

Thermodynamic description of the ternary compounds in the Cu-In-Se system

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Abstract: A set of thermodynamic descriptions of the ternary compounds (mainly α -CuInSe₂, δ -CuInSe₂, CuIn₃Se₅ and CuIn₅Se₈) in the Cu-In-Se system was established by adopting sub-lattice model. The model parameters are carefully evaluated by integrating the experimental data of thermodynamic properties, phase equilibrium and theoretical calculation of formation energies of different point defects. The evaluated Gibbs energies of the compounds reasonably agree with that estimated from EMF experiment and *ab initio* calculation. The calculated phase relationships in the Cu-In-Se system are in accord with the experimental phase diagrams. The obtained standard enthalpy of formation of CuInSe₂ is close to that reported in the literatures.

Key words: Cu-In-Se system; thermodynamics; Gibbs energy; defect compound

1. Introduction

Since the chalcopyrite CuInSe₂ (CIS) was first synthesized in 1953, the Cu-In-Se ternary system has attracted considerable attention due to its application as an absorber material in solar cells. CIS-based cells currently hold the world-record energy conversion efficiency (19.5%, AM 1.5 G, 100 mW/cm²) for thin film technologies [1]. This compound has a large homogeneity range of composition and complicated phase relationships with the other phases. A small deviation in composition about the stoichiometry or the existence of secondary phases produces large changes in CIS material properties and thus its device characteristics. There is a lack of reliable thermodynamic data for the ternary compounds in the Cu-In-Se system. Unfortunately these properties are essential to understanding reaction pathways to synthesis of CIS and development of novel processes to fabricate cost-effective high-quality CIS films.

Common experimental measurements of the thermodynamic properties cannot be directly used to

estimate the Gibbs energy of these ternary compounds as it is not easy to know their corresponding compositions due to the large homogeneity range of the ternary compounds as shown in Fig. 1.

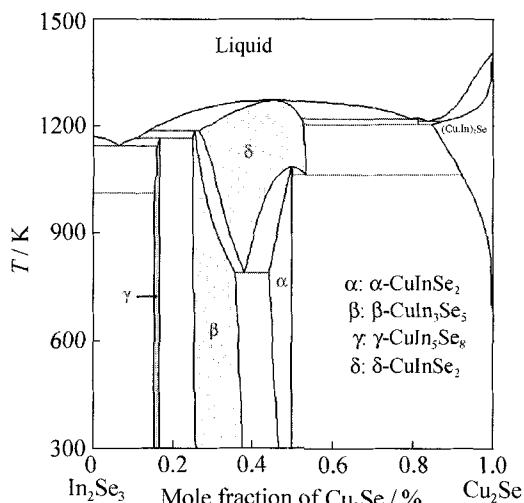


Fig. 1. Pseudo-binary In₂Se₃-Cu₂Se phase diagram [2].

In this work, a set of thermodynamic descriptions for the dominant ternary compounds in the Cu-In-Se

system is established by integrating the available information, which includes

(1) Experimental measurements of the thermodynamic properties of the Cu-In-Se ternary compounds.

(2) Experimental measurements of phase equilibria including Cu-In-Se ternary compounds.

(3) Established thermodynamic model of the three sub-binaries, i.e., Cu-Se, Cu-In and In-Se.

(4) *Ab initio* calculation on the defect formation energy in the Cu-In-Se ternary compounds.

2. Experimental

2.1. Ternary compounds

Four ternary compounds $\text{Cu}_{13}\text{In}_3\text{Se}_{11}$, CuInSe_2 , CuIn_3Se_5 and CuIn_5Se_8 , located on the $\text{Cu}_2\text{Se}-\text{In}_2\text{Se}_3$ pseudo-binary section (Fig.1), were identified as stable phases though several other compounds have been reported [2-4]. The CuInSe_2 , CuIn_3Se_5 and CuIn_5Se_8 phases have large homogeneity ranges. Under atmospheric pressure, the CuInSe_2 has two polymorphs separated by a first order transition between chalcopyrite (α) and sphalerite (δ) structures. The CuIn_3Se_5 has a tetragonal chalcopyrite-like structure and the CuIn_5Se_8 has a hexagonal structure. Interestingly, it was found that another phase often co-exists with a hexagonal CuIn_5Se_8 . This co-existing phase could be a trigonal [5] or tetragonal [6] structure. The $\text{Cu}_{13}\text{In}_3\text{Se}_{11}$ is reported as a line compound [2], which is stable within the narrow temperature range of 923-947°C.

