Thermochemistry of the Ga-Se System

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Solid state electrochemical cells were employed to obtain standard Gibbs energy of formation of \( \text{Ga}_2\text{Se}_3 \) as well as the temperature and enthalpy of the \( \alpha \) to \( \beta \)-\( \text{Ga}_2\text{Se}_3 \) transformation in the \( \text{Ga-Se} \) system. The reversible Emfs of the following solid-state electrochemical cells were measured: \( \text{Pt, Ga}(l), \text{Ga}_2\text{O}_3(s)|\text{YSZ}|\text{Ga}_2\text{O}_3(s), \text{GaSe}(s), \text{Ga}_2\text{Se}_3(s), \text{C, Pt I}; \text{Pt, Ga}(l), \text{Ga}_2\text{O}_3(s)|\text{YSZ}|\text{Ga}_2\text{O}_3(s), \text{GaSe}(s), \text{Ga}_2\text{Se}_3(s), \text{C, Pt II}; \text{Pt, Ga}(l), \text{Ga}_2\text{O}_3(s)|\text{YSZ}|\text{Ga}_2\text{O}_3(s), \text{GaSe}(s), \text{Ga}_2\text{Se}_3(s), \text{Liqud2, C, Pt III} \). The standard molar Gibbs energy of formation of \( \text{Ga}_2\text{Se}_3 \), which was calculated by analysis of measured data, is given by: \( \Delta G_m^r(\text{Ga}_2\text{Se}_3, \alpha) = 1.0012\pm0.0001 \text{kJ/mol} \). The thermodynamic and phase diagram data in the Ga-Se system were critically optimized based on literature and measured data. A self consistent set of thermochernistry and phase diagram data was obtained with the help of thermochemical measurements. The liquid phase was modeled by the associated solution model with two associates of GaSe and Ga2Se3. The \( \alpha \)-Ga2Se3 phase was described by the sublattice model with two sublattices according to the formula (Ga, Va)2 (Se, Va)3. The other two intermediate phases, GaSe and \( \beta \)-Ga2Se3 were treated as line compounds.

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Thermochemistry of the Ga-Se System

The Ga-Se system is of interest in developing CuInGa4.5Se2 (CIGS) based solar cell technologies. The Ga addition into CuInSe2 crystal structure was found to be improving its solar power efficiencies up to about 21% in laboratory devices. However, this 4-component compound semiconductor system includes complex chemistry and defect ternary structures with some regions of dispersement and lacking experimental data. The thermochernistry and phase diagram of the Cu-Ga and Ga-Se binaries are comparatively less studied. There is some controversial experimental data reported in the literature for the Ga-Se binary. Better understanding the role of Ga in determining the photo-electronic properties and defect structure of CIGS requires a complete thermodynamic description of not only the Ga-Se system but also other interacting binary and ternaries.

According to reported phase diagrams2-7 two well-defined compounds exist in the system. GaSe is characterized as a highly anisotropic compound with a layered crystal structure and \( \text{Ga}_2\text{Se}_3 \) is reported with a zincblende structure having \( \alpha \) and \( \beta \) modifications with a first order transition temperature at around 967 K. The presence of \( \text{Ga}_2\text{Se}_3 \) phase formation suggested by an earlier report8 was excluded by the later investigators because it was claimed unstable since it could not be prepared by direct synthesis.

Thermodynamic and some vapor pressure data for compounds in this system are reported in the literature. However, some of the literature data on the selenium-rich side of the phase diagram displays an unusual flat Se-rich liquids. Since there is limited data in this region an assessment would be useful to establish the measurability limits. A consistent thermodynamic description of the liquid phase and \( \alpha \)-Ga2Se3 defect compound would be helpful in predicting unknown regions of phase diagram.

In this work, some measured thermochemistry and phase diagram data in the Ga-Se system is reported. Solid state electrochemical cells were employed to measure liquid phase activity parameters (\( \alpha_{\text{Ga}}, \beta_{\text{Ga}} \)) in the two-phase region between solid GaSe and liquid with composition range of 15 to 45 at. % Se. The standard Gibbs energy of formation of \( \text{Ga}_2\text{Se}_3 \) as well as the temperature and enthalpy of the \( \alpha \) to \( \beta \)-\( \text{Ga}_2\text{Se}_3 \) transformation were also obtained by assessing these solid state Emf measurements.

The thermodynamic and phase diagram data in the Ga-Se system was critically optimized based on literature and measured data. A self consistent set of thermochemistry and phase diagram data were prepared. The liquid phase was described by the associated solution model with two associates GaSe and \( \text{Ga}_2\text{Se}_3 \). The \( \alpha \)-\( \text{Ga}_2\text{Se}_3 \) phase was modeled by the sublattice model with two sublattices according to the formula \((\text{Ga, Va})_2 (\text{Se, Va})_3\). The other two intermediate phases, GaSe and \( \beta \)-\( \text{Ga}_2\text{Se}_3 \) were treated as line compounds. The calculated phase diagram and thermochemical data show reasonable agreement except in some limits of the selenium rich liquidus line.

