

Design of $I_2-II-IV-VI_4$ Semiconductors through Element Substitution: The Thermodynamic Stability Limit and Chemical Trend

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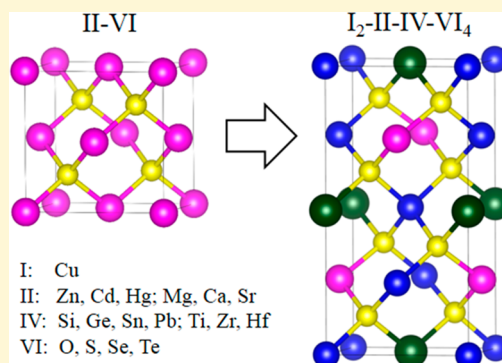
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ABSTRACT: Through element substitution in Cu_2ZnSnS_4 , a class of kesterite-structured $I_2-II-IV-VI_4$ semiconductors can be designed as novel functional materials. Using the first-principles calculations, we show that this element-substitution design is thermodynamically limited, that is, although $I_2-II-IV-VI_4$ with $I = Cu, Ag$, $II = Zn, Cd, Hg$, $IV = Si, Ge, Sn$, and $VI = S, Se, Te$ are stable quaternary compounds, those with $II = Mg, Ca, Sr, Ba$, $IV = Ti, Zr, Hf$, and $VI = O$ are unstable against the phase-separation into the competing binary and ternary compounds. Three main phase-separation pathways are revealed. In general, we show that if the secondary $II-VI$ or $I_2-IV-VI_3$ phases prefer to have nontetrahedral structures, then the $I_2-II-IV-VI_4$ semiconductors tend to phase separate. This finding can be used as a guideline for future design of new quaternary semiconductors.



I. INTRODUCTION

Because all component elements are earth-abundant and environment-friendly, the quaternary semiconductors Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe), and their alloys with band gaps between 1.0 and 1.5 eV have been intensively studied as low-cost and sustainable solar cell absorber materials during the last five years.^{1–5} Through substituting Cu by other group I (+1 valence) cations, Zn by group II (+2 valence) cations, Sn by group IV (+4 valence) cations, and S or Se by group VI anions (–2 valence), a class of $I_2-II-IV-VI_4$ quaternary semiconductors, such as Cu_2ZnGeS_4 ,^{4,6} $Ag_2CdSnSe_4$,⁷ and $Cu_2CdGeSe_4$,⁸ can be designed. These quaternary semiconductors have tetrahedrally coordinated crystal structures (derived from zincblende or wurtzite structure) and electronic structure (s–p band gap) similar to the binary II–VI semiconductors (ZnS , $CdTe$),⁹ but their properties are much more diverse given the increased number of elements, so they may have wide applications in electronic, optoelectronic, photovoltaic, or photocatalytic applications.^{10–13}

This element-substitution design had been proposed as early as 1960s,^{14,15} and a series of quaternary semiconductors had been synthesized, for example, $I_2-II-IV-VI_4$ with $I = Cu, Ag$, $II = Zn, Cd$, $IV = Si, Ge, Sn, Pb$, and $VI = S, Se$, as listed in the semiconductor handbooks.¹⁶ Recently, new design goes beyond these conventional elements; for example, Cu_2ZnTiS_4 , Cu_2MgSiS_4 , and Cu_2MgGeS_4 were proposed theoretically as new functional materials,^{17,18} and Cu_2MgGeS_4 had even been

synthesized, which shows X-ray diffraction pattern in good agreement with that of the theoretically proposed structure.¹⁷ The synthesis of some other $I_2-II-IV-VI_4$ compounds had also been reported. For example, $Cu_2ZnSn(S,O)_4$ (alloy of Cu_2ZnSnS_4 and Cu_2ZnSnO_4) was synthesized using chemical vapor deposition method by Washio et al.,¹⁹ and Cu_2BaSnS_4 , Ag_2BaSnS_4 and Cu_2SrSnS_4 were synthesized from a mixture of three binary sulfides by Teske et al.^{20,21} Since there are many elements with +1, +2, +4, and –2 valences, such as $II = Mg, Ca, Sr, Ba$ (group IIA), $IV = Ti, Zr, Hf$ (group IVB), and $VI = O, Te$, their combination can lead to a large number of potential $I_2-II-IV-VI_4$ compounds.

As more and more $I_2-II-IV-VI_4$ semiconductors are designed or reported, one fundamental issue is whether the proposed $I_2-II-IV-VI_4$ semiconductors are thermodynamically stable. Currently, this question is not yet systematically addressed. Furthermore, the possible factors or mechanism that may cause the instability are also unclear. The answer to these questions is important for theoretical design and experimental synthesis of novel and stable $I_2-II-IV-VI_4$ compounds.

