Karlsruhe, Germany, 2013].
[2] "The Materials Project," https://www.materialsproject.org/ (2013), [accessed September 1, 2013].
[3] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[4] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[5] G. K. H. Madsen and D. J. Singh, Comput. Phys. Commun. **175**, 67 (2006).
[6] G. Hautier, A. Miglio, G. Ceder, G.-M. Rignanese, and X. Gonze, Nat. Commun. **4**, 2292 (2013).
[7] G. Hautier, A. Miglio, D. Waroquiers, G.-M. Rignanese, and X. Gonze, Chem. Mater. **26**, 5447 (2014).

TABLE SI. Formula, space group (SG), inorganic crystal structure data base[1] identification number (icsd-id), materials project[2] identification number (mp-id), band gap E_g (eV), three principal hole effective masses m_1, m_2 and m_3 (m_o-free electron mass), components of valence band maximum (VBM) Sn-s, O-p and Sn-s (%) and remarks for all materials not matching with our model (NW-Networks and Clusters-CL).

Formula	SG	icsd-id	mp-id	E_g	m_1	m_2	m_3	Sn-s	O-p	Sn-p	Remarks
$NaSn_4(PO_4)_3$	$R3c$	409786	6226	3.74	4.66	4.71	4.71	26.2	59.9	12.8	No Sn−O NW
$SnMo_5O_8$	$P2_1/c$	68511	19524	1.0	2.20	2.31	12.70	0.0	2.4	6.0	75.8% Mo-d in VBM
$Sn_{15}Os_3O_{14}$	Cm	59312	28456	1.51	2.06	2.72	22.43	10.2	18.0	34.4	Little Sn-s in VBM
$Na_2Sn(CO_2)_4$	$C2/c$	388	554823	2.77	1.62	9.94	24.49	20.8	62.6	7.6	No Sn−O NW
$Na_4Sn_4H_{10}O_{11}$	$P2_1/c$	35420	772039	2.74	7.96	11.97	13.08	28.4	51.8	17.0	No Sn−O NW
$Sn_3H_4N_2O_{10}$	$P2_1/c$	80019	705520	2.67	4.45	11.75	20.98	31.1	56.5	11.0	No Sn−O NW
$K_2SnP_2O_7$	$P2_1/c$	419264	554825	4.18	17.86	20.30	20.49	27.1	62.1	7.0	No Sn−O NW
$SnP_2H_2O_8$	$C2/c$	200364	-	2.58	8.21	16.04	31.88	0.0	96.8	0.0	No Sn-s in VBM
$Sn_7S_2O_{20}$	$Pbca$	32673	-	1.53	32.23	38.40	112.93	0.3	96.0	0.6	No Sn-s in VBM
K_4SnO_3	$Pbca$	79101	14988	2.11	0.97	2.82	9.58	0.0	0.0	0.0	100% K-s in VBM
$KSn_4(PO_4)_3$	$R3c$	59857	6755	3.76	4.12	4.12	7.40	28.0	58.1	12.1	No Sn−O NW
Na_4SnO_3	Cc	49624	28261	1.89	1.38	2.41	7.0	12.0	64.6	19.5	No Sn−O NW
$Sn(SO_2)_2$	$P2_1/c$	32684	31004	2.71	1.41	2.51	11.33	9.0	39.9	31.0	No Sn−O NW
$VSnPO_5$	$P\bar{1}$	415455	566025	1.17	0.84	4.64	18.48	28.4	40.5	5.8	34.2% V-d in VBM
$SnPO_3$	Cc	25034	-	0.53	1.02	4.24	13.36	0.0	46.7	6.5	28% P-p in VBM
SnB_4O_7	$Pmn2_1$	249206	13252	3.57	1.63	2.08	2.18	31.4	64.3	2.9	No Sn−O NW
$SnSO_4$	$P\bar{1}$	2748	645774	4.07	2.28	4.69	8.22	24.6	68.9	5.4	No Sn−O NW
$SnSO_4$	$Pnma$	2748	542967	4.14	1.30	3.80	5.23	27.4	63.6	8.5	No Sn−O NW
$Sn_2P_2O_7$	$P2_1/c$	170847	556031	3.63	0.89	1.29	4.77	33.0	54.0	11.0	Sn−O CL
$Sn_2P_2O_7$	$P\bar{1}$	170845	554022	3.52	1.90	5.07	8.49	38.3	49.5	8.5	Sn−O CL
Sn_2PCO_6	$P2_1/c$	50969	559291	2.31	1.91	2.96	3.79	39.2	46.8	12.3	Sn−O CL
Sn_2SO_5	$P\bar{4}2_1c$	35101	28025	3.51	4.28	7.60	7.60	32.1	52.7	13.6	Sn−O CL
$Na_2Sn_2H_4O_5$	$P2_12_12_1$	35421	707767	2.33	0.69	1.75	4.26	34.1	48.8	14.2	Sn−O CL
$SnHC_2O_3$	$C2/m$	96547	697873	2.12	0.72	0.77	4.96	18.4	58.4	3.6	Sn−O CL
$SiSn_6O_8$	$P6_3mc$	156236	556100	1.90	3.38	3.93	3.93	39.4	38.9	20	Sn−O CL
Sn_3O_4	$P2/c$	174299	-	0.94	0.38	1.86	11.32	41.6	49.4	17.1	Both Sn^{2+} & Sn^{4+}
$SnWO_4$	$P2_13$	2840	19608	3.84	4.58	4.48	4.58	37.8	40.1	10.0	No Sn−O NW
$Sn_5(PO_5)_2$	$P\bar{1}$	418458	560715	2.70	0.810	4.826	9.320	37.8	45.0	15.9	Sn−O CL
$Sn_3H_2O_4$	$P-42_1c$	203206	625541	2.30	1.081	2.054	10.301	43.0	36.6	19.2	Sn−O CL