2.2. Thermodynamic properties

Only few thermodynamic data are available for CuInSe_2 compounds. The heat capacity of CuInSe_2 was measured by Boehnke *et al.* using the pulsed and semi-adiabatic calorimetric techniques, but only at very low temperatures (< 300 K) [7]. The literature values of the enthalpy of formation of CuInSe_2 at 298 K are summarized in Table 1. No thermodynamic information is available concerning the CuIn_3Se_5 and CuIn_5Se_8 compounds yet.

Electro-motive force (EMF) measurements were performed by Ider [8] to extract Gibbs energy information of ternary compounds (e.g., CuInSe_2 ,

CuIn_3Se_5 , and CuIn_5Se_8) from the appropriate galvanic cell reactions. It is noted that since the exact composition of the participating ternary compounds is generally unknown and may be far from the stoichiometry, the resulting thermodynamic properties directly calculated from cell reactions may not be quite reliable.

Table 1. Literature values of the standard formation enthalpy (ΔH_f^\ominus) and energy (ΔE_f^\ominus) of α - CuInSe_2

$-\Delta H_f^\ominus / (\text{kJ}\cdot\text{mol}^{-1})$	Method	Reference
267.4	Mass Spectrometry	[9]
260.2	Calculation	[10]
280.0	Calculation	[11]
189.8	Calculation	[12]
204.4	Calculation	[13]
$\Delta E_f^\ominus / (\text{kJ}\cdot\text{mol}^{-1})$	Method	Reference
190.30	<i>ab initio</i>	[14]

2.3. Phase diagrams

The phase diagram of $\text{Cu}_2\text{Se}-\text{In}_2\text{Se}_3$ pseudo-binary section [15-17] and projection of liquidus surface [5, 7, 15-16, 18] have been reported by several authors. These phase diagrams, however, are quite divergent and thus very difficult to assess. Gödecke *et al.* reported a series of phase diagrams of the Cu-In-Se system based on thorough experiments using more than 240 alloys [2-4], where the phase diagrams, including a projection of liquidus surfaces, a projection of four-phase plane, three isothermal sections and ten isopleths, are self-consistent.

3. *Ab initio* calculation on the ternary Cu-In-Se compounds

The formation energies of different point defects in various Cu-In-Se ternary compounds were calculated by Zhang [14] using an *ab initio* method. The existence of a series of unusual ordered defect compounds (ODC) along $\text{Cu}_2\text{Se}-\text{In}_2\text{Se}_3$ section and their large off-stoichiometry are explained by the particularly low formation energy of the $(2V_{\text{Cu}}+\text{In}_{\text{Cu}})$ defect pair in these compounds.

The CuIn_3Se_5 and CuIn_5Se_8 can be considered as ODC's of CuInSe_2 and formed by the reaction

$n(\text{CuInSe}_2) + m(\text{In}) \rightarrow \text{Cu}_{(n-3m)}\text{In}_{(m+n)}\text{Se}_{2n} + 3m(\text{Cu})$ (1)
 where $n = 2.5$, $m = 0.5$ for CuIn_3Se_5 and $n = 4$, $m = 1$ for CuIn_5Se_8 . The energy change of the reaction ΔE_r is calculated by

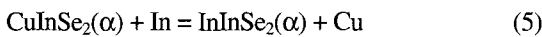
$$\Delta E_r = \Delta E_{\text{neu}} + \Delta E_{\text{int}} + \Delta E_{\text{ord}} \quad (2)$$

where ΔE_{neu} is the formation energy of non-interacting neutral defects, ΔE_{int} is the intra-pair interaction energy, and ΔE_{ord} is the pair-pair ordering energy. The formation energies of CuIn_3Se_5 and CuIn_5Se_8 compounds can then be calculated by

$$\Delta E_{\text{CuIn}_3\text{Se}_5}^f = 2.5\Delta E_{\text{CuInSe}_2}^f + 0.5E_{\text{In}} - 1.5E_{\text{Cu}} + \Delta E_r(\text{CuIn}_3\text{Se}_5) \quad (3)$$

$$\Delta E_{\text{CuIn}_5\text{Se}_8}^f = 4\Delta E_{\text{CuInSe}_2}^f + E_{\text{In}} - 3E_{\text{Cu}} + \Delta E_r(\text{CuIn}_5\text{Se}_8) \quad (4)$$

As the defect compounds are related to the end-members in the sub-lattice model, their formation energies are used to estimate Gibbs energy of the other end-members besides that corresponding to the stoichiometric composition. It can largely reduce the arbitrary aspects of the model parameters. For example, the formation energy of In_{Cu} is defined as the energy change of the reaction.