In this work, a series of kesterite-structured $I_2-II-IV-VI_4$ semiconductors are studied through the first-principles calculations. Based on the analysis of the calculated results, the thermodynamic limiting mechanism to the stability of I_2-

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II–IV–VI₄ semiconductors is revealed. The results show that although the substitution of II by Zn, Cd, Hg, IV by Si, Ge, Sn, and VI by S, Se, Te can lead to stable quaternary compound semiconductors, the substitution of II by Mg, Ca, Sr, Ba, IV by Ti, Zr, Hf, and VI by O has limited thermodynamic stability because the phase-separated competing binary and ternary compounds are more stable in different local environment than that in the tetrahedral environment of the I₂–II–IV–VI₄ compounds. When an I₂–II–IV–VI₄ compound is unstable, the corresponding elements can only be incorporated into a stable I₂–II–IV–VI₄ with low concentration; thus their contribution to tuning the material properties is limited.

II. COMPUTATIONAL DETAILS

The crystal and electronic structure calculations are performed based on the density functional theory as implemented in the Vienna ab initio simulation package (VASP) code.²² For the exchange correlation potential, we use the generalized gradient approximation (GGA) of Perdew and Wang.²³ The projector augmented-wave pseudopotentials²⁴ and the plane-wave basis functions are used with an energy cutoff of 400 eV in the study of all sulfide, selenide, and telluride compounds and an energy cutoff of 500 eV in the study of oxide compounds. For the Brillouin zone integration, an $8 \times 8 \times 4$ Monkhorst–Pack or equivalent k-point meshes are used. All lattice vectors and atomic positions are fully relaxed by minimizing the quantum-mechanical stresses and forces. The total energies used for assessing the heats of formation are converged to within 0.001 eV/atom. No temperature effects are considered, that is, the entropy influence at finite temperature is neglected, as discussed in section 3.2.4.

III. RESULTS AND DISCUSSION

3.1. Element-substitution Design of I₂–II–IV–VI₄. The quaternary I₂–II–IV–VI₄ semiconductors can be taken as derived from binary II–VI semiconductors,²⁵ for example, Cu₂ZnSnS₄ from ZnS, as shown schematically in Figure 1. In

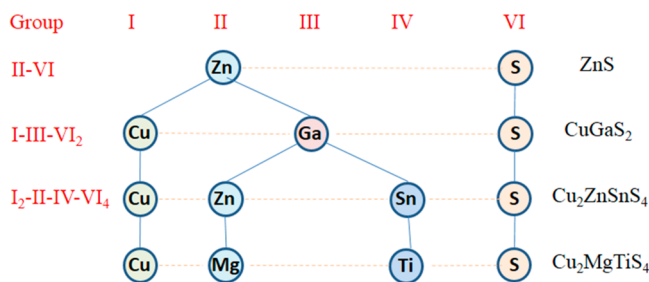


Figure 1. Schematic plot of the derivation of I₂–II–IV–VI₄ semiconductors from binary II–VI and ternary I–III–VI₂ parent compounds.

zincblende ZnS, the S^{2−} anion is tetrahedrally bonded with four Zn²⁺ cations. If the four Zn²⁺ are replaced by two Cu⁺ and two Ga³⁺ cations, the ternary CuGaS₂ semiconductor can be derived, and if the two Ga³⁺ cations are further replaced by one Zn²⁺ and one Sn⁴⁺ cation, quaternary Cu₂ZnSnS₄ can be derived. The elements of Cu₂ZnSnS₄ can also be replaced by other isovalent elements, such as Zn by Mg, Sn by Ti, and S by Se, then a series of I₂–II–IV–VI₄ semiconductors (such as Cu₂MgTiS₄) can be derived, as shown in Figure 1. In this study, we focus on the following series of component elements:

- I: Cu
- II: Zn, Cd, Hg; Mg, Ca, Sr
- IV: Si, Ge, Sn, Pb; Ti, Zr, Hf
- VI: O, S, Se, Te

During the replacement of the component elements, the local charge around each anion always satisfies the octet rule, so the tetrahedrally coordinated lattice framework of zincblende or wurtzite is kept when it mutates into quaternary structures, despite they have different symmetries depending on the ordering of the cations.²⁵ Among these quaternary crystal structures, five fundamental structures have been found with the smallest primitive cells and the lowest energy,^{25,26} including kesterite, stannite, primitive-mixed CuAu (PMCA), wurtzite–kesterite, and wurtzite–stannite. Two of those structures are shown in Figure 2. Their total energy difference is usually less

