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Formation of native defects in the $\gamma$-ray detector material Cs$_2$Hg$_6$S$_7$

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Semiconductor $\gamma$-ray detectors have broad applications, yet finding superior detector materials is a challenge because of its contradictory requirements. Here, we investigated a large set of native defects in Cs$_2$Hg$_6$S$_7$ that has been suggested as a promising candidate for detector materials. Using first-principles calculations, we showed that S-vacancy and Hg$_{Cs}$-antisite defect provide life-time limiting deep levels, and Cs-vacancy forms a shallow acceptor level, resulting in low resistivity. To decrease such detrimental effects, concentrations of defects and carriers were examined in various chemical environments, which reveal that carrier densities can be extremely reduced by adjusting Cs partial pressure. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4767368]

Semiconductor devices detecting hard radiation such as $\gamma$-rays have been receiving much attention because of their broad applications in many areas of scientific research and medical diagnostics. Furthermore, recent world events have increased the demand to develop such devices for nuclear safety, homeland security, and nuclear non-proliferation applications. However, the search for new detector materials is challenging since they should satisfy multiple criteria. For example, high stopping power for the high energy photon imposes the requirement of high average atomic number $Z$ and high density, and accurate measurement of the electrical signal from the event requires high purity, optimized band gap (1.6 eV–2.5 eV), and a high carrier mobility–carrier lifetime ($\mu\tau$) product. A few semiconductors have been proposed and utilized for detector materials (e.g., Si, high purity Ge, CdTe, Cd$_{1-x}$Zn$_x$Te (CZT), and HgI$_3$). To achieve higher resolution and higher efficiency at room temperature, new detector materials with better performance are needed.

To find a material that satisfies those conditions simultaneously, one needs to search and screen a set of ternary chalcogenide compounds having heavy (i.e., high $Z$) elements. Recently, we presented an effective screening strategy (called dimensional reduction) and applied it to the study of a set of compounds defined by the chemical expression $(A_2Q)_m(MQ)_n$ ($A$ = alkali metal ion; $M$ = Hg, Cd; $Q$ = S, Se, Te). From this strategy, Cs$_2$Hg$_6$S$_7$ was predicted to be superior to CZT which is the most widely used detector material, in terms of density, average value of $Z$, band gap, and $\mu\tau$. However, in spite of its properties, the practical use of Cs$_2$Hg$_6$S$_7$ can be limited by native defects which form inevitably during the growth. Native defects can degrade energy resolution of detectors by increased dark current and charge trapping. Therefore, investigating the stability of defects of Cs$_2$Hg$_6$S$_7$ is crucial to guide the optimal growth and improve the sample quality.

Here, we explore the stability of native defects of Cs$_2$Hg$_6$S$_7$ and their electronic properties using first-principles calculations. In order to understand the defect-related properties, we calculated the formation energy of the possible native defects, and identified the type of defect according to its defect levels. Furthermore, we examined the concentration of the defects as a function of chemical potentials and determined the chemical environments that minimize the concentration of the detrimental defects. Finally, we evaluated the net carrier density resulting from the native defects as a function of chemical environment and addressed the optimal condition to increase the resistivity of Cs$_2$Hg$_6$S$_7$.

In order to investigate the defect properties of Cs$_2$Hg$_6$S$_7$, we performed first-principles total energy calculations within the density functional theory (DFT) framework. We employed the plane-wave basis set and pseudo-potential scheme with the projector augmented wave method $^{14}$ implemented in the Vienna Ab initio Simulation Package (VASP) code. $^{12,13}$ The cut-off energy for the plane-wave basis was set to 350 eV and a regular $k$-point mesh was chosen by the Monkhorst-Pack scheme $^{14}$ with the density of 50 Å$^{-1}$ for Brillouin zone sampling. We used the generalized gradient approximation in the Perdew-Burke-Ernzerhof formalism $^{15}$ for the exchange correlation functional. To describe the isolated defect configurations, we calculated the formation energy of the defect (see details in Ref. 16) adopting $1 \times 1 \times 4$ super-cell which accommodates 120 atoms. In order to correct the finite cell-size effect from the super-cell scheme, correction terms of the band-filling effect and the image charge correction were considered. $^{17,18}$ The concentration of defects, carrier densities, and equilibrium Fermi level ($\Delta E_F$) were determined self-consistently within the charge neutrality condition $^{19}$ as a function of growth temperature ($T_g$).