$\text{InInSe}_2(\alpha)$ is regarded as an end-member in the sub-lattice model of $\text{CuInSe}_2(\alpha)$ and its Gibbs energy can be estimated from the formation energy of In_{Cu} .

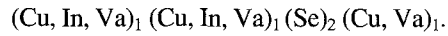
4. Establishment of thermodynamic descriptions

In this work, sub-lattice models [19] are used to describe thermodynamic properties of the ternary compounds. Unlike conventional thermodynamic optimization evaluating model parameters from abundant sources of phase diagrams and thermodynamic experiments, only one set of data was selected for this work to avoid the possible confusion caused by randomly mixing the divergent data for such a complicated system.

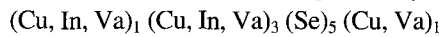
4.1. Sub-lattice model for different ternary compounds

The α - CuInSe_2 belongs to the family of I-III-VI₂

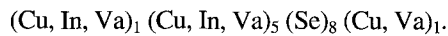
chalcopyrite semiconductors whose structure is similar to the zinc-blende structure where each of the two cations (Cu and In) is coordinated by four anions (Se), but the Se is coordinated by (2Cu + 2In) with different nearest-neighbors. The Se deficiency is mainly caused by Cu occupying an interstitial position [14]. The sub-lattice structure of α - CuInSe_2 is thus considered as:



Calculating Gibbs energy of this phase described by a sub-lattice model requires the information of the Gibbs energy for 18 end-members, e.g. $\text{Cu}_1\text{In}_1\text{Se}_2\text{Va}_1$, $\text{Cu}_1\text{Cu}_1\text{Se}_2\text{Va}_1$ and $\text{Va}_1\text{Cu}_1\text{Se}_2\text{Va}_1$. In the same manner, the sub-lattice structures of CuIn_3Se_5 and CuIn_5Se_8 are expressed by



and



The δ - CuInSe_2 is a disordered phase of α - CuInSe_2 with a sphalerite structure where the two metals (Cu and In) can be replaced by each other much more easily than in α - CuInSe_2 to achieve almost random mixing. The sub-lattice structure of the δ - CuInSe_2 is considered as $(\text{Cu}, \text{In}, \text{Va})_2(\text{Se})_1(\text{Se}, \text{Va})_2$ to keep its composition close to the section of Cu_2Se - In_2Se_3 , as observed experimentally.

4.2. Evaluation of Gibbs energies of end-members in the sub-lattice model

4.2.1. Gibbs energy of formation of $\text{CuInSe}_2(\alpha)$

To estimate the Gibbs energy of formation of $\text{CuInSe}_2(\alpha)$, the EMF results reported by Ider [8] were utilized. Three different kinds of galvanic cells were designed such as

Cell I: $\text{W}, \text{In}(\text{l}), \text{In}_2\text{O}_3(\text{s}) // \text{YSZ} // \text{In}_2\text{O}_3(\text{s}), \text{Cu}_2\text{Se}(\beta), \text{Cu}(\text{s}), \text{CuInSe}_2(\alpha \text{ or } \delta), \text{C}, \text{W}$.

Cell II: $\text{W}, \text{In}(\text{l}), \text{In}_2\text{O}_3(\text{s}) // \text{YSZ} // \text{In}_2\text{O}_3(\text{s}), \text{Cu}_1\text{In}_3\text{Se}_5(\text{s}), \text{CuInSe}_2(\alpha \text{ or } \delta), \text{C}, \text{W}$.

Cell III: $\text{W}, \text{In}(\text{l}), \text{In}_2\text{O}_3(\text{s}) // \text{YSZ} // \text{In}_2\text{O}_3(\text{s}), \text{Cu}_1\text{In}_5\text{Se}_8(\text{s}), \text{Cu}_1\text{In}_3\text{Se}_5(\text{s}), \text{C}, \text{W}$.