Review of the Experimental Data

The thermodynamics and phase diagram of the Ga-Se system has been measured by several investigators2-7 using differential thermal analysis (DTA), X-Ray diffraction (XRD), microscopy and vapor pressure methods. This system is characterized by the occurrence of two stable binary compounds: GaSe and \( \text{Ga}_2\text{Se}_3 \). \( \text{Ga}_2\text{Se}_3 \) has two stable polymorphisms: \( \beta \)-\( \text{Ga}_2\text{Se}_3 \) is the low temperature form and \( \alpha \)-\( \text{Ga}_2\text{Se}_3 \) is the high temperature form, which exists with a relatively narrow homogeneity range. In the equilibrium diagram of the Ga-Se system, a monotectic is found between Ga and GaSe at 1190 K and a miscibility gap with composition limits of 7.5 to 45.5 at. % Se at this temperature. The eutectic is formed at 1157 K in the composition region between GaSe and \( \text{Ga}_2\text{Se}_3 \). Above 60 at. % Se, \( \text{Ga}_2\text{Se}_3 \) and Se coexist. The thermodynamic value of \( \Delta H^f_{298} \) for \( \text{Ga}_2\text{Se}_3 \), which was studied by direct bomb calorimetry,8,9 existing data on \( \text{Ga}_2\text{Se}_3 \),10,11 and comparative calculation by Burylev,12 show marked discrepancies.

Rustamov7 proposed the existence of the compound \( \text{Ga}_2\text{Se}_3 \), but later investigators3,5 excluded the formation of solid GaSe in the equilibrium phase diagram. Ollitrut-Fichet1 predicted a Se-rich liquid miscibility gap, whereas others7,13 did not observe a monotectic in this region. Mikkelsen11 considered the unusual flat Se-rich liquidus may be due to an abrupt change in Ga solubility and probably a change in the liquid structure. \( \text{Ga}_2\text{Se}_3 \) is reported with other thermodynamically unstable polymorphisms, \( \beta \)-\( \text{Ga}_2\text{Se}_3 \) and \( \gamma \)-\( \text{Ga}_2\text{Se}_3 \). However, in the present optimization of the equilibrium phase diagram and thermodynamic properties, \( \text{Ga}_2\text{Se}_3 \), \( \beta \)-\( \text{Ga}_2\text{Se}_3 \), \( \gamma \)-\( \text{Ga}_2\text{Se}_3 \) and the Se-rich miscibility gap are not considered.

Fermei14 reviewed the properties of GaSe single crystal and organized the published literature by growth, structural, mechanical, electrical, thermal and optical properties. GaSe was categorized as a possible candidate material for optical frequency conversion in the near to far infrared (1–18 μm) wavelength. The published data prior to 1994 were summarized. A summary of the positives and negatives for nonlinear optical properties was also given.
Mamedov et al. reported $c_\text{p} = 0.329 \, \text{T}^{-1} \, (60 \text{ to } 87 \, \text{K}) / \text{mol K}$, and $c_\text{p} = 47.9 \, (300 \, \text{K}) / \text{J/mol K}$ by the measurements of vacuum adiabatic calorimeter. Jandl measured dispersion curves and calculated the $c_\text{p}$ data from a phonon frequency distribution function. The agreement with the measured heat capacity is excellent.

Sharifov measured $\Delta H_{\text{f, 298 K}} [\text{Ga}_2\text{Se}_3] = -88.1 \pm 3.1 \, \text{kcal/mol}$ for a cubic structure. His results differed considerably from earlier results of $-105.0 \, \text{kcal/mol}$ by Hahn and $-110.0 \, \text{kcal/mol}$ by Gadziev. However, he claimed that the earlier results might have contained some type errors related to measurement methods. Burylev investigated this discrepancy and estimated the standard enthalpy of formation by combining Kaputinski thermochemical log-arithmetic curve rule and linear dependence of enthalpies of formation assumption between homotopic substances. Burylev reported $\Delta H_{\text{f, 298 K}} [\text{Ga}_2\text{Se}_3] = -85.0 \pm 3.0 \, \text{kcal/mol}$ and $\Delta H_{\text{f, 298 K}} [\text{GaSe}] = -34.29 \pm 1.21 \, \text{kcal/mol}$ by comparative calculation including the experimental data of Naumov.

Mikkelsen measured the $\text{Se}$ vapor pressures in the temperature range 700 to 1050°C by the dew point method. The $\text{Se}$ vapor pressure was found to decrease rapidly near 60% Se. The $\text{S}$ and $\text{P}$-X liquidus curves were thermodynamically modeled by a regular associated solution model for the liquid phase, with a single associate, $\text{Ga}_2\text{Se}_5$.

