

Phase Equilibria and Thermodynamic Basis for the Cd-Se and Pb-Se Binary Systems

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Using the CALculation of PHase Diagrams (CALPHAD) method, the phase equilibria and thermodynamic basis for the Cd-Se and Pb-Se binary systems are critically studied in this work. The associated solution model is adopted for the liquid phases so as to reflect the V-shaped enthalpies of mixing, the abrupt change in activity plots, and the sharp maxima for the liquidus around intermediate phases. Due to the negligible solubilities in CdSe and PbSe, these two binary compounds are treated as stoichiometric phases. Solid Se, which has a hexagonal structure, is considered to be free of solubility with respect to Cd and Pb. The thermodynamic description provided in this work allows the experimental data to be well represented, thus providing a fundamental basis for semiconductor research.

Key words: Cd-Se, Pb-Se, thermodynamics, CALPHAD, associated solution model

INTRODUCTION

CdSe, having a wurtzite crystal structure, is an important semiconductor that has found wide applications in such fields as optoelectronic devices, laser diodes, nanosensing, and biomedical imaging.¹ In addition, this material is also being explored for use in high-efficiency solar cells and thin-film transistors.^{2–4} PbSe, characterized by a NaCl crystal structure, has been used to manufacture infrared detectors for thermal imaging.⁵ To fully harness the potential of these two materials, thorough and in-depth studies on their phase equilibria, phase diagrams, and thermodynamic basis are essential for both industry and academia, enabling significant decrease in the time and cost of semiconductor design and process optimization as well as improving modeling capabilities.

It is known that binary melts containing Se demonstrate anomalies in concentration-related properties, such as V-shaped enthalpies of mixing, sharp maxima for the liquidus curve around binary intermediate compounds, and abrupt changes in activity plots. There exist abundant experimental studies for the Cd-Se and Pb-Se systems in the literature. Assuming the associated solution model for the melts and treating the two binary intermediate compounds as stoichiometric phases, the thermodynamics of these two binary systems were systematically studied,^{6–8} the results of which allow the great majority of phase equilibria and thermochemical data to be well represented. However, the thermodynamic descriptions are based on the use of lattice stabilities of each phase, relative to the liquid phase, and the interaction parameters are not formulated within the current CALPHAD framework.⁹ There is thus a necessity to provide contemporary thermodynamic descriptions based on the Gibbs free energies of pure elements in the CALPHAD

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community, which can be used to predict phase stabilities under manufacture or service conditions for industry as well as academia.

LITERATURE INFORMATION

Cd-Se System

The Cd-Se binary system is fairly simple, and only one intermediate compound (CdSe) has been identified, which melts congruently and features negligible solubilities for Cd and Se. Studies on phase equilibria and thermochemical properties for this binary system are abundant, and the reported values are generally in good agreement. The liquidus data have been characterized by Reisman et al.¹⁰ and Sysoev et al.¹¹ The temperature and compositions for the monotectic invariant reaction in the CdSe-Se portion were reported by Reisman et al.¹⁰ The congruently melting temperature for CdSe was extensively identified by Reisman et al.,¹⁰ Sysoev et al.,¹¹ Chikashige and Hikosaka,¹² and Mason and O'Kane.¹³ The enthalpies of formation of CdSe were reported by Deore et al.,¹⁴ Wosten,¹⁵ Korneeva et al.,¹⁶ Terpilowski and Ratajczak,¹⁷ Seacrist and Munir,¹⁸ Sigai and Wiedemeir,¹⁹ Vardi et al.,²⁰ Goldfinger and Jeunehomme,²¹ and Shiozawa and Jost.²² The entropies of CdSe at 298 K were reported by Wosten,¹⁵ Terpilowski and Ratajczak,¹⁷ and Goldfinger and Jeunehomme.²¹ The partial vapor pressures of Cd and Se₂ in equilibrium with the liquid + CdSe two-phase mixtures at various temperatures were measured by Shiozawa and Jost²³ and Burmeister and Stevenson.²⁴ Such partial pressures are a measure of the chemical potentials of Cd and Se in the liquid phase, i.e., in an equilibrium state with CdSe and the gas, and can thus be converted into activities of Cd and Se in the liquid phase along the liquidus with the following relations:

