Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Role of native point defects and donor impurities on the electrical properties of $ZnSb_2O_4$: A hybrid density-functional study

(Supplementary Information)

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A. Crystal structure and atomic coordinates of $ZnSb_2O_4$

POSCAR files for the 28-atom primitive cell and 56-atom supercell of $ZnSb_2O_4$ used in the calculations are attached as a zip file: POSCARs.zip

B. Bader charge of $ZnSb_2O_4$, Sb_2O_3, and ZnO

Table S1 Bader charge analyses on $ZnSb_2O_4$, Sb_2O_3 and ZnO

	$ZnSb_2O_4$	Sb_2O_3	Sb_2O_5	ZnO
Sb	$+1.86e$	$+1.92e$	$+3.06e$	-
Zn	$+1.47e$	-	-	$+1.06e$
O1	$-1.27e$	$-1.31e$	$-1.19e$	$-1.06e$
O2	$-1.32e$	$-1.26e$	$-1.22e$	-
O3	-	-	$-1.24e$	-

C. Formation energy and transition levels of selected defects using 56- and 224-atom supercells.

Table S2 Formation energy of predominant defects at the VBM calculated using 56- and 224-atom supercells.

Defect	q	Supercell 56 atoms		Supercell 224 atoms	
		O-rich	O-poor	O-rich	O-poor
V_{O}	2+	2.44	1.68	2.54	1.78
	1+	0.09	−0.67	0.19	−0.57
	0	−2.57	−3.33	−2.67	−3.43
$\mathrm{Zn_{Sb}}$	1−	3.41	3.78	3.56	3.94
	0	2.17	2.55	2.31	2.69
$\mathrm{Ga_{Zn}}$	0	2.19	1.82	2.35	1.97
	1+	−2.15	−2.53	−2.00	−2.38

Table S3 Calculated transition level of the predominant defect using 56- and 224-atom supercells. All values are referenced to the VBM.

Defect	Supercell 56 atoms		Supercell 224 atoms	
	q, q'	$\varepsilon(q, q')$	q, q'	$\varepsilon(q, q')$
V_{O}	2+/0	2.50	2+/0	2.61
$\mathrm{Zn_{Sb}}$	0/−	1.24	0/−	1.25
$\mathrm{Ga_{Zn}}$	+/0	4.34	+/0	4.35

D. Local atomic structure of intrinsic defects

Vacancies

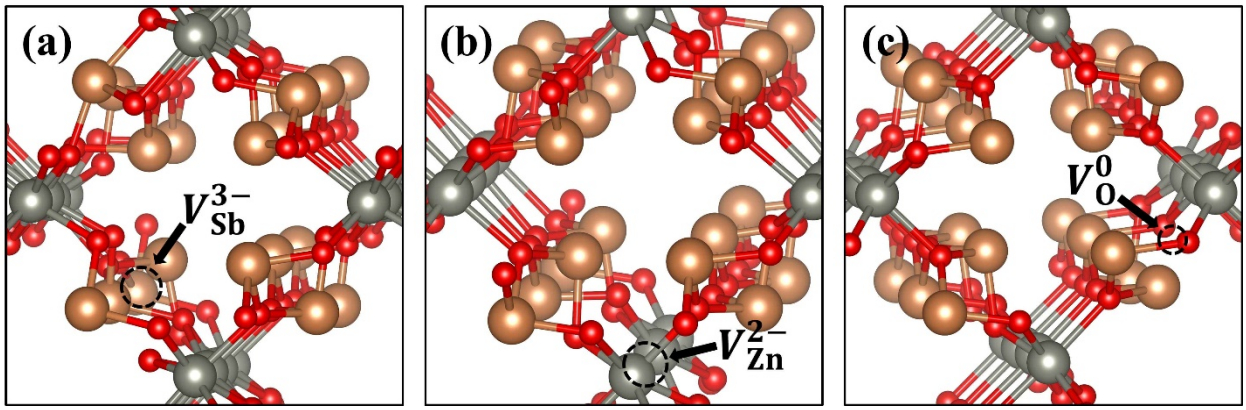

Figure S1 Local atomic structure of vacancy defects in their stable charge state at the pinned Fermi level; (a) V_{Sb}^{3-}, (b) V_{Zn}^{2-} and (c) V_{O}^{0}. The small red spheres are the O atoms; the large grey spheres and large copper spheres are Zn and Sb, respectively.