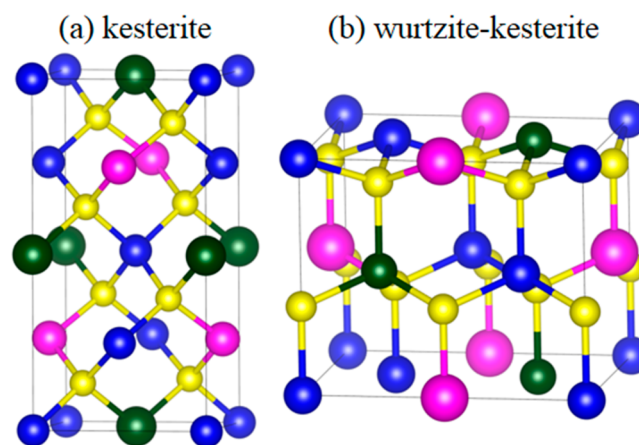


Figure 2. Unit cells of (a) zincblende-derived kesterite, (b) wurtzite-derived wurtzite–kesterite I₂–II–IV–VI₄ crystal structures. Blue, purple, green, and yellow balls show the I, II, IV, and VI atoms, respectively.

than 0.01 eV/atom, so their differences in the compound formation energies are small.^{24,25} Therefore, in our following study, we will use only the representative kesterite structure (Figure 2a) to study the chemical trend in the phase stability.

3.2. Thermodynamic Stability Limit. Although the charge-neutrality condition around each anion is satisfied in the element-substitution design of I₂–II–IV–VI₄ semiconductors, whether they can be synthesized under equilibrium conditions (thermodynamically stable) is a question. The formation of the quaternary compounds is limited, since these component elements can also form other elemental, binary and ternary phases, which are competing with the quaternary phases.^{5,27,28} This competition can be quantitatively described by the limit to the chemical potentials of the component elements.²⁹ As we know, the chemical potential of an element is defined as the partial molar derivative of the Gibbs free energy with respect to that elemental species. Higher chemical potential for element I in the synthesis environment will lead to higher molar concentration of element I in the sample, that is, making element I richer. Therefore, the chemical potential can be taken as a quantity that describes the richness of elements in an environment.^{30,31} The pure elemental phase is usually taken as the reference of the chemical potential; for example, if μ_I , μ_{II} , μ_{IV} , and μ_{VI} denote the chemical potentials of the group I, II, IV, and VI elements, respectively, $\mu_I = 0$ (similarly for $\mu_{II} = 0$, $\mu_{IV} = 0$, or $\mu_{VI} = 0$) means that the group I

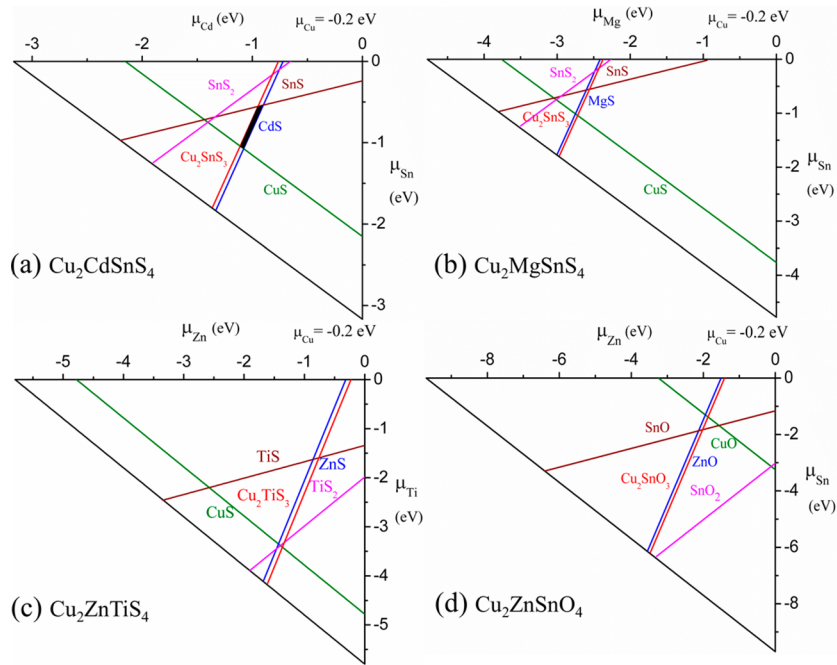


Figure 3. Limit to the chemical potential regions that stabilize single-phase $I_2-II-IV-VI_4$. Here the limit is imposed by a series of competing compounds, and the plot is in the $\mu_{Cu} = -0.2$ eV plane. The plot in other planes are also considered, but not shown here.

(II, IV, or VI) element has the chemical potential when it is in its most stable form (pure elemental phase).