The crystal structure of ordered $\text{Ga}_2\text{Se}_5$ was studied by Lubbers et al. It was claimed that the homogeneity range of this phase resulted from ordering of randomly distributed $\text{Ga}$ atoms and "structural vacancies" on the cation sides of the zincblende lattice. The results of Lubbers confirmed some general statements made by Newman, the $\text{Se}$ atoms according to Newman in which one-third of the anion sides occupied by $\text{Se}(\text{Y})$ and $\text{Ga}$ sites with one-third vacancy is modeled in our calculations as two different sublattices in the ordered structure. Earlier, Tonejc studied the lattice parameters of $(\text{Ga}_{x}\text{In}_{1-x})_2\text{Se}_3$ compounds. The phases, lattice parameters, and the linear coefficient of the lattice thermal expansion were determined by high-temperature X-Ray diffraction between room temperature and the melting temperature for the system $(\text{Ga}_{x}\text{In}_{1-x})_2\text{Se}_3 (1 >= x >= 0)$. A wide homogeneity range for this zincblende structure was found in the Ga-rich region when a certain temperature was reached. The lattice parameter of $\text{Ga}_2\text{Se}_5$ was given as a function of temperature. The polymorphic transformations as reported by Goryunova were not detected.

Suzuki determined the phase diagram of $\text{GaSe}$ system by differential thermal analysis. The peritectic single phase of $\text{Ga}_2\text{Se}_3$ which was observed by Rustamov did not appear in DTA analysis. A liquid miscibility was presented. The $\text{Ga}_2\text{Se}_3$ phase was assumed as a single phase line compound without polymorphism; however, the selenium rich liquidus line showed large discrepancy with the published data of Rustamov. As an example of the influence of $\text{Ga}$ or $\text{Se}$ on the stability of $\text{Ga}_2\text{Se}_3$ and $\beta$-$\text{Ga}_2\text{Se}_3$ phases and the transformation temperature were reported. XRD analysis performed in the composition region less than 50 at. % $\text{Se}$ indicated that $\text{Ga}_2\text{Se}_3$ and $\text{Ga}_2\text{Se}_5$ were coexisting phases. Between 50 at. % $\text{Se}$ and 60 at. % $\text{Se}$, $\text{Ga}_2\text{Se}_3$ and $\text{Ga}_2\text{Se}_5$ were observed. Samples at compositions higher than 60 at. % $\text{Se}$ consisted of only $\text{Ga}_2\text{Se}_3$ and selenium. The liquid miscibility gap was also reported between 7.5 at. % $\text{Se}$ and 45.5 at. % $\text{Se}$ closing at 994°C.

The compound $\text{GaSe}$ is well studied due to its interesting structural, optical, and photo-electronic properties for prospective semiconductor applications. The $\text{GaSe}$ structure was found to be highly anisotropic and chemical bonding in $\text{GaSe}$ layered structure showed strong structural anisotropy. Every layer consists of strongly covalent bonded four $\text{Ga}$ and selenium. The liquid miscibility gap was also reported between 7.5 at. % $\text{Se}$ and 45.5 at. % $\text{Se}$ closing at 994°C.

Amis studied the space-charge-limited current behavior for undoped $\text{p}$-$\text{GaSe}$ for the temperature range 200 K to 350 K. It was concluded that the frequently observed hole energy level of 0.195 eV was a single discrete trapping level with a density about $4 \times 10^{12} \, \text{cm}^{-3}$. The conduction was found to be extrinsic ($N_\text{A} - N_\text{D} = 3 \times 10^{19} \, \text{cm}^{-3}$). The energy of the shallow acceptor was decided to be structural defects rather than chemical impurities.

Minder measured the electron and hole drift velocity in the direction parallel to the $c$ axis between 80 and 400 K. A three dimensional character of carrier transport properties was found. The mobility values for electrons and holes at 300 K parallel to the $c$ axis were reported to be 80 cm$^2$/Vs, and 210 cm$^2$/Vs, correspondingly. The perpendicular mobility values are given as 300 cm$^2$/Vs for electrons, and 60 cm$^2$/Vs for holes.

Dobynde investigated the photoluminescence and absorption in $\text{GaSe}$ at 77 K. The $\text{p}$-$\text{GaSe}$ ingots were used in the experiments. The spontaneous photoluminescence (PL) spectra at different excitation and different excitation levels were investigated. Experiments supported the assumption of the presence of two minima in the conduction band.

Ludviksson studied the vacuum sublimation of $\text{Ga}_2\text{Se}_3$. Single crystal $\text{Ga}_2\text{Se}_3$ was grown on $\text{GaAs}(111)$ by vacuum sublimation from a single $\text{Ga}_2\text{Se}_3$ source without terminating the dangling bonds at the surface prior to deposition. Mass spectroscopy was used to determine the composition of the molecular source. It was found that the gaseous species are predominantly $\text{Ga}_2\text{Se}_3$ and $\text{Se}_2$.