For possible native defects in Cs$_2$Hg$_6$S$_7$, we considered several configurations, such as vacancy, antisite, and interstitial defects. As shown in Fig. 1, Cs$_2$Hg$_6$S$_7$ has one Cs-site, two different Hg-sites (tetrahedral site (Hg1) and 3-fold planar site (Hg2)), and three different S-sites (2-fold (S1), 3-fold (S2), and 4-fold (S3) coordinated sites). Accordingly, for vacancy defects, we considered one Cs-vacancy (VCs), two types of Hg-vacancy (VHg1 and VHg2), and three types of S-vacancy (V$_{S1}$, V$_{S2}$, and V$_S$). For an antisite defect, we substituted Hg for Cs (Hg$_{Cs}$), and Cs for Hg1 or Hg2 (Cs$_{Hg1}$ and Cs$_{Hg2}$), and for a self-interstitial defect, we added an extra atom (Cs$_i$, Hg$_i$, and S$_i$) at the largest empty space in Cs$_2$Hg$_6$S$_7$, denoted by A in Fig. 1.
In order to investigate the 12 types of native defects, we begin with an examination of the thermodynamic stability of Cs$_2$Hg$_6$S$_7$. Since the native defects are formed spontaneously when the host material grows, the formation of the defect is affected by the growth condition (i.e., the chemical environment and growth temperature $T_g$). In this procedure, the thermodynamic stability of the material imposes the possible range of the chemical environment in terms of the chemical potential ($\Delta \mu_a$) of a reservoir of each element $a$ (see details in Refs. 16–18). In Fig. 2, we present the thermodynamic stability of Cs$_2$Hg$_6$S$_7$ as a function of $\Delta \mu_{Cs}$, $\Delta \mu_{Hg}$, and $\Delta \mu_S$. Although the axis of $\Delta \mu_S$ is not shown here, the contours of $\Delta \mu_S$ are denoted by black dotted lines with isovales. The possible ranges of $\Delta \mu_a$ are identified as the grey-shaded region where Cs$_2$Hg$_6$S$_7$ is stable over all the other compounds composed of Cs, Hg, or S. Then, using several sets of $\Delta \mu_a$ in the stable region, we can evaluate the formation energy of each defect configuration in the various chemical environments. In this study, first, we focused on the two limiting cases, Cs-rich/S-poor and Cs-poor/S-rich limits which are denoted by red and blue dots in Fig. 2, to figure out the electrical and thermodynamic properties of the native defects. We then calculated the concentration of defects and carrier density in the whole thermodynamically stable region of Cs$_2$Hg$_6$S$_7$ in order to estimate the optimal growth condition.

The formation energy of defects in Fig. 3 shows that $V_{S_1}$, $Hg_{Cs}$, and $V_{Cs}$ are the dominant defects out of 12 possible native defects. In the Cs-rich/S-poor limit, $V_S$ is the most favorable out of the three dominant defects. Among the three $V_S$ configurations, $V_{S_1}$ and $V_{S_2}$, which correspond to the two lowest red dotted-lines, are electrically inactive defects. However, $V_{S_3}$, denoted by red solid-lines, has a deep donor level due to the large distortion of the $2^+$ charged configuration. Generally, it is well known that such a deep level can cause charge trapping or recombination of electrons and holes, which degrade the efficiency and the energy resolution of the $\gamma$-ray detector in terms of a low $\mu\gamma$ value. Therefore, $V_{S_3}$ can be considered as one of the detrimental defects of Cs$_2$Hg$_6$S$_7$. Moreover, due to the deep donor level of $V_{S_3}$, the equilibrium position of $\Delta E_F$ moves slightly to the conduction band maximum (CBM) and electron carriers are released to the conduction band. In Fig. 3(a), the equilibrium position of $\Delta E_F$ at the experimental growth temperature $T_g = 773$ K is depicted by the vertical dotted line at $\Delta E_F = 0.48$ eV, making a 0.01 eV shift from the pristine Cs$_2$Hg$_6$S$_7$.  

![Crystal structure of Cs$_2$Hg$_6$S$_7$](image1)

FIG. 1. Crystal structure of Cs$_2$Hg$_6$S$_7$ represented by a ball and stick model. Red, blue, and yellow balls correspond to Cs atom, Hg atom, and S atom, respectively. The location marked by A indicates the largest empty space of Cs$_2$Hg$_6$S$_7$, which can accommodate an interstitial defect.