$$a_{\text{Cd}} = \frac{p_{\text{Cd}}}{p_{\text{Cd}}^0}, \quad (1)$$

$$a_{\text{Se}} = \sqrt{\frac{p_{\text{Se}_2}}{p_{\text{Se}_2}^0}}, \quad (2)$$

where p_{Cd} and p_{Se_2} are the equilibrium partial pressures of Cd and Se₂ over the liquid + CdSe two-phase mixtures, respectively; p_{Cd}^0 and $p_{\text{Se}_2}^0$ are the equilibrium pressures of Cd and Se₂ over pure liquid Cd and pure liquid Se, respectively; a_{Cd} and a_{Se} are the activities of Cd and Se in the liquid phase, respectively. The relations of p_{Cd}^0 and $p_{\text{Se}_2}^0$ against temperature have been well established and can be obtained through Refs. 25, 26 as

$$\log p_{\text{Cd}}^0(\text{bar}) = -5317/T + 5.123, \quad (3)$$

$$\log p_{\text{Se}_2}^0(\text{bar}) = -7712/T + 19.346 - 1.7055 \ln(T). \quad (4)$$

Pb-Se System

The Pb-Se binary phase diagram shares a similar topology to the Cd-Se system, in which an intermediate phase, PbSe, is congruently formed. The binary Pb-Se system has been extensively studied. The liquidus curve was measured by Pelabon and Gernez,²⁷ Friedrich and Leroux,²⁸ Nozato and Isaki,²⁹ Pelzel,³⁰ Seidman et al.,³¹ Seidman,³² Miller and Komarek,³³ and Schneider and Guillaume.³⁴ The temperature and compositions for the monotectic invariant reaction were identified by Nozato and Isaki²⁹ and Seidman,³² and the eutectic reaction in the Pb-PbSe portion was reported by Greenwood and Worner.³⁵ The congruently melting temperatures for PbSe were reported by Friedrich and Leroux,²⁸ Nozato and Isaki,²⁹ Seidman et al.,³¹ and Miller and Komarek.³³ The enthalpies of formation of PbSe were reported by Deore et al.,¹⁴ Hajiev,³⁶ Boone and Kleppa,³⁷ Finch and Wagner,³⁸ Sadykov and Semenkovich,³⁹ and Shamsuddin.⁴⁰ Schneider and Guillaume³⁴ measured the Pb activities of liquid Pb-Se alloys with the electrochemical method in a large concentration and temperature regime, the results of which were interpreted with the associated solution model in which a mixture of PbSe associates, free Pb, and free Se were present. Kotchi et al.⁴¹ measured the enthalpies of formation for Pb-Se melts at nine temperatures in the Pb-PbSe region from 883 K to 1365 K, the results of which demonstrated that the enthalpies of mixing form a V-shaped geometry for the temperatures at which only the liquid phase is stable, indicating the formation of a stable melt structure around 50 at.% Se.

MODEL DESCRIPTION

For the thermodynamic framework established in this work for the Cd-Se and Pb-Se binary systems, the standard element reference state (SER) widely adopted in the CALPHAD community is used, and thus the Gibbs free energies of stable and metastable pure elements can be taken from the compilation of Dinsdale.⁴²

For Se-containing melts that demonstrate a certain degree of short-range order, formation of associates can be assumed when the attractive forces between metal and Se atoms are not strong enough to form stable molecules, but the lifetime of such associates can be significantly larger than the mean time between thermal collisions. For detailed discussion on the associated solution model, interested readers can refer to Ref. 43. For M-Se (M = Cd or Pb) binary melts, it can be assumed that M, Se, and MSe species are present in the liquid, constrained by the following equilibrium:



where { } denotes species present in the liquid state. With this assumption, M, Se, and MSe constitute the end-members for the Gibbs free energies of the binary melt, which can be given by

$$\begin{aligned}
G_m^{\text{liq}} = & y_M^{\text{liq}} G_M^{\text{liq}} + y_{\text{Se}}^{\text{liq}} G_{\text{Se}}^{\text{liq}} + y_{\text{MSe}}^{\text{liq}} G_{\text{MSe}}^{\text{liq}} \\
& + RT \left(y_M^{\text{liq}} \ln y_M^{\text{liq}} + y_{\text{Se}}^{\text{liq}} \ln y_{\text{Se}}^{\text{liq}} + y_{\text{MSe}}^{\text{liq}} \ln y_{\text{MSe}}^{\text{liq}} \right) \\
& + y_M^{\text{liq}} y_{\text{Se}}^{\text{liq}} \sum_i {}^i L_{\text{M,Se}}^{\text{liq}} \left(y_M^{\text{liq}} - y_{\text{Se}}^{\text{liq}} \right)^i \\
& + y_M^{\text{liq}} y_{\text{MSe}}^{\text{liq}} \sum_j {}^j L_{\text{M,MSe}}^{\text{liq}} \left(y_M^{\text{liq}} - y_{\text{MSe}}^{\text{liq}} \right)^j \\
& + y_{\text{Se}}^{\text{liq}} y_{\text{MSe}}^{\text{liq}} \sum_k {}^k L_{\text{Se,MSe}}^{\text{liq}} \left(y_{\text{Se}}^{\text{liq}} - y_{\text{MSe}}^{\text{liq}} \right)^k,
\end{aligned} \quad (6)$$

