Supporting Information:

Structural Stability and Defect-Tolerance of Ionic Spinel Semiconductor for High-Efficiency Solar Cells

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Part 1. Chemical potential conditions of HgX_2S_4 phase

Since the formation energy of defects is the function of chemical potential, we need to obtain the phase diagram which limits the region of chemical potential before calculating defects' formation energies. HgX_2S_4 phase diagram is thermodynamically limited by the following conditions. To avoid the pure phase of elements, the following conditions must be satisfied

$$\mu_{Hg} \le 0\ ,\ \mu_X \le 0,\ (X = In, Sc \text{ and } Y)\ ,\ \mu_S \le 0. \quad (S1)$$

Similarly, to exclude the formation of secondary phase of compounds, their formation enthalpies must satisfy eq. S2 for $HgIn_2S_4$, eq. S3 for $HgSc_2S_4$ and eq. S4 for HgY_2S_4.

$$\begin{cases} \mu_{Hg}+\mu_S \le \Delta H_{HgS}(-0.42\ eV) & 2\mu_{In}+3\mu_S \le \Delta H_{In_2S_3}(-4.03\ eV) \\ \mu_{Hg}+4\mu_S \le \Delta H_{HgS_4}(-1.37\ eV) & 3\mu_{In}+\mu_S \le \Delta H_{In_3S}(-1.27\ eV) \\ \mu_{In}+\mu_{Hg} \le \Delta H_{InHg}(-0.42\ eV) & 3\mu_{In}+4\mu_S \le \Delta H_{In_3S_4}(-5.08\ eV) \\ \mu_{In}+3\mu_{Hg} \le \Delta H_{InHg_3}(-0.46\ eV) & 5\mu_{In}+4\mu_S \le \Delta H_{In_5S_4}(-6.13\ eV) \\ 3\mu_{In}+\mu_{Hg} \le \Delta H_{In_3Hg}(-1.29\ eV) & 5\mu_{In}+8\mu_S \le \Delta H_{In_5S_8}(-8.48\ eV) \\ \mu_{In}+\mu_S \le \Delta H_{InS}(-1.61\ eV) & 6\mu_{In}+7\mu_S \le \Delta H_{In_6S_7}(-10.23\ eV) \\ \mu_{In}+2\mu_S \le \Delta H_{InS_2}(-0.64\ eV) & 11\mu_{In}+16\mu_S \le \Delta H_{In_{11}S_{16}}(-21.31\ eV) \end{cases} \quad (S2)$$

$$\begin{cases} \mu_{Hg}+\mu_S \le \Delta H_{HgS}(-0.42\ eV) & 3\mu_{Sc}+\mu_{Hg} \le \Delta H_{Sc_3Hg}(-1.14\ eV) \\ \mu_{Hg}+4\mu_S \le \Delta H_{HgS_4}(-1.37\ eV) & \mu_{Sc}+\mu_S \le \Delta H_{ScS}(-4.02\ eV) \\ \mu_{Sc}+\mu_{Hg} \le \Delta H_{ScHg}(-1.06\ eV) & \mu_{Sc}+2\mu_S \le \Delta H_{ScS_2}(-3.68\ eV) \\ \mu_{Sc}+3\mu_{Hg} \le \Delta H_{ScHg_3}(-1.18\ eV) & 2\mu_{Sc}+3\mu_S \le \Delta H_{Sc_2S_3}(-10.60\ eV) \end{cases} \quad (S3)$$

$$\begin{cases} \mu_{Hg}+\mu_S \le \Delta H_{HgS}(-0.42\ \text{eV}) & \mu_Y+\mu_S \le \Delta H_{YS}(-4.39\ \text{eV}) \\ \mu_{Hg}+4\mu_S \le \Delta H_{HgS_4}(-1.37\ \text{eV}) & \mu_Y+2\mu_S \le \Delta H_{YS_2}(-0.30\ \text{eV}) \\ \mu_Y+\mu_{Hg} \le \Delta H_{YHg}(-1.26\ \text{eV}) & 2\mu_Y+3\mu_S \le \Delta H_{Y_2S_3}(-11.64\ \text{eV}) \\ \mu_Y+2\mu_{Hg} \le \Delta H_{YHg_2}(-1.57\ \text{eV}) & 5\mu_Y+7\mu_S \le \Delta H_{Y_5S_7}(-27.94\ \text{eV}) \\ \mu_Y+3\mu_{Hg} \le \Delta H_{YHg_3}(-1.83\ \text{eV}) & \end{cases} \quad \text{(S4)}$$

Part 2. Degeneracy factor of intrinsic defects in HgX_2S_4 spinel system

The degeneracy factor g_q of a charged defect level and the arrangement of electron on defect energy levels of different defects are listed in the following Table S1.