A few epitaxial growth studies were published. Erkoc studied the electronic states of $\text{InSe}/\text{GaSe}$ superlattice. The potential and the charge density distribution for three different types of dopings were calculated. Lang studied the band lineup of mismatched $\text{InSe}/\text{GaSe}$ quantum well structures prepared by Van der Waals epitaxy. Palmer investigated the growth and characterization of $\text{GaSe}$ on $\text{As}_2\text{--passivated Si}(111)$ substrates. The epitaxial grown $\text{GaSe}$ layer was examined as a lattice mismatch/thermal expansion mismatch buffer layer in the $\text{GaAs} / \text{Si}$ system. The Van der Waals epitaxial growth of $\text{GaSe}$ on $\text{Si}(111)$ surface was also studied by Vinn. It was suggested according to the channeling measurements that a thin $\text{GaSe}$ film grown on silicon can be obtained with the same crystalline quality as the bulk form of $\text{GaSe}$.

Shigetomi studied impurity levels in $\text{p}$-$\text{GaSe}$ doped with $\text{Mn}$ and with $\text{Cu}$. Photoluminescence (PL), Hall Effect (HE), and deep-level transient spectroscopy (DLTS) measurements were performed. Hernandez studied temperature dependence of refractive index and absorption coefficient of $\text{GaSe}$ at 633 nm. Sanchez-Royo studied single crystal $\text{GaSe}$ crystals doped with tin by resistivity and Hall effect measurements. The transport properties of doped $\text{GaSe}$ single crystal were reported. The chemical bonding for $\text{GaSe}$ was characterized by strong anisotropy. Optical properties were also reported as anisotropic and the band gap value of 2.02 eV was reported.

Micocci studied the photo-electronic properties as a function of temperature and light intensity. It was stated that $\text{GaSe}$ single crystals can act as both $p$ and $n$ type semiconductors. $\text{GaSe}$ single crystal were grown by Bridgman-Stockbarger method and thermally stimulated current (TSC) and photo-conductivity of $n$-$\text{GaSe}$ doped with chlorine was studied. Micocci also studied the electrical properties of $n$-$\text{GaSe}$ chlorine doped single crystals. It was concluded that the electrical properties were dominated by a deep donor level at 0.57 eV below the conduction band.

Gurbulak studied the temperature dependencies of the Hall mobility of holes and the carrier concentration. The magneto-resistance and Hall Effect measurements were carried out in undoped and gadolinium doped $p$-$\text{GaSe}$ samples. Magnetic field dependencies of electrical properties were also investigated.

In summary, some thermodynamic data for the compounds and the liquid phase have been measured by means of vapor pressure, calorimetry, DTA, and electromotive force (Emf) methods. However, there is a considerable discrepancy in the measured data, and some parts of the phase diagram are not well-studied. Massalski assessed experimental phase diagram data for the binary Ga-Se system. The notations for phases and some stability ranges assessed by Massalski are adopted as reference parameters for initial boundary condition data in our calculations. In this work, selected thermochemistry and phase
diagram data in the Ga-Se system have been measured. Solid state electrochemical cells were employed to obtain chemical potential and standard Gibbs energy of formation of Ga$_2$Se$_3$ as well as the temperature and enthalpy of the α to β-Ga$_2$Se$_3$ transformation. Furthermore, a self-consistent phase diagram and set of thermodynamic data was obtained by critical assessment based on the Emf results and selected literature data through this assessment.

**Experimental**

*Cell materials.*— The solid alloys with compositions 15, 55, and 65 at. % Se were synthesized from pure Ga shots (Johnson Matthey) and Se pellets (Alpha Aesar). The samples were individually encapsulated in silica ampoules at a pressure less than 10 Pa and heated to 1273 K for 24 hours to ensure completion of the formation of the bi-phasic alloys. Then the silica ampoules were further heat treated in steps of 1173 K for 64 hr and 1073 K for 40 hr followed by annealing at 723 K for 24 hr. All the samples were characterized by powder X-Ray Diffractometry (XRD) method within its 5 mass % limit of detection for impurity phases. Gallium shots (Johnson Matthey, purity 99.99%) and Ga$_2$O$_3$ powders (Johnson Matthey, purity 99.99%) were used as received for the Emf measurements.