where ${}^0G_M^{\text{liq}}$, ${}^0G_{\text{Se}}^{\text{liq}}$, and ${}^0G_{\text{MSe}}^{\text{liq}}$ are the molar Gibbs free energies of pure liquid M, pure liquid Se, and pure liquid MSe, respectively; R is the gas constant; y_M^{liq} , $y_{\text{Se}}^{\text{liq}}$, and $y_{\text{MSe}}^{\text{liq}}$ are the site fractions of species in the liquid phase; and ${}^iL_{\text{M,Se}}^{\text{liq}}$, ${}^jL_{\text{M,MSe}}^{\text{liq}}$, and ${}^kL_{\text{MSe,Se}}^{\text{liq}}$ are the binary interaction parameters.

The two binary compounds, CdSe and PbSe, are considered to be stoichiometric phases, whose Gibbs free energies for one mole formula unit are expressed as

$$G_m^{\text{MSe}} = {}^0G_M^{\phi} + {}^0G_{\text{Se}}^{\text{hex}} + a^{\text{MSe}} + b^{\text{MSe}}T, \quad (7)$$

where ${}^0G_M^{\phi}$ ($\phi = \text{hcp}$ if $M = \text{Cd}$ and $\phi = \text{fcc}$ if $M = \text{Pb}$) and ${}^0G_{\text{Se}}^{\text{hex}}$ are the molar Gibbs free energies of pure M with the ϕ structure and hexagonal Se, respectively; a^{MSe} and b^{MSe} are the enthalpy parameter and the entropy parameter, respectively. The solid Se phase, which shows a hexagonal structure, is assumed to have no solubility of Cd and Pb, which is consistent with the current understanding for the Cd-Se and Pb-Se binary systems.

RESULTS AND DISCUSSION

The thermodynamic parameters necessary to formulate the Gibbs free energies of each phase were evaluated in this work using the Parrot module in Thermo-Calc,⁴⁴ which is based on the inverse evaluation of various kinds of experimental data such as enthalpies of mixing, enthalpies of formation, activities, liquidus curves, and congruent melting temperatures. All the experimental data

mentioned above were adopted to evaluate the thermodynamic descriptions. The assessment for the two binary systems followed the following steps. Firstly, the parameters for the Gibbs free energies of formation of associates in the liquid phase were optimized using the mixing enthalpies and activity data. Secondly, the enthalpies and entropies of formation of the binary compound were evaluated from measured enthalpies of formation and its congruent melting temperature. Thirdly, the interaction parameters between the associates and the remaining free atoms in the liquid phase were evaluated from thermochemical and liquidus data. As the interaction parameters between free atoms have little effect on the calculated phase diagrams, they were not evaluated in this work. Fourthly, once the phase diagram and the thermochemical data could be well represented, all the parameters were concurrently taken into the optimization process and thus the discrepancy between the calculated and measured data further minimized.

Cd-Se Binary System

The thermodynamic description for the Cd-Se binary system is given in Table I, and the calculated Cd-Se binary phase diagram is shown in Fig. 1, where the experimental data from Reisman et al.¹⁰ and Sysoev et al.¹¹ are also superimposed for comparison. It is evident that the experimentally measured liquidus can be well represented, especially for the Cd-CdSe portion. Figures 2 and 3 give the calculated and experimentally measured Cd and Se₂ partial pressures along the liquidus, where good agreement is evident.

The stability of Cd-Se melts can be evaluated from the thermodynamic factor, which is given as

$$\Phi = \frac{x_{\text{Se}}^{\text{liq}}}{RT} \frac{\partial \mu_{\text{Se}}^{\text{liq}}}{\partial x_{\text{Se}}^{\text{liq}}}, \quad (8)$$

where $x_{\text{Se}}^{\text{liq}}$ and $\mu_{\text{Se}}^{\text{liq}}$ are the mole fraction and the chemical potential of Se in the liquid phase, respectively. The physical significance of this stability

Table I. Thermodynamic parameters for the Cd-Se system (all in SI units)