The overall reaction of cell I is expressed as



In this work, the composition of CuInSe_2 is assumed to be in stoichiometry because the CuInSe_2 phase has a relatively narrow composition range

when it is in equilibrium with $\text{Cu}_2\text{Se}(\beta)$. Thus if the solubility of In in $\text{Cu}_2\text{Se}(\beta)$ phase is negligible, the Gibbs energy of formation of $\text{CuInSe}_2(\alpha)$ can be directly calculated by

$$G_{\text{CuInSe}_2(\alpha)}^f = \Delta G_{\text{R}(\text{cell I})} + 2G_{\text{Cu}_2\text{Se}(\beta)}^f \quad (7)$$

and ΔG_{R} was reported by Ider [8] as

$$\Delta G_{\text{R}} = -99520 + 54.50T \quad \text{J/mol (949-1044 K)} \quad (8)$$

From assessment of the Cu-Se system [20], the $G_{\text{Cu}_2\text{Se}(\beta)}^f$ is expressed by

$$G_{\text{Cu}_2\text{Se}(\beta)}^f = -60221.86 - 95.47T + 10.21T\ln(T) - 0.01T^2 + 3.70 \times 10^{-6}T^3 - 53288.13/T \quad \text{J/mol} \quad (9)$$

Plugging Eqs. (8) and (9) into Eq. (7) yields

$$G_{\text{CuInSe}_2(\alpha)}^f = -209963.72 - 36.43T + 20.41T\ln(T) - 0.02T^2 + 7.40 \times 10^{-6}T^3 - 106576.26/T \quad \text{J/mol} \quad (10)$$

The standard enthalpy of formation of $\text{CuInSe}_2(\alpha)$ at 298 K calculated from $G_{\text{CuInSe}_2(\alpha)}^f$ obtained by Eq. (10) is around 218.50 kJ/mol, which is similar to the literature values listed in Table 1.

4.2.2. Estimation of Gibbs energy of $\text{CuInSe}_2(\delta)$, CuIn_3Se_5 and CuIn_5Se_8

As mentioned before, EMF experimental results can provide only a rough estimation of the Gibbs energy of formation of $\text{CuInSe}_2(\delta)$, CuIn_3Se_5 and CuIn_5Se_8 mainly because of their non-stoichiometric composition during cell reactions. Ider [8] reported the Gibbs energy change of reaction for cell I through III as

$$G_{\text{R}(\text{Cell I})} = -89520 + 45.10T \quad \text{J/mol (1055-1150 K)} \quad (11)$$

$$G_{\text{R}(\text{Cell II})} = 90160.16 - 110.77T \quad \text{J/mol (868-1045 K)} \quad (12)$$

$$G_{\text{R}(\text{Cell III})} = 109180 - 125.90T \quad \text{J/mol (1054-1197 K)} \quad (13)$$

In the exactly same manner as $\text{CuInSe}_2(\alpha)$, the Gibbs energies of formation of other ternary compounds (i.e., $\text{CuInSe}_2(\delta)$, CuIn_3Se_5 and CuIn_5Se_8) were estimated as

$$G_{\text{CuInSe}_2(\delta)}^f = -209963.72 - 145.83T + 20.41T\ln(T) - 0.02T^2 + 7.40 \times 10^{-6}T^3 -$$

$$106576.26/T \quad \text{J/mol} \quad (14)$$

$$G_{\text{CuIn}_3\text{Se}_5}^f = -438646.71 - 1794.61T +$$

$$259.98T\ln(T) - 0.09844T^2 + 2.404 \times 10^{-5}T^3 - 528546.24/T \quad \text{J/mol} \quad (15)$$

$$G_{\text{CuIn}_5\text{Se}_8}^f = -717569.69 - 3404.57T + 499.55T\ln(T) - 0.1478T^2 + 4.0666 \times 10^{-5}T^3 - 1163668.00/T \quad \text{J/mol} \quad (16)$$

On the other hand, the Gibbs energy of CuIn_3Se_5 and CuIn_5Se_8 at their stoichiometry can also be estimated by *ab initio* calculation where they are considered as ordered defect compounds of CuInSe_2 . In the same pattern as Eqs. (3) and (4), the Gibbs energy of formation of CuIn_3Se_5 and CuIn_5Se_8 are expressed by

$$\Delta G_{\text{CuIn}_3\text{Se}_5}^f = 2.5\Delta G_{\text{CuInSe}_2}^f + 0.5G_{\text{In}} - 1.5G_{\text{Cu}} + \Delta G_r(\text{CuIn}_3\text{Se}_5) \quad (17)$$

$$\Delta G_{\text{CuIn}_5\text{Se}_8}^f = 4\Delta G_{\text{CuInSe}_2}^f + G_{\text{In}} - 3G_{\text{Cu}} + \Delta G_r(\text{CuIn}_5\text{Se}_8) \quad (18)$$