Interstitials

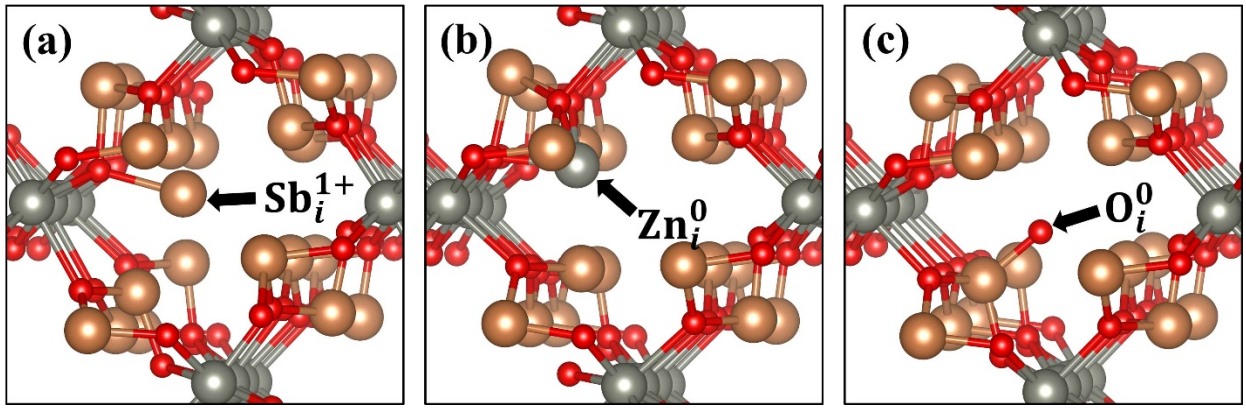

Figure S2 Local atomic geometry of interstitial defects in their stable charge state at the pinned Fermi level; (a) Sb_i^{1+}, (b) Zn_i^{0} and (c) O_i^{0}. The small red spheres are the O atoms; the large grey spheres and large copper spheres are Zn and Sb, respectively.