Phase	Model	Parameter
Liquid	(Cd, Se, CdSe) ₁	${}^0G_{\text{CdSe}}^{\text{liq}} = {}^0G_{\text{Cd}}^{\text{liq}} + {}^0G_{\text{Se}}^{\text{liq}} - 125372.45 + 17.25T$ ${}^0L_{\text{Cd,CdSe}}^{\text{liq}} = 25601.34 - 3.08T$ ${}^1L_{\text{Cd,CdSe}}^{\text{liq}} = 1201.35$ ${}^0L_{\text{Se,CdSe}}^{\text{liq}} = 16750.42$ ${}^1L_{\text{Se,CdSe}}^{\text{liq}} = -11987.45$ ${}^2L_{\text{Se,CdSe}}^{\text{liq}} = 13987.45$
CdSe	(Cd) ₁ (Se) ₁	$G_m^{\text{CdSe}} = {}^0G_{\text{Cd}}^{\text{hcp}} + {}^0G_{\text{Se}}^{\text{hex}} - 147032.45 + 15.54T$

Note: Solid hcp Cd and hexagonal Se are treated as phases without any solubilities, and thus their thermodynamic parameters are not included in this table.

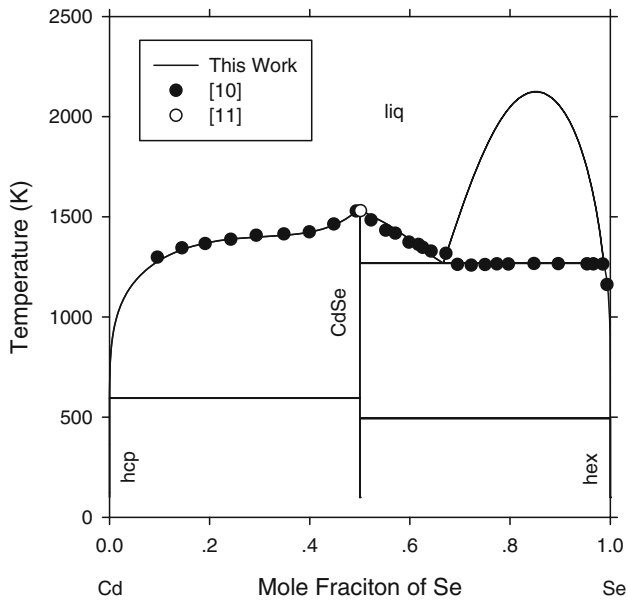


Fig. 1. Comparison between calculated and experimentally measured Cd-Se phase diagrams.

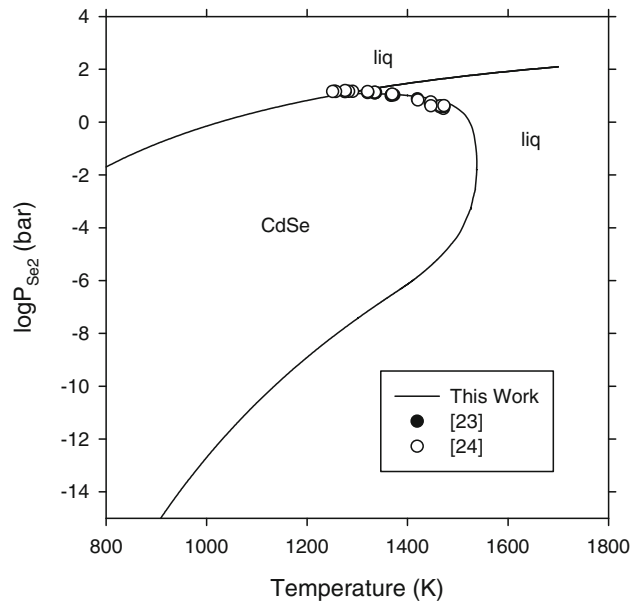


Fig. 3. Comparison between calculated and experimentally measured Se_2 partial pressures along the Cd-Se liquidus.

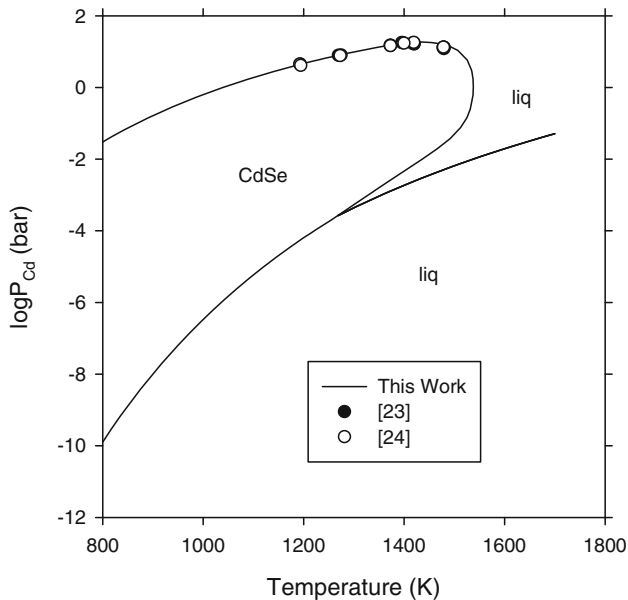


Fig. 2. Comparison between calculated and measured Cd partial pressures along the Cd-Se liquidus.