To synthesize $I_2-II-IV-VI_4$ and make it stable under the equilibrium condition, the chemical potential of the component elements in the synthesis environment, μ_I , μ_{II} , μ_{IV} , and μ_{VI} should satisfy the following conditions (see ref 29 for exact derivation),

$$2\mu_I + \mu_{II} + \mu_{IV} + 4\mu_{VI} = \Delta H_f(I_2 - II - IV - VI_4) \quad (1)$$

where $\Delta H_f(I_2-II-IV-VI_4)$ is the calculated formation energy of $I_2-II-IV-VI_4$, that is, the energy change of the reaction $2I + II + IV + 4VI \rightarrow I_2-II-IV-VI_4$ (from the I, II, IV, and VI pure elemental phases to the $I_2-II-IV-VI_4$ compound). To avoid the precipitation of the elemental phases in the synthesis environment, it is required that $\mu_I < 0$ and similarly $\mu_{II} < 0$, $\mu_{IV} < 0$, $\mu_{VI} < 0$. On the other hand, to avoid the formation of secondary phases such as binary I-VI (e.g., CuS), I₂-VI (Cu_2S), II-VI (ZnS), IV-VI (SnS), IV-VI₂ (SnS_2), and ternary $I_2-IV-VI_3$ (Cu_2SnS_3), as well as any phases that deviate from the stoichiometry (2:1:1:4) of the $I_2-II-IV-VI_4$ compound, the following conditions should also be satisfied:

$$\mu_I + \mu_{VI} < \Delta H_f(I-VI) \quad (\text{e.g., } \mu_{Cu} + \mu_S < \Delta H_f(CuS)) \quad (2a)$$

$$2\mu_I + \mu_{VI} < \Delta H_f(I_2-VI) \quad (\text{e.g., } 2\mu_{Cu} + \mu_S < \Delta H_f(Cu_2S)) \quad (2b)$$

$$\mu_{II} + \mu_{VI} < \Delta H_f(II-VI) \quad (\text{e.g., } \mu_{Zn} + \mu_S < \Delta H_f(ZnS)) \quad (2c)$$

$$\mu_{IV} + \mu_{VI} < \Delta H_f(IV-VI) \quad (\text{e.g., } \mu_{Sn} + \mu_S < \Delta H_f(SnS)) \quad (2d)$$

$$\mu_{IV} + 2\mu_{VI} < \Delta H_f(IV-VI_2) \quad (\text{e.g., } \mu_{Sn} + 2\mu_S < \Delta H_f(SnS_2)) \quad (2e)$$

$$2\mu_I + \mu_{VI} + 3\mu_{VI} < \Delta H_f(I_2-IV-VI_3)$$

$$(\text{e.g., } 2\mu_{Cu} + \mu_{Sn} + 3\mu_S < \Delta H_f(Cu_2SnS_3)) \quad (2f)$$

Only when all of these conditions are satisfied, the pure $I_2-II-IV-VI_4$ phase can be synthesized and stable thermodynamically. These constraints limit the values of μ_I , μ_{II} , μ_{IV} , μ_{VI} . Considering eq 1, only three of the four chemical potentials are variables, and the other one can be determined; for example, μ_{VI} can be determined if we take μ_I , μ_{II} , μ_{IV} as variables. Under the established constraints, the range of the three variables is bound in a polyhedron in the three-dimensional (μ_I , μ_{II} , μ_{IV}) space,²⁷ which defines the chemical potential range that stabilizes the $I_2-II-IV-VI_4$ compounds. In Figure 3, we plot the slices of the polyhedron in $\mu_{Cu} = -0.2$ eV plane for four representative $I_2-II-IV-VI_4$ compounds, Cu_2CdSnS_4 , Cu_2MgSnS_4 , Cu_2ZnTiS_4 , and Cu_2ZnSnO_4 .

3.2.1. Stability of $Cu_2-II-SnS_4$ ($II = Zn, Cd, Hg$, and Mg, Ca, Sr, Ba). In Figure 3a, the black region shows the chemical potential range that stabilizes Cu_2CdSnS_4 . Six competing secondary compounds, that is, binary Cu_2S , CuS, CdS, SnS, SnS_2 , and ternary Cu_2SnS_3 are considered, and their limit to the stable region is shown by the boundary lines with the same color as their labels. When the chemical potential crosses the line and goes beyond the black region, the corresponding secondary compounds can form, and thus the quaternary phase Cu_2CdSnS_4 becomes unstable. Besides the $\mu_{Cu} = -0.2$ eV plane, we also studied the limit to the stable region in other planes with different μ_{Cu} , which shows that single-phase Cu_2CdSnS_4 can be stabilized in a narrow chemical potential region, so it can be synthesized and is thermodynamically stable, which is consistent with the experimental observation that Cu_2CdSnS_4 had been synthesized by many groups.^{32–34}

Besides Cu_2CdSnS_4 , we also calculate the stable region for other $Cu_2-II-SnS_4$ compounds with $II = Zn, Hg$, and they all have a narrow stable region in the chemical potential space, which is also consistent with the widely reported experimental