*Emf measurements.*— The test electrodes were made by mixing the (gallium-selenium) alloys of compositions 15, 55 and 65 at % Se individually with one third of their mass of gallium oxide (Ga$_2$O$_3$) powder. The mixtures were allowed to equilibrate within the cell at the lowest temperature of measurement. The reference electrodes were prepared from a mixture of 4:1 weight ratios of Ga shots and Ga$_2$O$_3$ powders. The cell configuration of the Emf experiments for each cell can be outlined as:

\[
\text{Pt, Ga(I), Ga}_2\text{O}_3\text{(s) \parallel YSZ \parallel Ga}_2\text{O}_3\text{(s)}, GaSe(s), Liquid1, C, Pt, cell I (0 < x_{Se} < 0.5)}
\]

\[
\text{Pt, Ga(I), Ga}_2\text{O}_3\text{(s) \parallel YSZ \parallel Ga}_2\text{O}_3\text{(s), GaSe(s), Ga}_2\text{Se}_3\text{(s), C, Pt, cell II (x_{Se} = 0.55) Liquid2, C, Pt, cell III (x_{Se} = 0.65)}
\]

where YSZ denotes 15 mass percent Y$_2$O$_3$ (yittria) stabilized ZrO$_2$ (zirconia) solid electrolyte and C denotes high density graphite cups. Pt denotes platinum wire which was used as the electrical contact. Liquid1 and Liquid2 represent the Ga rich and Se rich liquids respectively. Cylindrical YSZ crucibles with 15 mm in diameter and 3 mm thickness were used to contain electrode mixtures. High density nu-clear grade graphite cups and alumina crucibles were employed to contain the test electrode materials. The graphite and YSZ crucibles enclosing the test and reference electrodes were sealed with magnesia based ceramic sealant (Aremco 571) to avoid the vaporization of selenium from the test electrode sample as well as to enclose liquid Ga in the reference electrode. The absence of asymmetric potentials due to graphite cups were verified by the observation of null Emf (± 1 mV) over the range 800 to 1200 K in a symmetric cell with identical Ga(l) + Ga$_2$O$_3$ electrodes. The absence of asymmetric potentials and the location of the electrodes in the isothermal zone of the furnace were carefully verified. In measurements, both cell electrodes were located in isothermal zone of the furnace. This enabled the solid oxide ion conductor to be in its ionic conduction domain at both electrodes. The temperature range of adopted measurements was high enough that there was no detrimental influence from the partial electronic conduction. A nearly static atmosphere of purified argon was provided for the electrodes of the cell compartment. The temperature of the cell was measured using a Pt-10%Rh/Pt thermocouple whose junction was located near the electrodes of the cell in the isothermal zone of the furnace. The reversibility of the Emf readings was ascertained by checking the reproducibility in thermal cycling as well as micro-polarization. The equilibrium nature of the Emf was verified by a 5 to 10% variation in the composition of the co-existing phases of the test electrodes from one experimental run to another. The test electrodes were examined by XRD at the end of each experiment to confirm the absence of changes in phase composition. Other experimental details such as temperature control, purification of argon, and voltage measurement are given in references.

**Experimental Procedure and Results**

The Emf results on cell I, cell II and cell III for the composition of gallium-selenium alloys encompassing 15, 55 and 65 at. % Se is presented in Figure 1, Figure 2 and Figure 3. The solution parameters and transformation enthalpies were calculated depending on the constitution of the electrochemical cell from the following general relation,

\[
\Delta G_R = \Delta G^0_{R} + RT \ln K = -nFE
\]

where $\Delta G_R$ is the Gibbs energy change of the overall cell reaction which is directly related to the measured EMF, E is the measured open circuit value between test and reference electrodes, n is the number of equivalent charges transferred per mole of reaction and Faraday’s constant, F is equal to 96485.3 C/mol.

**Liquid phase activity measurements.*— The electrochemical half-cell reactions for the cell I, which was employed for the liquid phase activity measurements, can be represented schematically as:

Reference electrode: \[ \text{Ga}_{\text{pure}}, l + 3/2 \text{O}^{2-} \leftrightarrow \frac{1}{2} \text{Ga}_2\text{O}_3 + 3 \text{e}^{-} \]

![Figure 1. Temperature dependence of the Emfs of cell I with 15 at. % Se.](image1.png)

![Figure 2. Temperature dependence of the Emfs of cell II with 55 at. % Se.](image2.png)
The α to β transition in Ga2Se3.— The galvanic cell employed for cell II is represented by
Pt, Ga(l), Ga2O3(s) || YSZ || Ga2O3(s), GaSe(s), Ga2Se3(s), C, Pt

The Emf expressions for the above cell are given as follows:

\[ E_{II(a)} = 2.32 \text{ (mV)} = 417.27 - 0.27477 T \text{ (K)} \] \]

\[ E_{III(b)} = 2.25 \text{ (mV)} = 476.63 - 0.33454 T \text{ (K)} \] \]

The half cell reactions of the cell II could be written as:

Reference electrode:

\[ \text{Ga (pure, l)} + 3/2 \text{O}^{2-} (g) \leftrightarrow \text{Ga} \text{(se)} (s) + 3 e^- \] \]

