Journal of Alloys and Compounds 604 (2014) 363–372

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Thermochemistry of the Cu_2Se–In_2Se_3 system

M. Ider [a,*], R. Pankajavalli [b], W. Zhuang [c], J.Y. Shen [d], T.J. Anderson [e]

[a] Department of Chemical Engineering, Usak University, 64200 Usak, Turkey
[b] Thermodynamics and Kinetics Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India
[c] General Research Institute for Nonferrous Metals, Grirem Advanced Materials Co., Ltd., Beijing 100088, China
[d] General Research Institute for Nonferrous Metals, Beijing 100088, China
[e] Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, United States

ARTICLE INFO

Article history:
Received 20 February 2014
Received in revised form 15 March 2014
Accepted 17 March 2014
Available online 1 April 2014

Keywords:
System Cu_2Se–In_2Se_3
Phase diagram
Gibbs energy of formation
Copper indium di-selenide
Solid electrolyte EMF measurements
Thermodynamic assessment

ABSTRACT

Solid state electrochemical cells were employed to obtain standard Gibbs energy of formation of $CuInSe_2$ as well as the temperature and enthalpy of the α to δ-$CuInSe_2$ transformation in the Cu_2Se–In_2Se_3 pseudo-binary system. The reversible EMF data of the following solid-state electrochemical cell were measured:

$$Pt, In(l), In_2O_3(s) \,\|YSZ\|\, In_2O_3(s), Cu_2Se(s), Cu(s), CuInSe_2(\alpha \text{ or } \delta), C, Pt \quad \text{Cell I}$$

The calculated standard molar Gibbs energy of formation of α and δ-$CuInSe_2$ from measured data are given by

$$\Delta G_f^\circ\ CuInSe_2\ (\alpha) \pm 0.0003 = 0.0051T\ (K) - 220.92\ kJ/mol\ (949–1044\ K)$$

$$\Delta G_f^\circ\ CuInSe_2\ (\delta) \pm 0.0004 = -0.0043T\ (K) - 210.92\ kJ/mol\ (1055–1150\ K)$$

The α to δ phase transition temperature T_{trans} and the enthalpy of transition ΔH°_{trans} for $CuInSe_2$ were determined to be 1064 K and 10.0 kJ/mol respectively. ΔS°_{trans} was calculated as 9.4 J/mol K.

The thermodynamic and phase diagram data in the Cu_2Se–In_2Se_3 pseudo-binary system were critically assessed. A self consistent set of thermochemistry and phase diagram data was obtained with the help of measured data. The liquid phase along the Cu_2Se–In_2Se_3 pseudo-binary was calculated with the Redlich–Kister model. The β-$Cu_1In_3Se_5$ and γ-$Cu_1In_5Se_8$ phases were represented by the sub-regular model. The ordered non-stoichiometric α-$CuInSe_2$ and δ-$CuInSe_2$ phases were modeled by using a three-sublattice formalism. The calculated phase diagram and thermochemical data show reasonable agreement.

1. Introduction

$CuInSe_2$ (CIS) is becoming one of the most promising materials for solar cell applications. Its band gap (1.04 eV) and good absorption coefficient ($10^5\ cm^{-1}$) for solar spectrum make this material an excellent candidate for a solar cell absorber layer. Although the electrical properties of CIS are relatively well-known, some ternary phase diagram regions were not completely studied experimentally. The knowledge of phase diagram and thermochemistry of CIS along with its constituent binaries will provide helpful information on the processing conditions and development of new thin film and bulk production methods. For the thermodynamic assessment of phase diagram, the phase stability and Gibbs energy of compounds are essential. According to the recent pseudo-binary diagram reported by Chang [1], four ternary compounds $CuInSe_2$, $Cu_2In_4Se_7$, $CuIn_3Se_5$ and $CuIn_5Se_8$ exist in the Cu_2Se–In_2Se_3 section. However; critically assessed Gibbs energy expressions are missing and the stability of the compounds are not experimentally established. For this reason, the thermochemical data for Cu_2Se–In_2Se_3 pseudo-binary region was assessed. Solid state galvanic cell experiments were performed to measure Gibbs energy data of selected ternary compounds and the pseudo-binary phase diagram was calculated by optimizing the experimental data.