Antisites

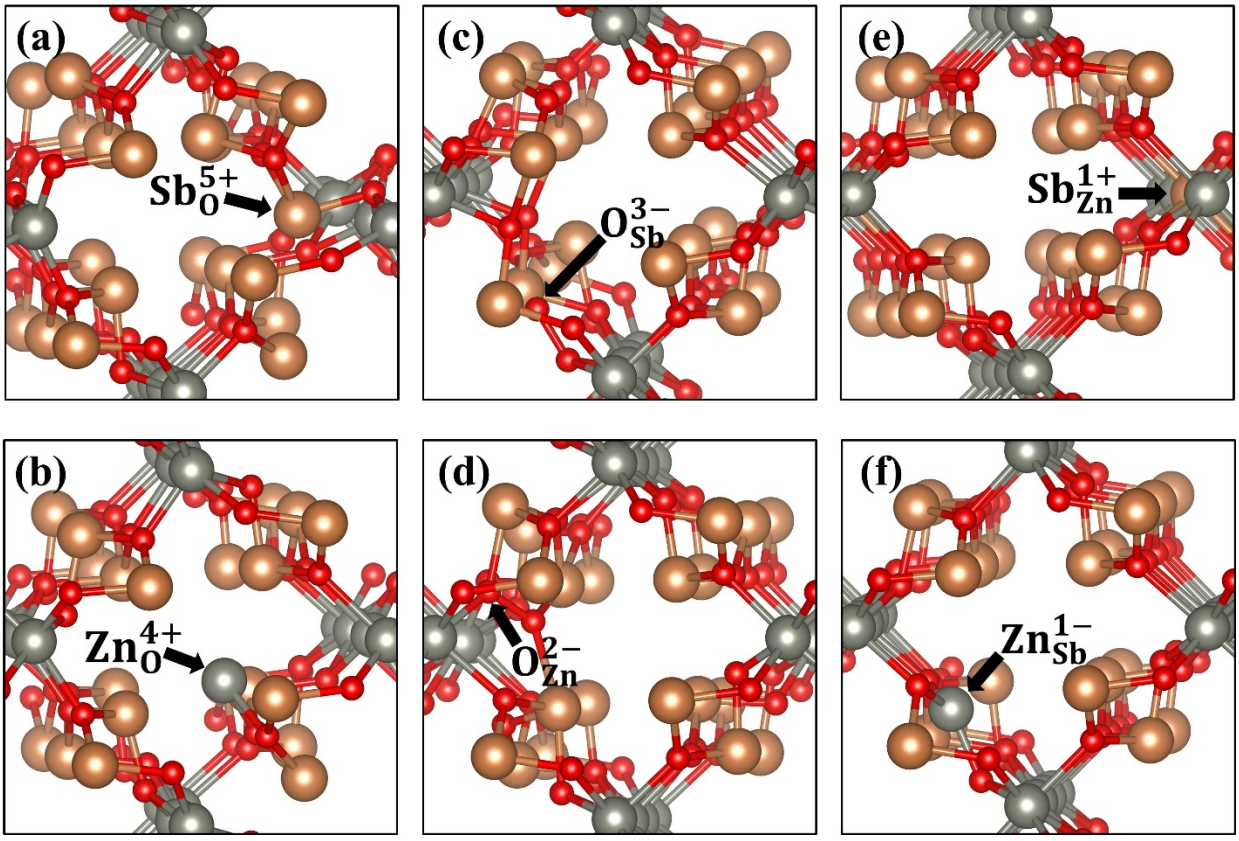

Figure S3 Local atomic structure of antisite defects in their stable charge state at the pinned Fermi level; (a) Sb_O^{5+}, (b) Zn_O^{4+}, (c) O_{Sb}^{3-}, (d) O_{Zn}^{2-}, (e) Sb_{Zn}^{1+} and (f) Zn_{Sb}^{1-}. The small red spheres are the O atoms; the large grey spheres and large copper spheres are Zn and Sb, respectively.

E. Local atomic structure of Al, In, Ga, and F impurities

In impurities

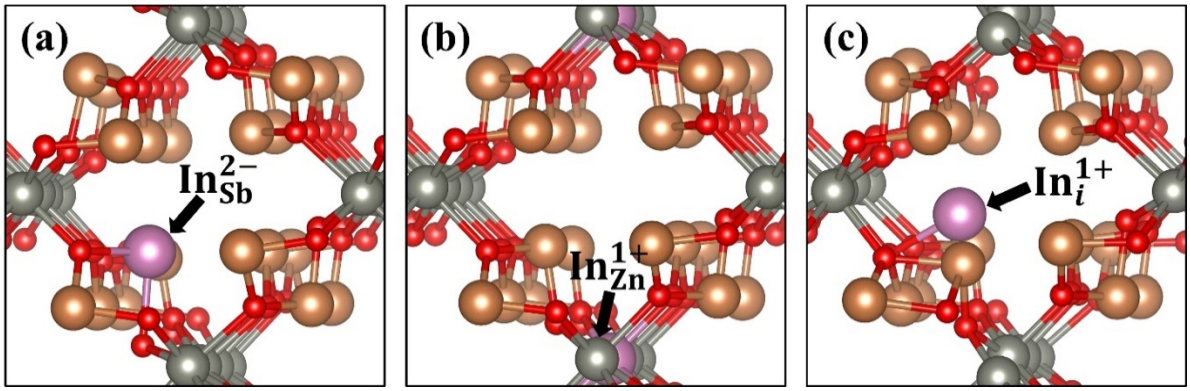

Figure S4 Local atomic geometry of indium (In) impurities in their stable charge state at the pinned Fermi level; (a) In_{Sb}^{2-}, (b) In_{Zn}^{1+} and (c) In_{i}^{1+}. The small red spheres are the O atoms; the large grey spheres, large copper spheres and large purple spheres are Zn, Sb, and In, respectively.