In this work, the volume and entropy change for the defect formation reaction is assumed to be negligible and thus the values of $\Delta G_r(\text{CuIn}_3\text{Se}_5)$ and $\Delta G_r(\text{CuIn}_5\text{Se}_8)$ are identical to $\Delta E_r(\text{CuIn}_3\text{Se}_5)$ and $\Delta E_r(\text{CuIn}_5\text{Se}_8)$ calculated by equation (3) and (4) where the values of ΔE_{neu} , ΔE_{int} , and ΔE_{ord} are taken from [14] as shown in Table 2. The value of $\Delta G_{\text{CuInSe}_2(\alpha)}^f$ is directly calculated from equation (10).

Table 2. Parameters used to calculate ΔE^f of CuIn_3Se_5 and CuIn_5Se_8

Compound	ΔE_{neu}	ΔE_{int}	ΔE_{ord}	ΔE_r
CuIn_3Se_5	2.27	-2.105	-0.225	-0.06
CuIn_5Se_8	4.54	-4.21	-0.43	-0.10

In summary, the estimated Gibbs energies of formation from *ab initio* study are

$$G_{\text{CuIn}_3\text{Se}_5}^f = -557341.00 - 337.26T + 51.036T\ln(T) - 0.0551T^2 + 1.85 \times 10^{-5}T^3 - 266441.00/T \quad \text{J/mol} \quad (19)$$

$$G_{\text{CuIn}_5\text{Se}_8}^f = -892788.00 - 538.09T + 81.657T\ln(T) - 0.0881T^2 + 2.96 \times 10^{-5}T^3 - 426305.00/T \quad \text{J/mol} \quad (20)$$

4.2.3. Estimation of Gibbs energy of other end-members

The Gibbs energy of other end-members in the α -CuInSe₂, β -CuIn₃Se₅, γ -CuIn₅Se₈ compounds is estimated using defect formation energy calculated by Zhang [14] according the reaction to form point defect such as (5).

For example,

$$G_{\text{Va}_1\text{In}_1\text{Se}_2\text{Va}_1}^0 = G_{\text{CuInSe}_2(\alpha)}^0 + E_{\text{Va}(\text{Cu})} - G_{\text{Cu}}^0 \quad (21)$$

$$G_{\text{Cu}_1\text{In}_1\text{Se}_2\text{Cu}_1}^0 = G_{\text{CuInSe}_2(\alpha)}^0 + E_{\text{Cu}(i)} + G_{\text{Cu}}^0 \quad (22)$$

4.2.4. Optimization of parameters in Gibbs energy expressions

The Gibbs energy expressions of the ternary compounds are adjusted to satisfy the relevant experimental phase relationships reported in Refs. [2-4]. The results are compared with the available data. It is believed that the complicated phase relationships may play an important role in controlling the chemical potentials of these compounds within a reasonable range. The parameters for Gibbs energy are optimized as

$$G_{\text{CuInSe}_2(\alpha)}^0 = -251102.38 - 688.51T - 135.95T\ln(T) + 0.03T^2 - 3.47 \times 10^{-6}T^3 - 265806.00/T \quad \text{J/mol} \quad (23)$$

$$G_{\text{CuInSe}_2(\delta)}^0 = -186607.3408 + 505.39T - 114.87T\ln(T) \quad \text{J/mol} \quad (24)$$

$$G_{\text{CuIn}_3\text{Se}_5}^0 = -550466.88 + 1175.69T - 249.24T\ln(T) - 0.00102T^2 - 1.22 \times 10^{-7}T^3 - 582645.00/T \quad \text{J/mol} \quad (25)$$

$$G_{\text{CuIn}_5\text{Se}_8}^0 = -940623.58 + 1916.46T - 389.81T\ln(T) + 7.32 \times 10^{-6}T^2 - 2.90 \times 10^{-7}T^3 - 1006060.00/T \quad \text{J/mol} \quad (26)$$

The optimized Gibbs energy (G^0) and Gibbs en-

ergy of formation (ΔG^f) are compared with the results of EMF experiment and *ab initio* calculation, as represented in Fig. 2.