2. Literature review

$CuInSe_2$ has two solid modifications separated by a first order transition between chalcopyrite and sphalerite structures. The δ-$CuInSe_2$ sphalerite phase is stable with a wide homogeneity range between the temperatures of 1090 and 1280 K. The low temperature α-$CuInSe_2$ phase crystallizes in the chalcopyrite form with a contracting homogeneity range at low temperature. The melting point $T_m(CuInSe_2) = 1254 \pm 5$ K and lattice constants ($a = 0.577$ nm $c = 1.156$ nm) of

* Corresponding author. Tel.: +90 27622121362720; fax: +90 2762212137.
E-mail address: muhsin.ider@usak.edu.tr (M. Ider).

http://dx.doi.org/10.1016/j.jallcom.2014.03.129
0925-8388/

$CuInSe_2$ were reported by Rigan et al. [2]. Mechkovski et al. [3] also studied the melting and phase transition temperatures. He determined the melting enthalpy of $CuInSe_2$ by DTA experiments as ΔH_{melt} = 83.6 kJ/mol.

Wei et al. [4] stated a first order transition for $CuInSe_2$ and calculated the order–disorder transition temperature as T_{tr} = 1125 ± 20 K, which is similar to the experimental value of 1083 K reported by Shay and Wernick [5].

Bachmann et al. [6] measured the low temperature $CuInSe_2$ heat capacity by pulsed calorimetry and semi-adiabatic techniques. He derived the entropy value at 298 K as S°_{298} = 1.5773 kJ/mol K and reported the Debye temperature for $CuInSe_2$. However, his heat capacity data is limited to only low temperature (<300 K).

Khriplovich et al. [7] measured the heat capacity of $CuIn_2Se_{3.5}$ at low temperatures with a vacuum adiabatic calorimeter. On the other hand, these results were not supported by structural analysis to check whether it was a single phase or two-phase sample.

A number of papers were also published stating the lattice parameters and stability of intermediate phases; however, some results are inconsistent. Range [8] reported the formation of a cubic high-pressure zincblende structure for $CuInSe_2$. Kotkata and Al-Kotb [9] reported lattice parameters of $CuInSe_2$. The lattice parameters of $Cu_1In_3Se_5$ were measured by Palatnik and Rogacheva [10]. Neuman [11] also reported the lattice parameters for $CuInSe_2$ and $CuGaSe_2$. Fearheiley and Bachmann [12] reported the lattice parameters of $CuInSe_2$ (a = 5.814 ± 0.003 Å and c = 11.63 ± 0.04 Å) and compared his results with Hahn et al.'s [13] results which were close (a = 5.782 Å c = 11.621 Å). He concluded that the lattice constant of $CuInSe_2$ and non-stoichiometric defect structures vary within its homogeneity range. This suggestion is supported by the fact that a few other authors also observed slightly different lattice parameters within homogeneous single-phase CIS.

Matsuhita et al. [14] determined the melting and transition points of I–III–VI compounds by DTA, including those for CIS. It was stated that enthalpies of fusion and transition depend on mean atomic weight and ionicity, that the melting point was influenced by the lattice strain. It was found that fusion and transition enthalpies of their solid solutions are much lower than the end members of their compounds.

Zargarova et al. [15] constructed the $CuInSe_2$–InSe phase diagram section and reported a transition temperature between α-$CuInSe_2$ and δ-$CuInSe_2$ at 1103 K. Two phase coexistence between $CuInSe_2$ and InSe was observed by micro-structural examination at low temperatures. An event at 1083 K that was attributed to cation ordering was reported. Above 868 K only liquid, L + α-$CuInSe_2$ and L + InSe stability were reported. No other experimental information is available for (α,δ)-$CuInSe_2$–In_2Se_3, and (α,δ)-$CuInSe_2$–In_4Se_3, (α,δ)-$CuInSe_2$–In_6Se_7. Aside from Zargarova's results, there is not much stability information about $Cu_1In_3Se_5$–In_xSe_y and $Cu_1In_5Se_8$–In_xSe_y (x = 1, 2, 4, 6; y = 1, 3, 7) systems.