Table 1. Calculated Energy Change ΔE (in eV/formula unit) of Different Phase-Separation Reactions of $\text{Cu}_2\text{-II-SnS}_4$ (II = Zn, Cd, Hg, and Mg, Ca, Sr, Ba)^a

compd.	phase separation	ΔE	ref.	compd.	phase separation	ΔE	ref
$\text{Cu}_2\text{ZnSnS}_4$	$\text{Cu}_2\text{S} + \text{ZnS} + \text{SnS}_2$	0.56	40	$\text{Cu}_2\text{MgSnS}_4$	$\text{Cu}_2\text{S} + \text{MgS} + \text{SnS}_2$	0.47	
	$2\text{CuS} + \text{ZnS} + \text{SnS}$	0.40	36		$2\text{CuS} + \text{MgS} + \text{SnS}$	0.31	
	$\text{Cu}_2\text{SnS}_3 + \text{ZnS}$	0.08	35		$\text{Cu}_2\text{SnS}_3 + \text{MgS}$	-0.01	
$\text{Cu}_2\text{CdSnS}_4$	$\text{Cu}_2\text{S} + \text{CdS} + \text{SnS}_2$	0.51	32	$\text{Cu}_2\text{CaSnS}_4$	$\text{Cu}_2\text{S} + \text{CaS} + \text{SnS}_2$	-0.23	
	$2\text{CuS} + \text{CdS} + \text{SnS}$	0.35	33		$2\text{CuS} + \text{CaS} + \text{SnS}$	-0.39	
	$\text{Cu}_2\text{SnS}_3 + \text{CdS}$	0.03	41		$\text{Cu}_2\text{SnS}_3 + \text{CaS}$	-0.71	
$\text{Cu}_2\text{HgSnS}_4$	$\text{Cu}_2\text{S} + \text{HgS} + \text{SnS}_2$	0.56	38	$\text{Cu}_2\text{SrSnS}_4$	$\text{Cu}_2\text{S} + \text{SrS} + \text{SnS}_2$	-0.35	
	$2\text{CuS} + \text{HgS} + \text{SnS}$	0.37	39		$2\text{CuS} + \text{SrS} + \text{SnS}$	-0.51	
	$\text{Cu}_2\text{SnS}_3 + \text{HgS}$	0.08			$\text{Cu}_2\text{SnS}_3 + \text{SrS}$	-0.83	
				$\text{Cu}_2\text{BaSnS}_4$	$\text{Cu}_2\text{S} + \text{BaS} + \text{SnS}_2$	-0.48	
					$2\text{CuS} + \text{BaS} + \text{SnS}$	-0.64	
					$\text{Cu}_2\text{SnS}_3 + \text{BaS}$	-0.97	

^aThe initial and final states of the reactions are listed in the “Compound” and “Phase Separation” columns, respectively. ΔE is in the unit of eV per formula unit of the initial quaternary compound. If the compound has been synthesized, the references are listed.

Table 2. Calculated Energy Change ΔE (in eV/formula unit) of $\text{Cu}_2\text{Zn-IV-VI}_4$ (IV = Si, Ge, Sn, Pb, and Ti, Zr, Hf, VI = O, S, Se, Te), through Different Phase-Separation Reactions^a

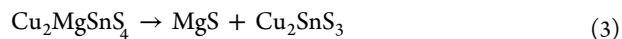
compd.	phase separation	ΔE	ref	compd.	phase separation	ΔE	ref
$\text{Cu}_2\text{ZnSiS}_4$	$\text{Cu}_2\text{S} + \text{ZnS} + \text{SiS}_2$	0.48	42	$\text{Cu}_2\text{ZnTiS}_4$	$\text{Cu}_2\text{S} + \text{ZnS} + \text{TiS}_2$	0.15	
	$2\text{CuS} + \text{ZnS} + \text{SiS}$	1.89	43		$2\text{CuS} + \text{ZnS} + \text{TiS}$	1.14	
	$\text{Cu}_2\text{SiS}_3 + \text{ZnS}$	0.16			$\text{Cu}_2\text{TiS}_3 + \text{ZnS}$	-0.05	
$\text{Cu}_2\text{ZnGeS}_4$	$\text{Cu}_2\text{S} + \text{ZnS} + \text{GeS}_2$	0.73	6	$\text{Cu}_2\text{ZnZrS}_4$	$\text{Cu}_2\text{S} + \text{ZnS} + \text{ZrS}_2$	-0.27	
	$2\text{CuS} + \text{ZnS} + \text{GeS}$	0.79	44		$2\text{CuS} + \text{ZnS} + \text{ZrS}$	1.20	
	$\text{Cu}_2\text{GeS}_3 + \text{ZnS}$	0.08			$\text{Cu}_2\text{ZrS}_3 + \text{ZnS}$	-0.03	
$\text{Cu}_2\text{ZnSnS}_4$	$\text{Cu}_2\text{S} + \text{ZnS} + \text{SnS}_2$	0.56	40	$\text{Cu}_2\text{ZnHfS}_4$	$\text{Cu}_2\text{S} + \text{ZnS} + \text{HfS}_2$	-0.40	
	$2\text{CuS} + \text{ZnS} + \text{SnS}$	0.40	36		$2\text{CuS} + \text{ZnS} + \text{HfS}$	1.73	
	$\text{Cu}_2\text{SnS}_3 + \text{ZnS}$	0.08	35		$\text{Cu}_2\text{HfS}_3 + \text{ZnS}$	0.04	
$\text{Cu}_2\text{ZnPbS}_4$	$\text{Cu}_2\text{S} + \text{ZnS} + \text{PbS}_2$	1.00		$\text{Cu}_2\text{ZnSnO}_4$	$\text{Cu}_2\text{O} + \text{ZnO} + \text{SnO}_2$	-1.71	
	$2\text{CuS} + \text{ZnS} + \text{PbS}$	-0.60			$2\text{CuO} + \text{ZnO} + \text{SnO}$	-0.38	
	$\text{Cu}_2\text{PbS}_3 + \text{ZnS}$	-0.11			$\text{Cu}_2\text{SnO}_3 + \text{ZnO}$	-0.07	
$\text{Cu}_2\text{ZnSnSe}_4$	$\text{Cu}_2\text{Se} + \text{ZnSe} + \text{SnSe}_2$	0.76	45	$\text{Cu}_2\text{ZnSnTe}_4$	$\text{Cu}_2\text{Te} + \text{ZnTe} + \text{SnTe}_2$	0.78	46
	$2\text{CuSe} + \text{ZnSe} + \text{SnSe}$	0.38	40		$2\text{CuTe} + \text{ZnTe} + \text{SnTe}$	0.08	
	$\text{Cu}_2\text{SnSe}_3 + \text{ZnSe}$	0.05			$\text{Cu}_2\text{SnTe}_3 + \text{ZnTe}$	0.03	