[8] R. Dronskowski and P. E. Blöchl, J. Phys. Chem. **97**, 8617 (1993).
[9] V. L. Deringer, A. L. Tchougreeff, and R. Dronskowski, J. Phys. Chem. A **115**, 5461 (2011).
[10] S. P. Ong, W. D. Richards, A. Jain, G. Hautier, M. Kocher, and *et al.*, Comput. Mater. Sci. **68**, 314 (2013).
[11] J. F. Nye, "Physical properties of crystals: Their representation by tensors and matrices," (Clarendon Press, 1985) Chap. I, p. 24.

TABLE SII. Formula, space group (SG), inorganic crystal structure data base [1] identification number (icsd-id), three principal hole effective masses m_1, m_2 and m_3 (m_o-free electron mass), average Sn−O−Sn angle $\measuredangle_a$ (°) and average Sn−O distance d_a (Å) for all materials matching with our model.

Formula	SG	icsd-id	m_1	m_2	m_3	$\measuredangle_a$	d_a
$K_2Sn_2O_3$	$R\bar{3}m$	2216	0.231	0.231	0.429	180	2.07
$K_2Sn_2O_3$	$I2_13$	40463	0.274	0.274	0.274	167.6	2.09
$Rb_2Sn_2O_3$	$R\bar{3}m$	24816	0.265	0.265	0.369	180	2.1
Rb_2SnO_2	$P2_12_12_1$	24805	1.797	2.227	2.489	131.1	2.12
SnO	$Pmn2_1$	20624	0.557	0.624	7.852	115.6	2.16
SnO	$P4/nmm$	60619	0.588	2.822	2.822	118.0	2.26
$Nb_2Sn_2O_7$	$Fd\bar{3}m$	163817	4.744	4.744	4.744	98.3	2.65
Nb_2SnO_6	$C2/c$	163815	0.425	2.126	5.634	104.0	2.3
$Sn_3(PO_4)_2$	$P2_1/c$	966	0.995	1.997	3.155	110.1	2.31
$Sn_4P_2O_9$	$P2_1/c$	418459	2.433	2.631	5.772	107.6	2.12
$SnWO_4$	$Pnna$	2147	1.034	2.231	2.417	101.4	2.3
$Ta_2Sn_2O_7$	$Fd\bar{3}m$	163818	6.921	6.921	6.921	98.0	2.66
Ta_2SnO_6	Cc	54078	1.222	3.498	5.094	103.1	2.28
$TiSn_2O_4$	$P4_2/mbc$	163230	0.962	0.962	1.427	126.2	2.12
$BaSn_2H_2O_4$	$P2_1$	37115	1.471	2.274	5.256	116.5	2.09
$SnPHO_4$	$P2_1/c$	658	0.959	1.088	4.524	109.2	2.39
$Cs_2Sn_2O_3$	$Pnma$	24392	2.675	3.575	9.537	123	2.1
$Sn(CO_2)_2$	$C2/c$	150101	0.766	10.214	12.231	113.6	2.63