![Calculated ranges of chemical potential in the thermodynamic stability of Cs$_2$Hg$_6$S$_7$](image2)

FIG. 2. Calculated ranges of chemical potential in the thermodynamic stability of Cs$_2$Hg$_6$S$_7$. The grey shaded region represents the possible ranges of the chemical potentials. The chemical potential of Cs ($\Delta \mu_{Cs}$) changes along the x-axis and the chemical potential of Hg ($\Delta \mu_{Hg}$) changes along the y-axis. The chemical potential of S ($\Delta \mu_S$), which changes along the z-axis, is not shown here. Instead, the contour of $\Delta \mu_S$ is denoted by black dotted lines for $\Delta \mu_S = 0.0$ eV, $-0.22$ eV, and $-0.45$ eV. The Cs-rich/S-poor limit and the Cs-poor/S-rich limit are denoted by red and blue dots, respectively.

![Calculated formation energies of 12 native defects in Cs$_2$Hg$_6$S$_7$](image3)

FIG. 3. Calculated formation energies of 12 native defects in Cs$_2$Hg$_6$S$_7$ as a function of the Fermi level, $\Delta E_F$. (a) Formation energies of defects in the Cs-rich/S-poor limit and (b) formation energies of defects in the Cs-poor/S-rich limit. $\Delta E_F = 0$ eV is set as the valence band maximum. Each defect type is denoted in the legend at the bottom. The vertical dotted line in each panel represents the equilibrium $\Delta E_F$ at the growth temperature $T_g = 773$ K.
In the Cs-poor/S-rich limit, \(H_{\text{Cs}}\) and \(V_{\text{Cs}}\) are the most dominant native defects. As shown in Fig. 3(b), \(H_{\text{Cs}}\) forms a deep level similar to \(V_{\text{S}3}\), so this defect can be considered as detrimental as well. On the other hand, another dominant defect, \(V_{\text{Cs}}\), forms a shallow acceptor level with the charge transition level \(E(0/-) = 0.1\) eV above the valence band maximum (VBM). The low formation energy and low ionization energy of \(V_{\text{Cs}}\) move the position of the equilibrium \(\Delta E_F\) down to the VBM. As shown in Fig. 3(b), the equilibrium \(\Delta E_F\) equals 0.24 eV at \(T_\text{g} = 773\) K, which is 0.23 eV lower than that of the pristine crystal. Thus, more hole carriers are released from \(V_{\text{Cs}}\) into the valence band as compared to electron carriers in the Cs-rich/S-poor limit. While \(H_{\text{Cs}}\) can partially compensate the hole from \(V_{\text{Cs}}\), \(\text{Cs}_2\text{Hg}_6\text{S}_7\) has a net p-type carrier because the lower formation energy near the equilibrium \(\Delta E_F\) makes \(V_{\text{Cs}}\) dominate over \(H_{\text{Cs}}\).

From the formation energy of the defects, we evaluated the concentration of defects and the carrier density as a function of the chemical environment and \(T_\text{g}\). In Figs. 4(a) and 4(b), the concentrations of two detrimental defects, \(n[\text{V}_{\text{S}3}]\) and \(n[\text{H}_{\text{Cs}}]\), are presented, at the experimental growth temperature \(T_\text{g} = 773\) K. In the case of \(\text{V}_{\text{S}3}\), \(n[\text{V}_{\text{S}3}]\) is predicted to have the minimum value \((8.8 \times 10^{14}\text{cm}^{-3})\) at point A and the maximum value \((3.2 \times 10^{17}\text{cm}^{-3})\) at point B as shown in Fig. 4(a). However, \(n[\text{H}_{\text{Cs}}]\) is minimized \((2.4 \times 10^{13}\text{cm}^{-3})\) at point B and maximized \((2.0 \times 10^{15}\text{cm}^{-3})\) at point C, as shown in Fig. 4(b). Thus, the conditions for minimum values of \(n[\text{V}_{\text{S}3}]\) and \(n[\text{H}_{\text{Cs}}]\) cannot be satisfied simultaneously; rather, the condition for the minimum value of \(n[\text{H}_{\text{Cs}}]\) and the condition for the maximum value of \(n[\text{V}_{\text{S}3}]\) coincide.