^aIf the compound has been synthesized, the references are listed in the Ref. column. Because SiS, PbS₂, SnTe₂, Cu₂TiS₃, Cu₂ZrS₃, Cu₂HfS₃, and Cu₂SnO₃ have not yet been synthesized or their structures have not been reported, we assume that they take the corresponding structures of SnS, SnS₂, and Cu₂SnS₃ when calculating ΔE of the possible phase-separation reactions.

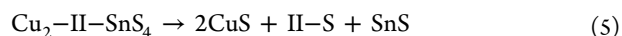
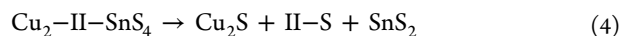
synthesis.^{35–39} The stable regions for all the three compounds are narrow, indicating that the composition control is very important for synthesizing these single-phase materials. The most stringent constraints come from CdS and Cu₂SnS₃; that is, when Cd is relatively poor (left side of the black region) in the synthesis environment, Cu₂SnS₃ will coexist in the samples, while when Cd is relatively rich (right side of the black region), CdS will coexist. This highlights the necessity to detect these secondary phases in the synthesized samples before the characterization of their properties, otherwise the properties may not be intrinsic to the quaternary I₂-II-IV-VI₄.

In contrast to I₂-II-IV-VI₄ with II = Zn, Cd, Hg, those with II = Mg, Ca, Sr, Ba do not have a stable region in the chemical potential space, indicating that they cannot be synthesized and stable from a thermodynamic perspective. For example, Cu₂MgSnS₄ does not have a stable (black) region in the $\mu_{\text{Cu}} = -0.2$ eV plane (see Figure 3b), as well as in other planes with different μ_{Cu} , which are not shown here. The main reason for the disappearing of the stable region is from the constraint of MgS and Cu₂SnS₃, that is, the MgS line is on the

left side of the Cu₂SnS₃ line in Figure 3b. This constraint can be described by the following phase-separation reaction,



The calculated energy change of this reaction is exothermic ($\Delta E < 0$ in Table 1), meaning that the phase separation of Cu₂MgSnS₄ will proceed spontaneously, in accordance with the disappearance of the stable region in the chemical potential space. Similarly, for Cu₂CaSnS₄, Cu₂SrSnS₄, Cu₂BaSnS₄, they do not form stable regions either, and their phase-separation reactions corresponding to eq 3 are exothermic. Furthermore, these three compounds also have other phase-separation pathways,



which are also exothermic (Table 1) and can proceed spontaneously. Our analysis showing that the instability for these compounds are directly related to the fact that for group IIA elements they are more stable in the ionic rocksalt structure with S than in the more covalent tetrahedral environment as in

kesterite. The instability increases (ΔE becomes more negative) when the ionicity increases as the II changes from Mg to Ca to Sr to Ba. According to the calculated results, we predict that the kesterite-structured $I_2-II-IV-VI_4$ with II = Mg, Ca, Sr, Ba are not thermodynamically stable, and their synthesis and application in real devices are questionable. There are several experimental reports about the synthesis of Cu_2MgGeS_4 ,¹⁷ Cu_2SrSnS_4 , and Cu_2BaSnS_4 .²⁰ We suggest that these samples may crystallize in structures different from kesterite, or are only metastable and secondary phases may exist in these samples. More experimental study on these samples is needed.