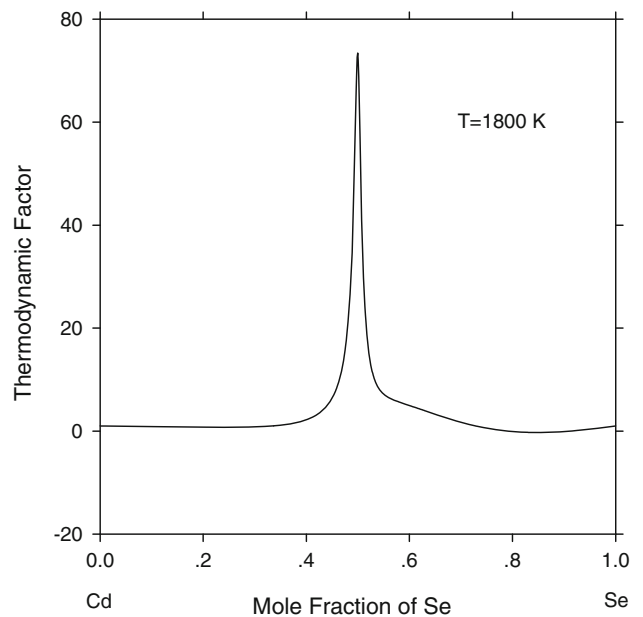


Fig. 4. Thermodynamic factor of Cd-Se melts for 1800 K.

function is obvious. A negative value indicates the presence of an unstable region seeking phase decomposition, while a positive value demonstrates a stable structure. The calculated phase stability according to Eq. 8 is presented in Fig. 4 against the mole fraction of Se, which features a sharp positive peak around 50 at.% Se and a region characterized by negative values around the Se edge. Such nice geometric characteristics are consistent with the appearance of sharp maxima for the liquidus in the Cd-Se phase diagram and also the presence of

miscibility gap at 1800 K. The calculated enthalpies of mixing of the liquid phase at 1600 K are given in Fig. 5, where the V-shaped geometry is evident, indicating the formation of a stable melt structure around 50 at.% Se.

The calculated and experimentally measured invariant reactions are given in Table II. For the three invariant reactions, only the monotectic one has been experimentally measured, and the thermodynamic description provided in Table I allows the invariant temperature and concentrations to be

well reproduced. The comparison between the calculated and experimentally measured congruent melting points of CdSe is given in Table III, where the current value is in the favor of temperature from Sysoev et al.¹¹ The calculated enthalpies of formation for CdSe compound compare well with the great majority of the experimental values listed in Table IV, where pure hcp Cd and pure hexagonal Se are utilized as the reference state. The calculated entropies of CdSe for 298 K are given in Table V, agreeing fairly well with the values from Wosten¹⁵ and Terpilowski and Ratajczak.¹⁷

Pb-Se Binary System

The thermodynamic description obtained in this work is provided in Table VI, and the calculated Pb-Se binary phase diagram is given in Fig. 6, together with the experimental data from Pelabon and Gernez,²⁷ Friedrich and Leroux,²⁸ Nozato and Isaki,²⁹ Pelzel,³⁰ Seidman et al.,³¹ Seidman,³² Miller and Komarek,³³ and Schneider and Guillaume.³⁴ The calculated phase diagram agrees with the great

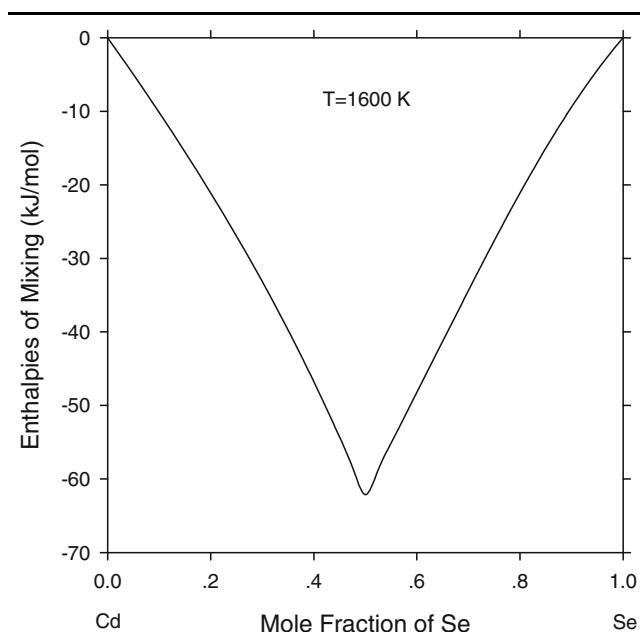


Fig. 5. Enthalpies of mixing for Cd-Se melts at 1600 K.