Test electrode:

\[ \text{Ga}_{2} \text{Se}_3 (\alpha \text{or } \beta) + 1/2 \text{Ga}_2 \text{O}_3 (l) + 3 e^- \leftrightarrow 3 \text{GaSe (s)} + 3/2 \text{O}^{2-} (g) \] \]

For the passage of 3 Faraday of electricity, the overall cell reaction can be represented by the following reaction:

Overall: \[ \text{Ga (pure, l)} + \text{Ga}_{2} \text{Se}_3 (\alpha \text{or } \beta) \leftrightarrow 3 \text{GaSe (s)} \] \]

The Gibbs energy changes \[ \Delta G_{(R(a))} \] and \[ \Delta G_{(R(b))} \] for the reaction were calculated using the Nernst equations and are given below.

\[ \Delta G_{(R(a))} = 3 \Delta G^\circ \text{f (GaSe (s))} - \Delta G^\circ \text{f (Ga}_{2}\text{Se}_3(\alpha \text{or } \beta)) \] \]

\[ \Delta G_{(R(b))} \pm 0.65 \text{ (kJ/mol)} = -137.97 + 0.09684 T \text{ (K)} \]

Equations 17 and 18 are valid for the \( \alpha \) and \( \beta \) forms of Ga2Se3, respectively, in the temperature ranges indicated in Equations 11 and 12. Since there is no phase transition predicted for either GaSe or Ga in the temperature range 823 to 1100 K, the difference in \( \Delta G_R \) calculated from Equations 17 and 18 corresponds to the standard Gibbs energy change, \( \Delta G_{(R(\alpha \rightarrow \beta))} \) for the \( \alpha \) to \( \beta \) transition in Ga2Se3. Thus, by solving the expressions 17 and 18, one obtains the following Gibbs energy expression for the transformation:

\[ \Delta G_{(R(\alpha \rightarrow \beta))} (\text{Ga}_{2}\text{Se}_3) \pm 1.32 \text{ (kJ/mol)} = -17.19 - 0.01730 T \text{ (K)} \] \]

This leads to values of 993.6 K and 17.2 kJ/mol for \( T_{\text{trans}} \) and \( \Delta H_{\text{trans}} \) of Ga2Se3. This transformation enthalpy value was directly used in the optimization of the phase diagram, which is explored in the following sections.

The α to β transition in Ga2Se3 from cell II. — The electrochemical reactions for the cell III can be represented as:

Pt, Ga(l), Ga2O3(s) || YSZ || Ga2O3(s), GaSe(s), Ga2Se3(s), C, Pt

Reference electrode:

\[ \text{Ga}_{2} \text{O}_3 (s) + 3 e^- \leftrightarrow \text{Ga} \text{(l)} + 3/2 \text{O}^{2-} \] \]

Test electrode:

\[ \text{Ga}_{2} \text{Se}_3 (\alpha \text{or } \beta) + \text{Ga} \text{(l)} + 3/2 \text{O}^{2-} \leftrightarrow 3 \text{GaSe (s)} + 3 e^- \] \]
The random scatter of values of \( \Delta H^f \) at 1004 K for Ga\(_2\)Se\(_3\). This is in good agreement with the data obtained by the following relation:

\[
\Delta H^f (\text{GaSe}) (\text{kJ/mole}) = -460.2 + 0.11816 T (\text{K})
\]

(25)

The assessed phase diagram of Ga-Se system is shown in Figure 6. The mean value of \( \Delta H^f_{\text{GaSe}} \) for Ga\(_2\)Se\(_3\) was found to be \(-405.6\) kJ/mol. The random scatter of values of \( \Delta H^f_{\text{GaSe}} \) around its mean value in this plot indicates the absence of significant temperature dependent errors in the Emf measurements. This value is also found to be in excellent agreement with \(-408.8\) kJ/mol reported by Barin.45 These values are compared with those of other literature values along with \( S^0_{298} \) in Table II.

### Table II. Comparison of the standard enthalpy of formation and absolute entropy of \( \alpha\)-Ga\(_2\)Se\(_3\).

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>( -\Delta H^f_{\text{GaSe}} ) (kJ/mol)</th>
<th>Ref.</th>
<th>( S^0_{298} ) (kJ/mole)</th>
<th>Ref.</th>
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<tr>
<td>1</td>
<td>368.6</td>
<td>10</td>
<td>179.9</td>
<td>45</td>
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<td>11</td>
<td>98.6</td>
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<td></td>
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<tr>
<td>6</td>
<td>408.8</td>
<td>45(^*)</td>
<td></td>
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<tr>
<td>7</td>
<td>405.6</td>
<td>This Work</td>
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\(^*\) calculated using Ref. 11

\(^*\) calculated using Ref. 10

Figure 5. Third law treatment of standard enthalpy of formation of \( \alpha\)-Ga\(_2\)Se\(_3\) (\( \alpha \)).