Figures 4(c) and 4(d) present the net carrier density, \(N = N_{\text{electron}} + N_{\text{hole}}\), of \(\text{Cs}_2\text{Hg}_6\text{S}_7\) at 300 K with different \(T_\text{g}\): \(773\) K and 900 K, respectively. From the calculation, we found several distinct features for \(N\). First, as the chemical environment changes from the Cs-rich/S-poor limit (point B) to the Cs-poor/S-rich limit (point D), the type of carrier changes from electron to hole because the dominant defect configuration changes from electron donor, \(\text{V}_{\text{S}3}\), to the electron acceptor, \(V_{\text{Cs}}\). This feature indicates that in a certain range of chemical potentials, both the electron from \(\text{V}_{\text{S}3}\) and the hole from \(V_{\text{Cs}}\) can be suppressed, and thus \(N\) can be reduced to a low value. Such conditions are found in the white-colored region where \(N < 10^{12}\text{cm}^{-3}\) in Figs. 4(c) and 4(d). Second, \(N\) changes mainly depending on \(\Delta\mu_{\text{Cs}}\); especially, near the minimum value, \(N\) is only affected by \(\Delta\mu_{\text{Cs}}\). This can be explained by the relationship between the equilibrium position of \(\Delta E_F\) and \(\Delta\mu_{\text{Cs}}\). Due to the lower thermal ionization energy of \(V_{\text{Cs}}\) than that of other electron donor defects, \(\text{V}_{\text{S}3}\) and \(\text{H}_{\text{Cs}}\), the equilibrium \(\Delta E_F\) highly depends on \(\Delta\mu_{\text{Cs}}\). Accordingly, \(N\) also highly depends on \(\Delta\mu_{\text{Cs}}\) because \(N\) is determined as a function of \(\Delta E_F\) \((N = m^{1/2}_e\exp[-\Delta E_F/kT] - m^{1/2}_h\exp[-(E_F - \Delta E_F)/kT])\). Additionally, Figs. 4(c) and 4(d) show the \(T_\text{g}\)-dependence of \(N\). While the maximum value of \(N\) is increased at higher \(T_\text{g}\), the effect on the minimum region is negligible.

Based on these results, we can determine the optimal growth condition of \(\text{Cs}_2\text{Hg}_6\text{S}_7\) for \(\gamma\)-ray detector materials. From Ref. 9, we found that experimentally measured resistivity of \(\text{Cs}_2\text{Hg}_6\text{S}_7\) is low \(\approx 2 \times 10^{12}\Omega\cdot\text{cm}\), while the \(\mu\tau\) values are comparable with those of CZT. Therefore, the primary obstacle for the practical application of \(\text{Cs}_2\text{Hg}_6\text{S}_7\) is to achieve the high resistivity. As shown in Figs. 4(c) and 4(d), the chemical environment of \(\Delta\mu_{\text{Cs}}\), corresponding to the white-colored region minimizes \(N\). Accordingly, this...
chemical environment can be the optimal growth condition for Cs$_2$Hg$_6$S$_7$ to have higher resistivity, from the relationship of resistivity $\rho \propto 1/N$. However, the growth condition reducing $n[\text{VS}_3]$ or $n[\text{HgCs}]$ which can decrease $\mu\tau$ values is not perfectly compatible with the optimal growth conditions for the high resistivity as shown in Fig. 4. Nevertheless, from our results, we can control chemical potentials to decrease $n[\text{VS}_3]$ and $n[\text{HgCs}]$ within the conditions of the minimum $N$, and can enhance further the performance of the $\gamma$-ray detector. For instance, under the optimal chemical potentials of Cs for the high resistivity, we can decrease the partial pressure of Hg to the value that corresponds to $\Delta P_{\text{Hg}}$ near point A in Fig. 4(a). Then, this condition leads to decreasing $n[\text{VS}_3]$ and $n[\text{HgCs}]$ in appropriate levels.

In conclusion, we have investigated the formation energy of possible native defects of Cs$_2$Hg$_6$S$_7$ and its concentration as a function of the chemical environment using first-principles DFT calculations. From the results, we found that $\text{VS}_3$, $\text{HgCs}$, and $\text{VC}_s$ are the most dominant defects. Out of all defects, however, $\text{VS}_3$ and $\text{HgCs}$ form deep levels, and thus they could limit the mobility and life-time of carriers of Cs$_2$Hg$_6$S$_7$. Furthermore, we calculated the concentration of defects and carrier density, and found that $N$ can be suppressed by controlling the Cs partial pressure, which leads to the high resistivity of Cs$_2$Hg$_6$S$_7$.

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