Al impurities

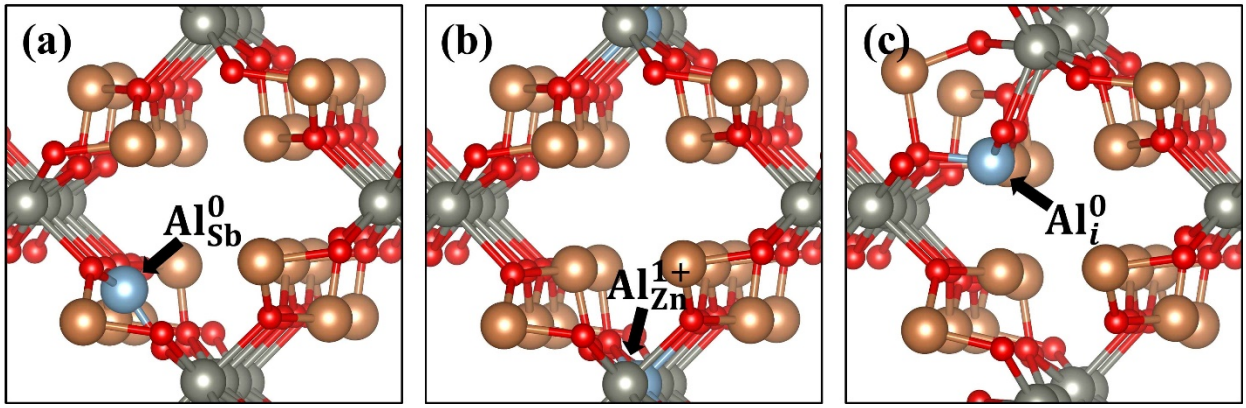

Figure S5 Local atomic geometry of aluminum (Al) impurities in their stable charge state at the pinned Fermi level; (a) Al_{Sb}^{0}, (b) Al_{Zn}^{1+}, and (c) Al_{i}^{0}. The small red spheres are the O atoms; the large grey spheres, large copper spheres and large blue spheres are Zn, Sb and Al, respectively.

Ga impurities

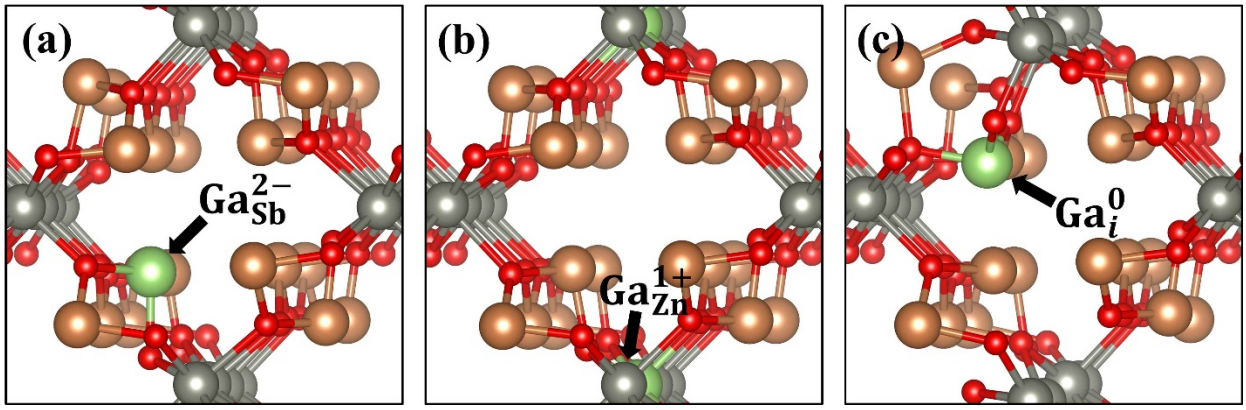

Figure S6 Local atomic geometry of gallium (Ga) impurities in $ZnSb_2O_4$ as shown (a) Ga_{Sb}^{2-}, (b) Ga_{Zn}^{1+} and (c) Ga_{i}^{0}. The small red spheres are the O atoms; the large grey spheres, large copper spheres and large green spheres are Zn, Sb and Ga, respectively.

F impurities

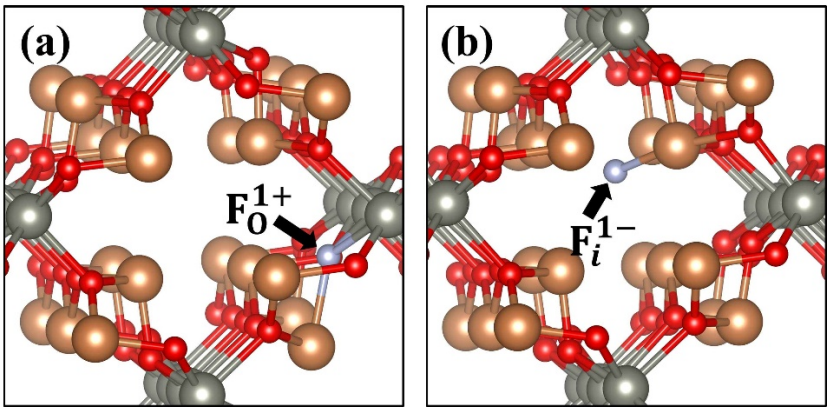

Figure S7 Local atomic geometry of fluorine (F) impurities in their stable charge state at the pinned Fermi level (a) F_{O}^{1+} and (b) F_{i}^{1-}. The small red spheres are the O atoms; the large grey spheres, large copper spheres and small light purple spheres are Zn, Sb and F respectively.