majority of the experimental data. The Pb-Se binary phase diagram shares similar characteristics to the Cd-Se phase diagram, except that the width and the consolute temperature for the miscibility around Se-rich edge are much smaller. The liquidus curve in the Pb-PbSe portion shows an inflection point, around which the curvature of the liquidus changes sign. This inflection point indicates the presence of a metastable liquid miscibility gap.

The calculated Pb activities along the liquidus are given in Fig. 7, together with the experimental data from Schneider and Guillaume.³⁴ Pure liquid Pb is utilized as the reference state. The calculated and experimentally measured enthalpies of mixing for various temperatures are given in Fig. 8 as a function of Se molar fraction, where liquid Pb and liquid Se are used as the reference state. At 1365 K, where only the liquid phase is stable, a V-shaped geometry for the enthalpies of mixing is evident, indicating the formation of relatively stable structure in the melt. The calculated curves for the temperatures of 1243 K and 883 K incorporate the formation of solid PbSe compound, and are thus the characteristics of two-phase mixtures within some concentration regimes.

When PbSe associates are taken into consideration for the liquid phase, there will be one more concentration variables in terms of site fractions. From the thermodynamic point of view, the amount of such associates can be evaluated from the minimization of the Gibbs free energies for the liquid phase alone, as the Gibbs free energies of formation for PbSe associates and the interaction parameters among Pb, Se, and PbSe in Pb-Se melts can provide such information. Based on the thermodynamic description obtained in this work, the calculated degrees of association, i.e., the site fractions of Pb,

Table III. Congruent melting temperatures of CdSe for the Cd-Se binary system (all in SI units)

Temperature (K)	Reference
1512	10
1537	11
1623	12
1531	13
1538	This work

Table II. Invariant reactions involving the liquid phase in the Cd-Se system (all in SI units)

Reaction	Temperature (K)	Compositions of Respective Phases (at.% Se)			Reference
liq \leftrightarrow (Cd) + CdSe	594	~ 0	~ 0	0.5	This work
liq#1 \leftrightarrow liq#2 + CdSe	1264	0.675–0.70	~ 0.99	0.5	10
	1269	0.66	0.99	0.5	This work
liq \leftrightarrow (Se) + CdSe	494	~ 1.0	1	0.5	This work

Table IV. Enthalpies of formation of CdSe obtained from various techniques

Method	Value (kJ/mol)	Reference
Oxide melt drop solution calorimetry	-139.40	14
Vapor pressure measurements	-158.00	15
Vapor pressure measurements	-139.00	16
EMF measurements	-136.60	17
Vapor pressure measurements	-144.10	18
Vapor pressure measurements	-147.70	19
Vapor pressure measurements	-142.60	20
Vapor pressure measurements	-136.50	21
Vapor pressure measurements	-141.96	22
Calculated	-147.03	This work

Note: The unit is for one mole formula; pure hcp Cd and pure hexagonal Se are used as the reference state; *EMF* Electromotive force.

Table V. Standard entropies of CdSe at 298 K (all in SI units)

Method	Value (J/mol/K)	Reference
Vapor pressure measurements	78.12	15
EMF measurements	78.12	17
Vapor pressure measurements	97.02	21
Calculated	78.20	This work

EMF Electromotive force.

Table VI. Thermodynamic parameters for the Pb-Se system (all in SI units)

Phase	Model	Parameter
Liquid	(Pb, Se, PbSe) ₁	${}^0G_{\text{PbSe}}^{\text{liq}} = {}^0G_{\text{Pb}}^{\text{liq}} + {}^0G_{\text{Se}}^{\text{liq}} - 91032.45 + 29.88T$ ${}^0L_{\text{Pb,PbSe}}^{\text{liq}} = 19500.32$ ${}^1L_{\text{Pb,PbSe}}^{\text{liq}} = -1003.26 + 0.58T$ ${}^2L_{\text{Pb,PbSe}}^{\text{liq}} = 8352.21 - 5.64T$ ${}^0L_{\text{Se,PbSe}}^{\text{liq}} = 17503.24 - 7.95T$ ${}^1L_{\text{Se,PbSe}}^{\text{liq}} = -4201.24 + 1.42T$ ${}^2L_{\text{Se,PbSe}}^{\text{liq}} = 16498.24 - 3.61T$
PbSe	(Pb) ₁ (Se) ₁	$G_{\text{m}}^{\text{PbSe}} = {}^0G_{\text{Pb}}^{\text{fcc}} + {}^0G_{\text{Se}}^{\text{hex}} - 99783.25 + 22.58T$

Note: Solid fcc Pb and hexagonal Se are treated as phases without any solubilities, and thus their thermodynamic parameters are not included in this table.