3.2.2. Stability of $Cu_2Zn-IV-S_4$ (IV = Si, Ge, Sn, Pb, and Ti, Zr, Hf). Besides the substitution of the group II elements, the substitution of the group IV elements also leads to a series of $I_2-II-IV-VI_4$ semiconductors. Here, we take $Cu_2Zn-IV-S_4$ with IV = Si, Ge, Sn, Pb, and Ti, Zr, Hf as examples, to see whether these element substitutions are limited by the thermodynamic stability.

Table 2 lists the calculated energy change for the possible phase-separation reactions of these compounds. Obviously, Cu_2ZnSiS_4 , Cu_2ZnGeS_4 , and Cu_2ZnSnS_4 are stable against all the studied phase-separation pathways, consistent with the wide report of their synthesis. However, when IV = Pb, Ti, Zr, Hf all the $Cu_2Zn-IV-S_4$ compounds prefer phase-separation to binary or ternary compounds, because at least one of their phase-separation reactions have negative energy change. This indicates that the chemical binding in the binary and ternary compounds is stronger (thus lower formation energy) than in the quaternary ones. Two trends can be found in the energy change ΔE : (i) for the reaction corresponding to eq 5, $Cu_2Zn-IV-S_4 \rightarrow 2CuS + ZnS + IV-S$, ΔE decreases from Si to Ge to Sn, and turning to be negative for IV = Pb. This is because for the heavy element Pb, due to relativistic effects, it prefers to be in the 2+ ionization state as in the rocksalt PbS instead to be in the 4+ ionization state as in the tetrahedral environment associated with kesterite structure; (ii) for the reaction corresponding to eq 4, $Cu_2Zn-IV-S_4 \rightarrow Cu_2S + ZnS + IV-S_2$, ΔE decreases from positive to negative as IV changes from Ti to Zr to Hf, indicating that for Hf with more delocalized 5d valence orbital, it prefers to form more ionic binary HfS_2 structure rather than the tetragonal $Hf-S$ bond in quaternary Cu_2ZnHfS_4 . (iii) for $Cu_2Zn-IV-S_4 \rightarrow Cu_2-IV-S_3 + ZnS$, the stability of $Cu_2Zn-IV-S_4$ increases slightly when group IV elements change from Ti to Zr to Hf due to increased strain relaxation in the quaternary compounds than in the ternary Cu_2-IV-S_3 when the size of group IV elements increases. Considering these trends, we predict that it should be more difficult to form $I_2-II-IV-VI_4$ compounds when group IV elements become heavy due to the separation to the binary and ternary competing compounds.

The above-discussed instability is reflected by the absence of favorable regions in chemical potential space for the formation of $Cu_2Zn-IV-S_4$ with IV = Pb, Ti, Zr, Hf. In Figure 3c, the limits are plotted for Cu_2ZnTiS_4 , where no stable (black) region exists, because of the relative stability of Cu_2TiS_3 . Experimentally, Cu_2TiS_3 has not yet been synthesized, and appears to be unstable with respect to further phase-separation into Cu_4TiS_4 and TiS_2 ,⁴⁷ indicating that the energy change of the phase-separation reaction $2Cu_2ZnTiS_4 \rightarrow 2ZnS + Cu_4TiS_4 + TiS_2$ can have even larger value (more negative). Recently, Cu_2ZnTiS_4 ($Cu_2ZnTiSe_4$) had been designed and proposed as candidate solar cell absorber materials for their band gaps comparable with Cu_2ZnSnS_4 ($Cu_2ZnSnSe_4$) and higher

absorption coefficient.¹⁸ However, the present calculation of their thermodynamic stability shows that the two quaternary compounds with Ti are only metastable, which is a serious challenge to their real application besides other issue related to this compound such as poor transport property.

3.2.3. Stability of $Cu_2Zn-Sn-VI_4$ (VI = O, S, Se, Te). In Table 2, we also listed the phase-separation energy change of $Cu_2ZnSn-VI_4$ with VI = O, S, Se, Te. We find that when VI = O, the Cu_2ZnSnO_4 compound is not stable. The phase-separations into $Cu_2O + ZnO + SnO_2$ and $2CuO + ZnO + SnO$ are both exothermic, which means that the bonding in some of the binary oxides is much stronger than in the quaternary Cu_2ZnSnO_4 . Indeed, when bound to oxygen, Cu^I tends to favor linear coordination environments as demonstrated in Cu_2O and related delafossite ternary oxides and SnO_2 like to form the rutile structure. In Figure 3(d), the chemical potential limit is plotted for Cu_2ZnSnO_4 , in which the strong stability of SnO_2 makes the stable region disappear. Considering the large negative energy-change of the phase-separation reactions and the strong constraint to the chemical potential range, the synthesis of single-phase Cu_2ZnSnO_4 would be challenging.