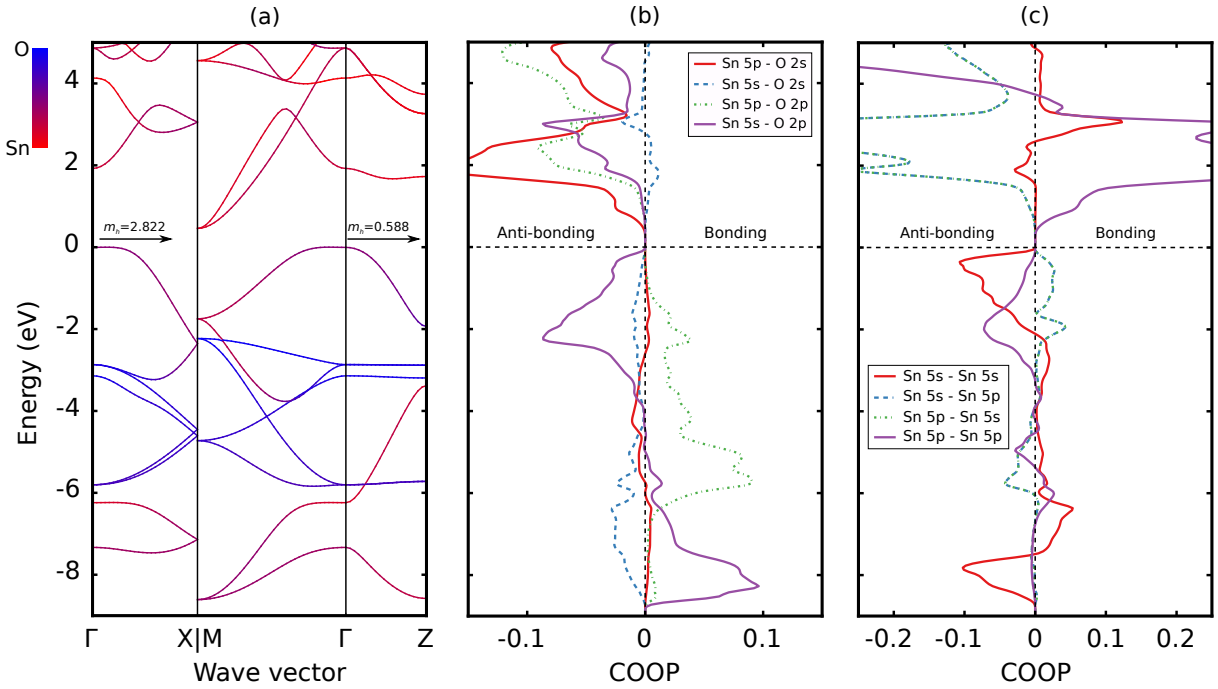

FIG. S1. The projected band structure of SnO on Sn (red colors) and O (blue colors) atoms (a) and the projected Crystal Orbital Overlap Populations (COOP) for Sn-O (b) and Sn-Sn (c) interactions.