Se, and PbSe, are illustrated in Fig. 9, where the high degree of association around 50 at.% Se is consistent with the appearance of sharp maxima for the liquidus in Fig. 6 and also the presence of PbSe associates in the melts.

The calculated invariant reactions in the Pb-Se binary system are given in Table VII, along with the experimental data. It is evident that the experimental data are only available for the eutectic reaction in the Pb-PbSe portion as well as the monotectic reaction in the PbSe-Se region. The thermodynamic description obtained in this work

generally allows the temperature and invariant concentrations to be represented within experimental errors. The calculated and experimentally measured congruent melting temperatures are presented in Table VIII, where the current result is consistent with the reports from Nozato and Isaki,²⁹ Seidman et al.,³¹ and Miller and Komarek.³³ The calculated enthalpies of formation for PbSe compound are compared with the experimental data in Table IX. It is seen that the experimental values are generally distributed around -99.78 kJ/mol which is proposed in this work.

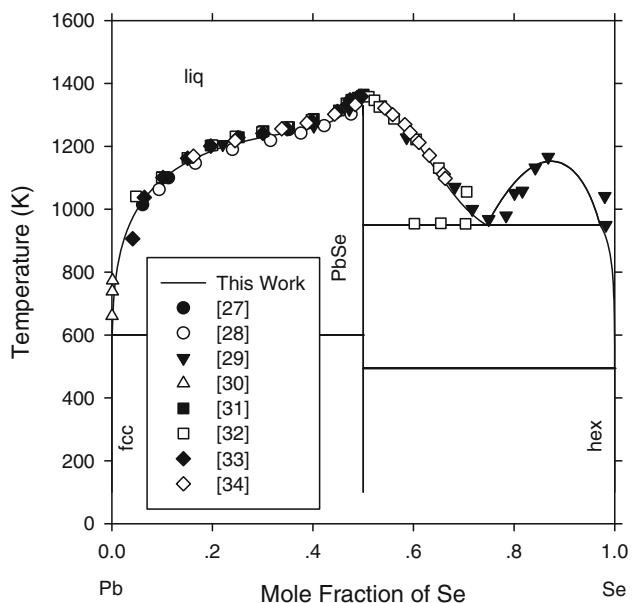


Fig. 6. Comparison between calculated and experimentally measured Pb-Se phase diagrams.

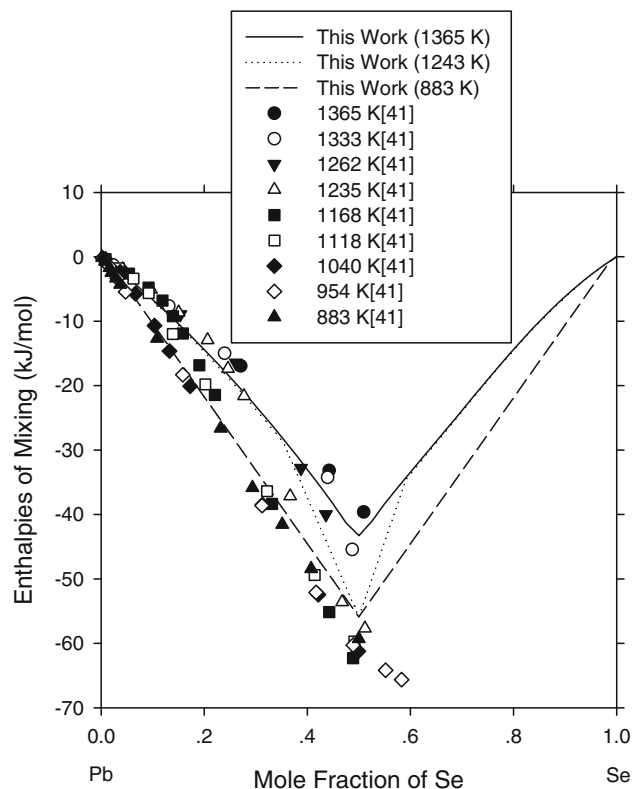


Fig. 8. Comparison between calculated and experimentally measured enthalpies of mixing for the Pb-Se melts (reference states: pure liquid Pb and pure liquid Se).