In general, there is a lack of experimental data on the thermochemistry of CIS and related ternaries except a few estimation calculations. Mooney and Lamoreaux [16] reported the enthalpy of formation of $CuInSe_2$ and presented enthalpy data of binary associates. The Gibbs energy of formation data was also calculated using approximate equality equation by Lamoreaux et al. [17]. Neumann [18] also reported the heats of atomization for CIS and Nomura et al. [19] analyzed the mechanism of the phase change from $Cu_{2-x}Se$ to $CuInSe_2$ by the absorption of indium selenide. Some of literature enthalpy and transformation data are summarized in Tables 1 and 2.

A few studies on phase equilibrium in the Cu_2Se–In_2Se_3 pseudo-binary system have been reported. Cu_5InSe_4, $CuInSe_2$, $Cu_2In_4Se_7$, $CuIn_3Se_5$ and $CuIn_5Se_8$ are the most widely referred intermediate compounds. Many other compounds were also stated to exist between chalcopyrite and In_2Se_3 compositions in the pseudo-binary section. However, X-ray and structural data are not in good agreement and this region requires further structure studies and justification. There is not much thermodynamic data available on the stability of these ternary phases except the standard enthalpy and absolute entropy of formation, $\Delta H^{\circ}_{f,298}$ and S°_{298} of $CuInSe_2$.

A general review was published on production methods of CIS films by Rockett and Birkmire [20]. Production analysis and performance of photovoltaic devices based on CIS materials were discussed. Cahen and Noufi [21] summarized thermodynamic data available on CIS related compounds. Gibbs energies of compounds and species that are involved in preparation of CIS films were calculated. A number of possible formation reaction Gibbs energy and free energy function data, as well as formation enthalpy data are available in this paper.

Bachmann et al. [22] published a Cu_2Se–In_2Se_3 pseudo-binary phase diagram. He reported the congruent melting point for Cu_5InSe_4 as T = 943 °C with two eutectics at $x_{In_2Se_3}$ = 0.11 and $x_{In_2Se_3}$=0.17. Folmer et al. [23] studied the composition range greater than 50 mol% In_2Se_3 and suggested three new hexagonal phases in high In_2Se_3 region of Cu_2Se–In_2Se_3 pseudobinary.

Fearheiley et al. [24] reviewed the phase relations in the Cu–In–Se system and the crystal growth of single crystals. Cu–In, In–Se and Cu–Se phase diagrams were reported. He also reported the pseudo-binary section of Cu_2Se–In_2Se_3 containing the intermediate compounds $Cu_2In_4Se_7$ [25] $Cu_1In_3Se_5$ [26], $Cu_3In_5Se_9$ [27], Cu_5InSe_4 [22] and $CuIn_5Se_8$ [28]. The pseudo-binary section of Cu–$CuInSe_2$ was reported with a wide range of coexistence up to 900 K.

Fearheiley et al. [24] reported $Cu_2In_4Se_7$ as incongruently melting and $Cu_1In_3Se_5$ as congruent melting compounds. However, Schock [29] did not report a $Cu_2In_4Se_7$ phase although he reported an incongruent $CuIn_3Se_5$ intermediate. Schock [29] also stated that the solubility of excess Cu in $CuInSe_2$ is very small. A summary of collected phase diagram data from several references was presented.