Phase Diagram Assessment and Optimization

The assessed phase diagram of Ga-Se system is shown in Figure 6 with the temperature of transition values marked for 55 and 65 at. \% Se for cells II and III along with a selected set of various assessments and experimental data. The optimized parameters of the invariant reactions in the Ga-Se system are listed in Table III. The phase diagram and thermodynamic properties of this system were calculated with the Poly-3 module of the Thermo-Calc program package. The optimized phase diagram is given in Figure 7.

Figure 6. Comparison of the calculated Ga-Se phase diagram with various assessments and experimental data.
Table III. Assessed temperatures and compositions of the invariant reactions in the Ga-Se system.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Composition, at. % Se</th>
<th>Temperature [K]</th>
<th>Reaction Type</th>
<th>Reference</th>
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<td>L&lt;sub&gt;1&lt;/sub&gt;/L&lt;sub&gt;2&lt;/sub&gt;</td>
<td>∼23/∼23</td>
<td>1268</td>
<td>Critical</td>
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<td>L&lt;sub&gt;1&lt;/sub&gt;/L&lt;sub&gt;2&lt;/sub&gt;/GaSe</td>
<td>5.5/4/50</td>
<td>1188</td>
<td>Monotectic</td>
<td>4</td>
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<td>∼23.9/23.9</td>
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<td>∼24/∼24</td>
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<td>7.1/4.2/9.50</td>
<td>1183</td>
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<td>This work</td>
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<td>Ga/L&lt;sub&gt;1&lt;/sub&gt;/GaSe</td>
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<td>Eutectic (or peritectic)</td>
<td>7</td>
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<td></td>
<td>0/0/50</td>
<td>303</td>
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<td>4</td>
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<tr>
<td></td>
<td>0/0/50</td>
<td>303</td>
<td></td>
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<td></td>
<td>0/0/50</td>
<td>303</td>
<td></td>
<td>5</td>
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<td></td>
<td>0/0/50</td>
<td>303</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>∼23.9/23.9</td>
<td>1267</td>
<td></td>
<td>5</td>
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<tr>
<td>GaSe/L&lt;sub&gt;2&lt;/sub&gt;</td>
<td>50/50</td>
<td>1233</td>
<td>Congruent</td>
<td>7</td>
</tr>
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<td></td>
<td>50/50</td>
<td>1223</td>
<td></td>
<td>6</td>
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<td>50/50</td>
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<td>5</td>
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<td>50/50</td>
<td>1215</td>
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<td></td>
<td>50/54.9/59.5</td>
<td>1163</td>
<td></td>
<td>5</td>
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<tr>
<td>α-Ga&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;/L&lt;sub&gt;2&lt;/sub&gt;</td>
<td>60/60</td>
<td>1293</td>
<td>Congruent</td>
<td>7</td>
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<td></td>
<td>60/60</td>
<td>1283</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>60/60</td>
<td>1280</td>
<td></td>
<td>5</td>
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<tr>
<td></td>
<td>60/60</td>
<td>1292</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>GaSe/α-Ga&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;/β-Ga&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;</td>
<td>50/~59.9/~60.2</td>
<td>898</td>
<td>Eutectoid</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>50/59.3/60</td>
<td>898</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>β-Ga&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;/α-Ga&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;</td>
<td>60/60</td>
<td>1003</td>
<td>Polymorphic</td>
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<tr>
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<td>60/60</td>
<td>1003</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>60/60</td>
<td>968</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>60/60</td>
<td>967</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>β-Ga&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;/α-Ga&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;/L&lt;sub&gt;2&lt;/sub&gt;</td>
<td>~60/76/15</td>
<td>918</td>
<td>Peritectic</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>60/61/0/99.1</td>
<td>918</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>β-Ga&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;/Se/L&lt;sub&gt;3&lt;/sub&gt;</td>
<td>60/100/100</td>
<td>493</td>
<td>Eutectic (or peritectic)</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>60/100/100</td>
<td>493</td>
<td></td>
<td>4</td>
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<tr>
<td></td>
<td>60/100/100</td>
<td>494</td>
<td></td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 7. Optimized phase diagram of the Ga-Se system.

Pure elements and stoichiometric compound phases.—A set of crystallographic literature data and band gap information is given in Table IV. After evaluation of structural and phase diagram information, GaSe and the two polymorphisms of α-Ga<sub>2</sub>Se<sub>3</sub> and β-Ga<sub>2</sub>Se<sub>3</sub> were accepted as stable compounds in calculation of Ga-Se binary line. The Gibbs energy of Ga was obtained from Ref. 46, and that of Se from Ref. 47 The Gibbs energies of GaSe and β-Ga<sub>2</sub>Se<sub>3</sub> were obtained from Refs. 48 and 49, respectively. The equation given below is used to represent the temperature dependence of the Gibbs energies of pure elements and stoichiometric compound phases of GaSe and β-Ga<sub>2</sub>Se<sub>3</sub>.