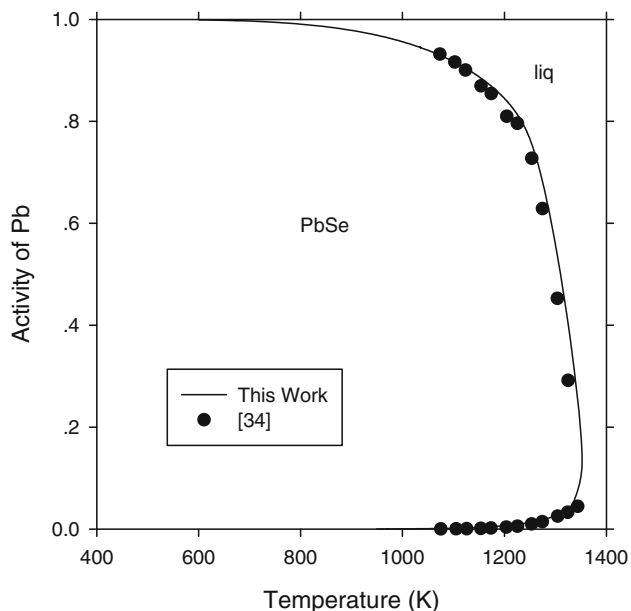


Fig. 7. Comparison between calculated and experimentally measured Pb activities along the Pb-Se liquidus. Pure liquid Pb is used as the reference state.

CONCLUSIONS

Based on the experimental data in the literature, the phase equilibria and thermodynamic basis for the Cd-Se and Pb-Se binary systems are extensively explored. The Cd-Se and Pb-Se melts are treated with the associated solution model so as to reflect the formation of CdSe and PbSe associates. This

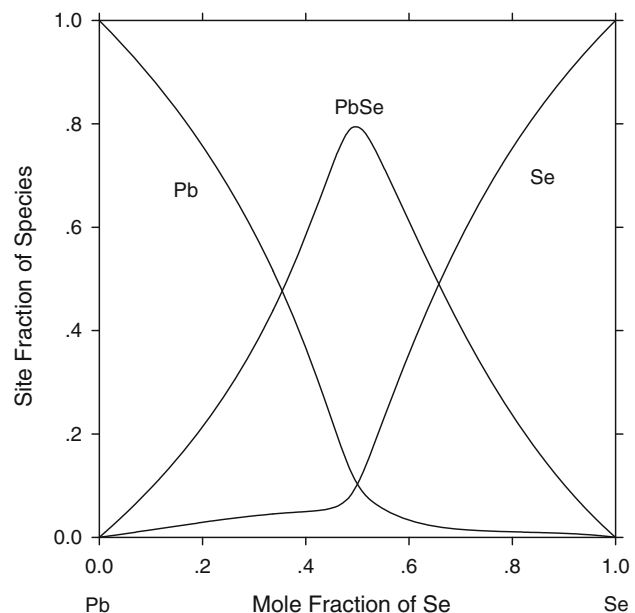


Fig. 9. Calculated site fractions of Pb, Se, and PbSe in Pb-Se melts at 1600 K.

treatment allows the anomalies for the liquid phase and liquidus curve to be well represented. The CdSe and PbSe compounds are treated as stoichiometric

Table VII. Invariant reactions in the Pb-Se binary system (all in SI units)

Reaction	Temperature (K)	Compositions of Respective Phases (at.% Se)			Reference
liq ↔ (Pb) + PbSe	600.3	~0	~0	0.5	35
	600	~0	~0	0.5	This work
liq#1 ↔ liq#2 + PbSe	954	0.76	0.988	0.5	29
	951.3	0.761	—	—	32
	947.2	0.746	0.971	0.5	This work
liq ↔ (Se) + PbSe	493.9	~1.0	1	0.5	This work

Table VIII. Congruent melting temperatures of PbSe for the Pb-Se binary system (all in SI units)

Temperature (K)	Reference
1361	28
1349	29
1353.7	31
1353.7	33
1352	This work

Table IX. Enthalpies of formation of PbSe obtained from various techniques

Method	Value (kJ/mol)	Reference
Oxide melt drop solution calorimetry	-99.26	14
Oxygen vessel calorimetry	-105	36
Direct combination drop calorimetry	-96.3	37
EMF measurements	-99.5	38
EMF measurements	-95.1	39
EMF measurements	-100.3	40
Calculated	-99.78	This work

Note: The unit is for one mole formula. Pure fcc Pb and pure hexagonal Se are used as the reference state. *EMF* Electromotive force

phases. The thermodynamic parameters necessary to formulate the Gibbs free energies of each phase are obtained in this work with the CALPHAD method, which allows the great majority of the experimental data to be well represented.

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