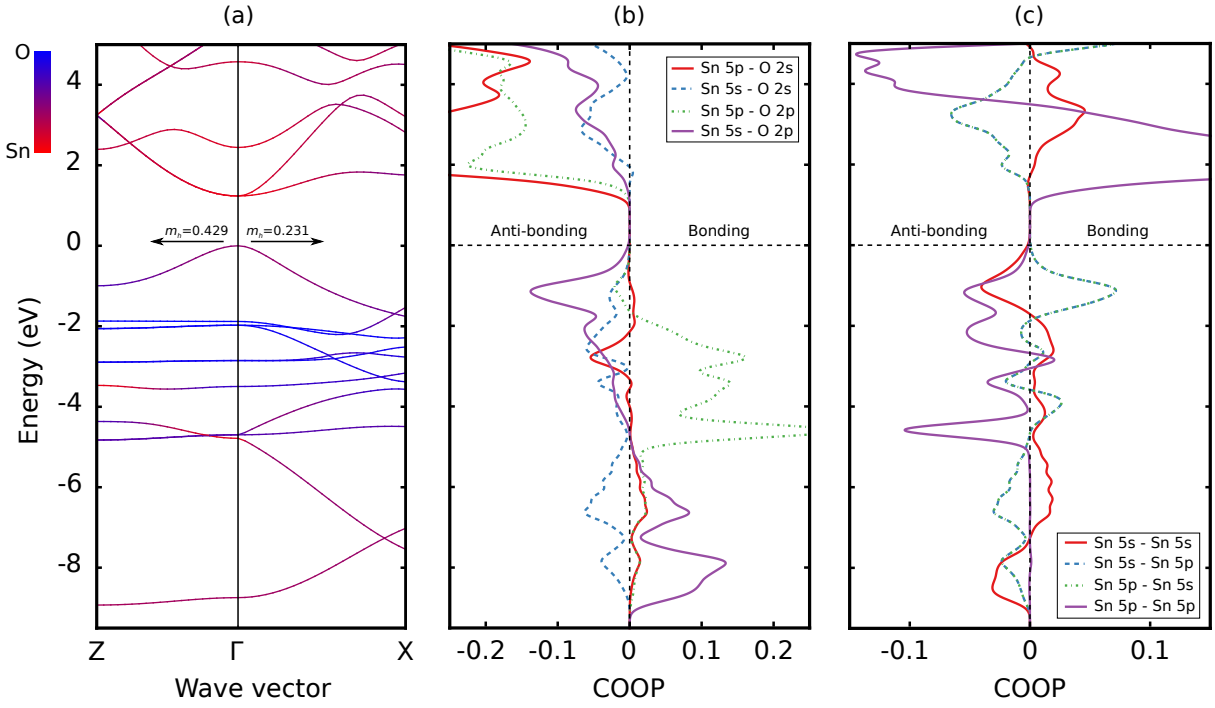

FIG. S2. The projected band structure of $K_2Sn_2O_3$-$R\bar{3}m$ on Sn (red colors) and O (blue colors) atoms (a) and the projected Crystal Orbital Overlap Populations (COOP) for Sn-O (b) and Sn-Sn (c) interactions.

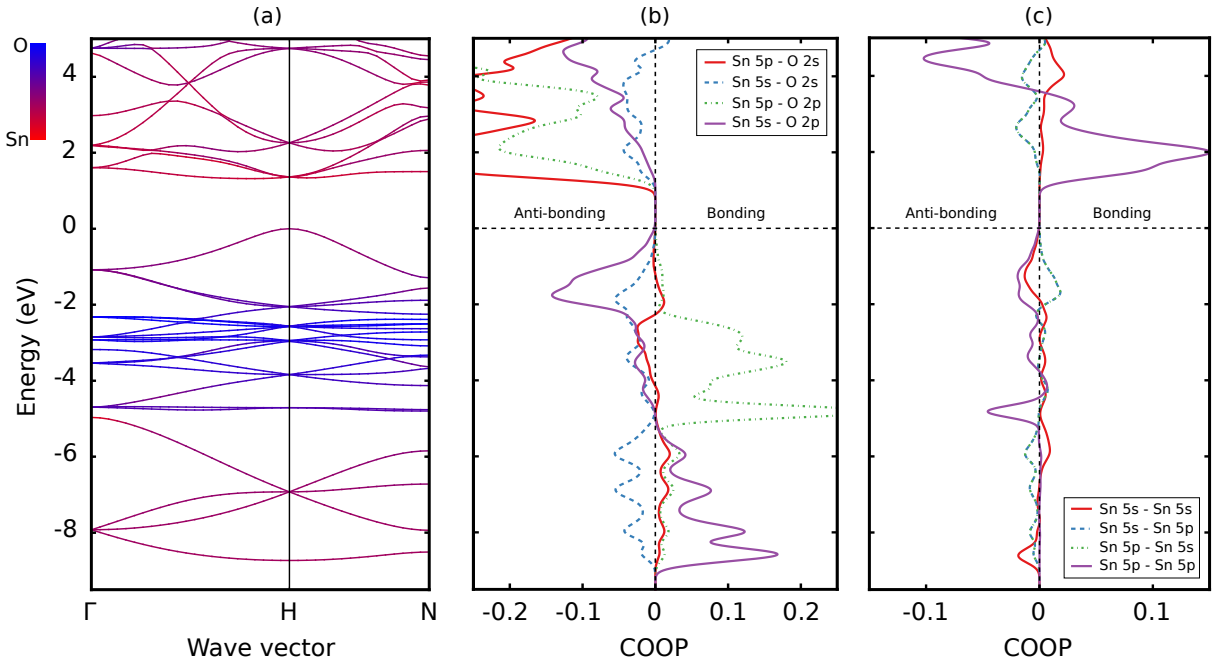

FIG. S3. The projected band structure of $K_2Sn_2O_3$-$I2_13$ on Sn (red colors) and O (blue colors) atoms (a) and the projected Crystal Orbital Overlap Populations (COOP) for Sn-O (b) and Sn-Sn (c) interactions.