Hanada et al. [30] studied the crystal structure of $CuIn_3Se_5$ by combination of electron and X-ray diffractions. He determined that $CuIn_3Se_5$ is a stable compound semiconductor, which is different from CIS and not a vacancy ordered compound or a defect chalcopyrite. He measured lattice parameters by XRD at 700 °C as a = 0.574 nm and c = 1.1518 nm. Schumann et al. [31] measured diffraction patterns of $CuIn_2Se_{3.5}$ compound. It was claimed that $CuIn_2Se_{3.5}$ has a structure type with defects that is a derivative of chalcopyrite. However, the lattice parameters reported by Schumann et al. [31] for $CuIn_2Se_{3.5}$ do not agree with two earlier reports. The fact that the diffraction patterns of $Cu_2In_4Se_7$ are very similar to CIS with the chalcopyrite structure suggest a possibility that $Cu_2In_4Se_7$ composition range may lie in a homogeneity range or in a two phase region of $CuInSe_2$–$Cu_1In_3Se_5$ or $CuInSe_2$ and some other composition.

Koneshova et al. [32] constructed a Cu_2Se–In_2Se_3 phase diagram from previously published results and suggested the co-existence of $CuInSe_2$ and $Cu_1In_3Se_5$ phases in the phase diagram. Koneshova et al. [32] also claimed that some of the ternary phases, which were previously assumed to be stable, in fact were two phase regions. Instead of the $Cu_2In_4Se_7$ modification, a stable phase corresponding to the $Cu_1In_3Se_5$ composition was outlined in the phase diagram. Two phase coexistence between the $CuInSe_2$ and $Cu_1In_3Se_5$ modifications was also assumed. On the other hand the limits of high temperature stable modification were greater than other reports and $Cu_1In_3Se_5$ phase was reported to be stable only below 900 °C. Additionally, a thin range of coexistence between $Cu_1In_3Se_5$ and possibly a compound, which lies in the composition range of $Cu_1In_5Se_8$ compositions, was depicted. However, the limits seem too narrow.

Boehnke and Kuhn [33] emphasized that numerous compounds were stated in the literature to exist along Cu_2Se–In_2Se_3 line and the reported data showed evident differences in structure and homogeneity ranges and thermal behavior. Boehnke and Kuhn [33] concluded from X-ray, EPMA (electron microprobe analysis), optical microscopy and DTA measurements that only 4 ternary phases with extended homogeneity range were stable. He verified δ (sphalerite) phase first time by high temperature X-ray diffraction. It was asserted that a beta phase extending between $x_{In_2Se_3}$ = 0.67 and $x_{In_2Se_3}$ = 0.80 crystallizes in an ordered chalcopyrite-like defect structure. From a comparison of X-ray data with those of literature data for $Cu_2In_4Se_7$, $Cu_1In_3Se_5$, $Cu_8In_{18}Se_{32}$, and $Cu_7In_{19}Se_{32}$, he concluded that all belong to a β ($Cu_1In_3Se_5$) phase. He also reports that the γ ($Cu_1In_5Se_8$) phase has a typical layered structure with hexagonal and trigonal modifications along with strong lattice parameter dependence on compositions. This approach with respect to limits of stabilities of ternary compounds seems reasonable.

Godecke et al. [34] published a detailed paper about phase diagram of CIS and related binaries. His results are consistent with Boehnke et al.'s [33] results, except the limits of two phase region of high temperature sphalerite phase and β

Table 1
Comparison of α-$CuInSe_2$ to δ-$CuInSe_2$ enthalpy of transformation data.

Solid phase	T_{trans} (K)	ΔH°_{trans} (kJ/mol)	References
$CuInSe_2$	1058–1083	–	[47]
	1083	–	[48,3]
	1125	10.0	[4]
	–	15.9	[49]
	1095–1099	16.2	[14]
	1064	10.0	This work (Cell I)
	1050	21.7	[35]

Solid phase	Melting temperature (K)	$\Delta H_{melting}$ (kJ/mol)	Heat of fusion (kJ/mol)	$\Delta S_{melting}$ (kJ/mol)	References
$CuInSe_2$	1259	83.6	–	0.0664	[3]
	1269	–	88.62	–	[14]