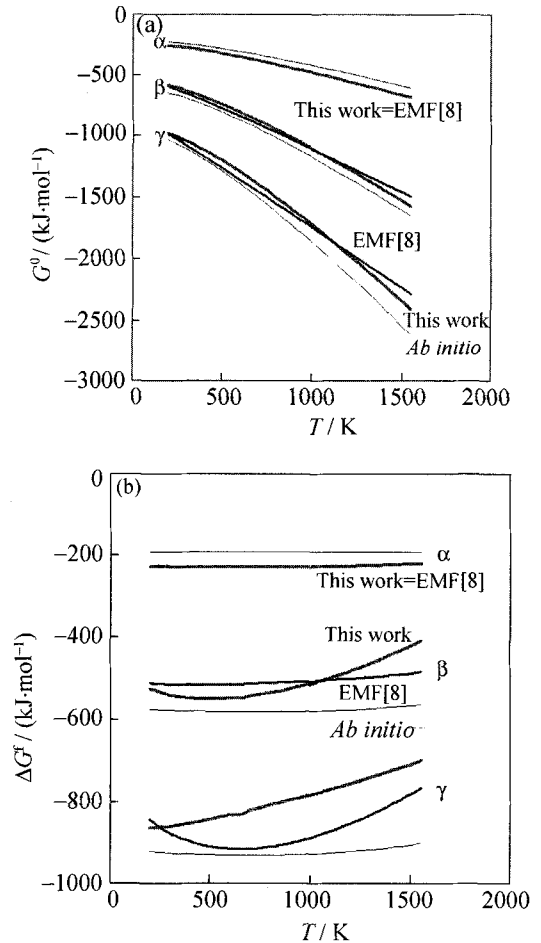
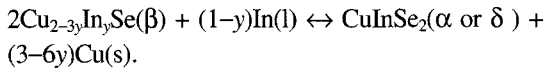


Fig. 2. Optimized (a) Gibbs energy (G^0), and (b) Gibbs energy of formation (ΔG^f) of α -CuInSe₂, β -CuIn₃Se₅ and γ -CuIn₅Se₈ compared with those estimated from EMF experiments and *ab initio* calculation.

5. Conclusions

The EMF experimental results, *ab initio* calculation and phase equilibrium data were successfully combined to establish the reliable descriptions of Gibbs energy for ternary compounds in the Cu-In-Se system. The EMF result was directly adopted only for the estimation of Gibbs energy of CuInSe₂(α) by

assuming the stoichiometric composition. The influence of the solubility of indium in $\text{Cu}_2\text{Se}(\beta)$ on the electronic transfer and thus the Gibbs energy of formation was also considered. The reaction was considered as



The number of electron to be transferred is $(3-6y)$ to form one mole of $\text{CuInSe}_2(\alpha)$. The difference of Gibbs energy of formation between $\text{Cu}_{2-3y}\text{In}_y\text{Se}(\beta)$ and Cu_2Se is calculated using the formation energy of the defect pair $(2V_{\text{Cu}}+\text{In}_{\text{Cu}})$ in Ref. [14]. This approach, however, yields an unreasonable value of

enthalpy of formation for CuInSe_2 at 298.15 K, whereas the calculation using $G_{\text{Cu}_2\text{Se}(\beta)}^f$ expression in Eq. (9) shows the reasonable results, which are in a good agreement with most of literature values.

The comparison of the optimized Gibbs energy of the $\text{CuInSe}_2(\delta)$, CuIn_3Se_5 and CuIn_5Se_8 with that estimated by EMF experiment and *ab initio* calculation demonstrates reasonable agreement. The phase relationships concerning these ternary compounds follow the experimental isothermal section of the Cu-In-Se system at 500, 800, and 900 °C shown in Figs. 3-5, respectively. The obtained standard enthalpy of formation of CuInSe_2 is close to that reported