Table S1. Degeneracy factor of intrinsic defects in HgX_2S_4 spinel system combing with the consideration of energy level splitting in crystal field.

Defects	q	g_q X=In	g_q X=Sc/Y	Crystal fields X=In	Crystal fields X=Sc/Y	Configurations (take $q=+1/q=-1$ as an example) X=In	Configurations X=Sc/Y
Hg_i	0	$C_2^2=1$		D_{3d}		Hg 6s	
	1+	$C_2^1=2$					
	2+	$C_2^0=1$					
X_i	0	$C_2^1=2$	$C_2^1C_2^1=4$	D_{3d}		In: 5p, 5s	X: 3d, 4s; E_g', A_{1g}, E_g
	1+	$C_2^2=1$	$C_2^2=1$				
	2+	$C_2^1=2$	$C_2^1=2$				
	3+	$C_2^0=1$	$C_2^0=1$				
X_{Hg}	0	$C_2^1=2$	$C_2^1=2$	T_d		In: 5p, 5s	X: 3d; T_2, E
	1+	$C_2^0=1$	$C_2^0=1$				
V_S	0	$C_2^1(C_2^1)^3=16$				Hg + 3Sc): 6s, 3d, 4s	
	1+	$C_2^1(C_2^1)^3=16$					
	2+	$C_2^0(C_2^0)^3=1$					(take X=Sc as an example)
V_X	0	$C_2^1C_3^2C_2^1C_3^1=36$				(S): 3p, 3s	
	1-	$C_2^1C_3^1=6$					
	2-	$C_2^1C_3^2=6$					
	3-	$C_3^0=1$					
V_{Hg}	0	$C_2^1C_3^1=6$				(S): 3p, 3s	
	1-	$C_2^1C_3^2=6$					
	2-	$C_3^0=1$					
Hg_X	0	$C_2^1C_3^2=6$		O_h		(S): 3p, 3s	
	1-	$C_3^0=1$					

Part 3. Optical absorption coefficient and partial charge density of CBM

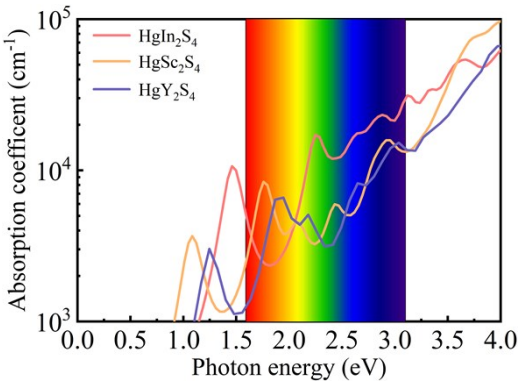

Fig. S1. Optical absorption coefficient of HgX_2S_4 spinel semiconductors (X=In, Sc and Y).

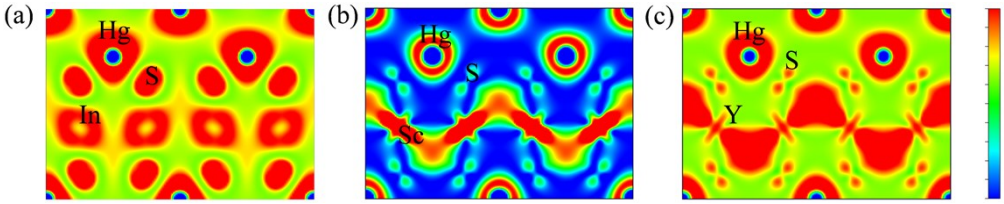

Fig. S2. Partial charge density of CBM for (a) $HgIn_2S_4$, (b) $HgSc_2S_4$ and (c) HgY_2S_4.