Recently, Washio et al. and Yang et al. both reported synthesis of the mixed-anion $Cu_2ZnSn(S_{1-x}O_x)_4$ alloys with the O composition (x) as high as 60% and 27% respectively.^{19,48} They stated that "Oxygen is another group VI element and can replace S in CZTS without disturbing valence. Therefore, $Cu_2ZnSnS_{4-x}O_x$ (CZTSO) can also be suitable for thin film solar cells." However, our calculations show that Cu_2ZnSnO_4 compound is unstable due to the preference of oxides to have different structure and coordination, thus makes this suggestion questionable. Since Cu_2ZnSnS_4 is stable, while Cu_2ZnSnO_4 in the kesterite structure is unstable with respect to phase separation, the stability of $Cu_2ZnSn(S_{1-x}O_x)_4$ alloys should depend on the O composition. For the alloy samples that have been synthesized,^{19,48} there should exist a critical value for the O composition, below which $Cu_2ZnSn(S_{1-x}O_x)_4$ alloys isostructural to kesterite Cu_2ZnSnS_4 may be stabilized. When the O composition is higher than the critical value, $Cu_2ZnSn(S_{1-x}O_x)_4$ alloys will be unstable, and the secondary compounds—particularly binary metal oxides—are likely to form in the synthesized samples. Based on this, it is necessary to investigate the phase separation in the synthesized samples of these alloys, especially when O composition is high. In contrast to $Cu_2ZnSn(S,O)_4$, the alloys formed by mixing Cu_2ZnSnS_4 , $Cu_2ZnSnSe_4$, and $Cu_2ZnSnTe_4$ are stable; for example, the $Cu_2ZnSn(S_{1-x}Se_x)_4$ alloys have been synthesized with the composition parameter x tunable from 0 to 1,^{49,50} so the properties can be tuned continuously in a wide composition range.

3.2.4. Temperature Effect on the Thermodynamic Stability. It should be noted that the above calculations are athermal and at zero pressure, so only total energy (formation energy) differences are considered. At finite temperatures, such as 300–900 K (synthesis temperature) or 300–400 K (device working temperature), the contribution of entropy should also be considered to calculate the Gibbs free energy and to predict the thermodynamic stability of quaternary semiconductors.

For the phase separation reactions that we considered in this paper (as shown in Tables 1 and 2), both the reactants (quaternary compounds) and products (binary and ternary compounds) are in the crystal state, so the entropy can be partitioned into two parts, the configurational and vibrational

entropy. The configurational entropy can be neglected if the crystal structures are fully ordered (and excluding point defects). As $I_2-II-IV-VI_4$ (such as Cu_2ZnSnS_4) and $I_2-IV-VI_3$ (such as Cu_2SnS_3) semiconductors may be partially disordered in the cation sublattices at finite temperatures,^{51,52} configurational entropy may play some role in their stability. The vibrational contributions are known to largely cancel for solid-state reactions. As the reactants and products are similar to Cu_2ZnSnS_4 , Cu_2SnS_3 , and ZnS whose structures are all derived from the zincblende structure, the influence of the vibrational entropy difference should be particularly small.

As a result of the structural complexity and the possible partial disorder of the quaternary and ternary semiconductors, the direct calculation of both their configurational and vibrational entropy is still challenging. The prediction of the thermodynamic stability of the quaternary $I_2-II-IV-VI_4$ semiconductors at finite temperature deserves further consideration. When comparing the current predictions with experimental synthesis at high temperature, it should be noted that the stability or instability of $I_2-II-IV-VI_4$ with small phase-separation energy change ΔE (as listed in Tables 1 and 2) may change due to the influence of entropy.

IV. CONCLUSIONS

Using the first-principles calculations, we have studied the thermodynamic stability of three classes of tetrahedral $I_2-II-IV-VI_4$ compound semiconductors in the kesterite structure. We show that only those with $II = Zn, Cd, Hg$, $IV = Si, Ge, Sn$, and $VI = S, Se, Te$ are stable, but those with $II = Mg, Ca, Sr, Ba$, $IV = Ti, Zr, Hf$, and $VI = O$ are unstable because of the phase-separation into the competing binary and ternary compounds. We find that for those unstable compounds, the materials are more ionic and their binary and ternary secondary phases tend to form nontetrahedral structures such as 6-fold rock salt structure. As a result of the limited stability, these elements can only be alloyed into the stable $I_2-II-IV-VI_4$ semiconductors with a low composition, and thus, their contribution to tuning the material properties such as band gaps is limited. Some unstable $I_2-II-IV-VI_4$ compounds have been reportedly synthesized, including Cu_2SrSnS_4 , Cu_2BaSnS_4 , Cu_2MgGeS_4 , and $Cu_2ZnSn(S_{1-x}O_x)_4$ alloys with a high O composition. We suggest that further study is needed, especially the detection of the secondary compounds in the synthesized samples, which could have similar X-ray diffraction patterns.⁵² Our results could provide guideline of understanding the thermodynamic stability limit in the design of new quaternary semiconductors.

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Notes

The authors declare no competing financial interest.

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