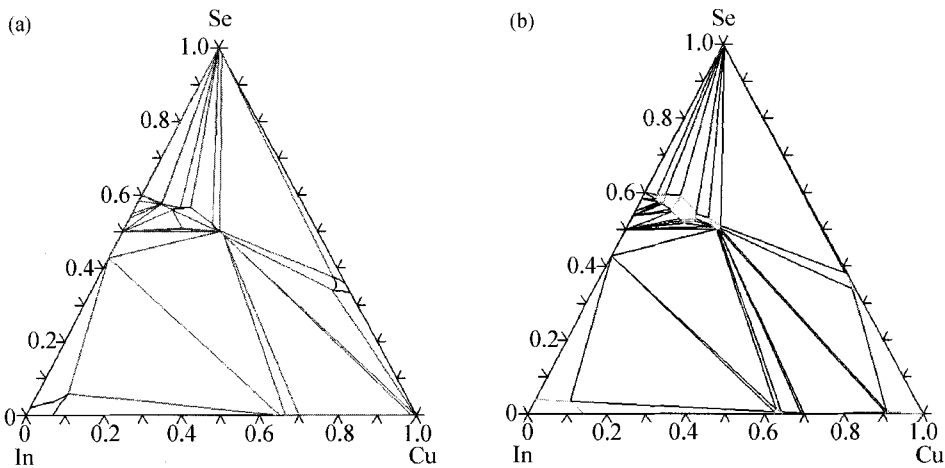


Fig. 3. Isothermal sections of Cu-In-Se at 500 °C: (a) calculation and (b) experimental evaluation [4].

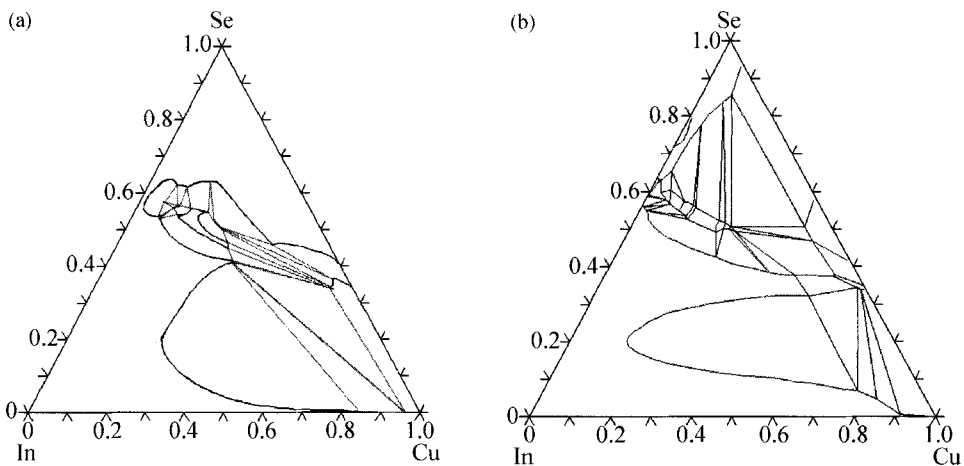


Fig. 4. Isothermal sections of Cu-In-Se at 800 °C: (a) calculation and (b) experimental evaluation [4].

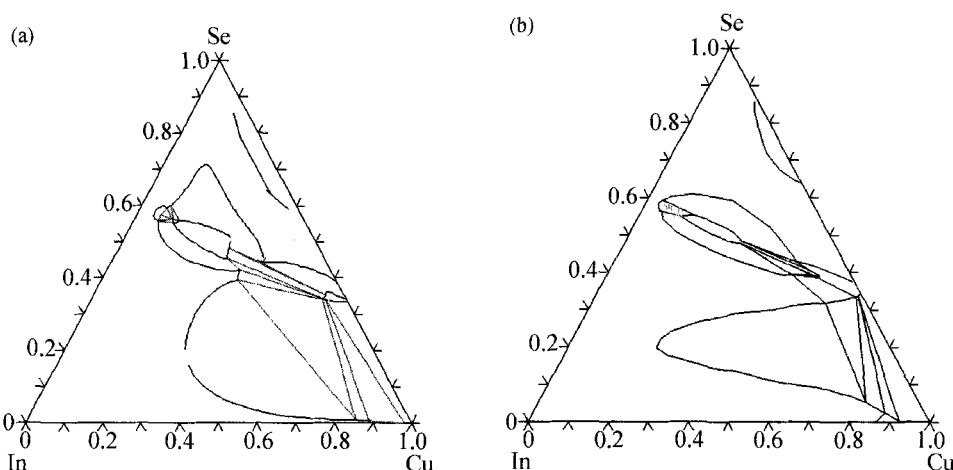


Fig. 5. Isothermal sections of Cu-In-Se at 900 °C: (a) calculation and (b) experimental evaluation [4].

in the literatures. It can be concluded that a set of reliable Gibbs energy expression was obtained, although its precision would be further improved with additional experimental and theoretical study.

Acknowledgements

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