\[ \Delta G = a + bT + cT \ln T + dT^2 + eT^3 + fT^4 \]  

[27]

where \( \Delta G \) is the standard Gibbs energy, T is the absolute temperature.
### Table IV. Lattice structures of the compounds in the Ga-Se System.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal system</th>
<th>Lattice parameter (Å)</th>
<th>$E_g$ (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaSe</td>
<td>Hexagonal several polytypes</td>
<td>$a = 3.755$</td>
<td>$E_g, direct = 2.1275$</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>$\beta$-$D_{6h}^3 \sim P6_3/mmc$</td>
<td>$c = 16-34$ (depending on polytypes)</td>
<td>$E_g, indirect = 2.103$ (5.2 K)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\gamma$-$C_{6v}^3 \sim R3m$</td>
<td>$c = 15.94$</td>
<td>$E_g, direct = 2.1021$ (300 K)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\delta$-$C_{6v}^1 \sim P6_3/mmc$</td>
<td>$c = 15.94$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$-$D_{3h}^1 \sim P6m2$</td>
<td>$c = 15.94$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$-$GaSe$</td>
<td>$a = 3.775$</td>
<td>$E_g, direct = 2.02$ (300 K)</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>hexagonal($\delta$), trigonal($\gamma$)</td>
<td>$a = 3.755$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga$_2$Se$_3$</td>
<td>cubic</td>
<td>$a = 5.444$</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>$\alpha$-$Ga_2Se_3$ monoclinic</td>
<td>$a = 6.6068$</td>
<td></td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>$\alpha$-$Ga_2Se_3$ tetragonal</td>
<td>$a = 7.760$</td>
<td></td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>$\alpha$-$Ga_2Se_3$ orthorhombic</td>
<td>$a = 7.760$</td>
<td></td>
<td>63, 64, 65</td>
</tr>
<tr>
<td></td>
<td>$\beta$-$Ga_2Se_3$ (metastable phase of zinblende by fast quenching)</td>
<td>$a_{0}(oct.) = 5.435$</td>
<td>$a_{0}(even) = 5.416 \pm 0.002$</td>
<td>63, 64, 65</td>
</tr>
<tr>
<td></td>
<td>$\gamma$-$Ga_2Se_3$</td>
<td>$a_0(oct.) = 5.463 \pm 0.003$</td>
<td>$a_0(even) = 5.43 \pm 0.001$</td>
<td>60, 63, 64, 65</td>
</tr>
<tr>
<td></td>
<td>liquid phase</td>
<td>$a_0 = 5.4595 \pm 0.0005$</td>
<td>$a_0 = 5.463 \pm 0.003$</td>
<td>5, 63, 64, 65</td>
</tr>
</tbody>
</table>

**Liquid phase.**—The associated solution model developed by Sommer\textsuperscript{50} is used to describe the Gibbs energy of the liquid phase. Two associates, GaSe and Ga$_2$Se$_3$, are used in this modeling:

$$(Ga, GaSe, Ga_2Se_3, Se)_l$$  [28]

The Gibbs energy of this phase (given for 1 mole of atoms) is expressed as:

$$G_l = G_l^{ref} + G_l^{id} + G_l^{eg}$$  [29]

where $l$ represents liquid. The term $G_l^{ref}$ is equal to:

$$G_l^{ref} = x_{Ga}^0 C_{Ga}^l + x_{GaSe}^0 C_{GaSe}^l + x_{Ga_2Se_3}^0 C_{Ga_2Se_3}^l + x_{Se}^0 C_{Se}^l$$  [30]

where $x_i$ refers to the site fractions of species $i$ with $x_{Ga} + x_{GaSe} + x_{Ga_2Se_3} + x_{Se} = 1$.

The terms $G_l^{id}$ represent the standard Gibbs energies of the liquid phases of species $i$. The ideal mixing Gibbs energy $G_l^{id}$ is expressed as:

$$G_l^{id} = R T (x_{Ga} \ln x_{Ga} + x_{GaSe} \ln x_{GaSe} + x_{Ga_2Se_3} \ln x_{Ga_2Se_3} + x_{Se} \ln x_{Se})$$  [31]

The excess Gibbs energy $G_l^{eg}$ is represented by the following formula:

$$G_l^{eg} = x_{Ga} x_{GaSe} (G_l^{eg} + G_l^{eg}) + x_{Ga} x_{Ga_2Se_3} (G_l^{eg} + G_l^{eg}) + x_{Ga_2Se_3} x_{Se} (G_l^{eg} + G_l^{eg})$$  [32]

where $L$ is the interaction parameter between the species to be optimized in the present work. $L$ is considered as the linear function of the absolute temperature $T$ or temperature independent.
Ordered nonstoichiometric compound phase.— The high temperature modification of Ga₂Se₃, α-Ga₂Se₃, is related to the zincblende structure with the space group \( \overline{F} \overline{T} \overline{3} \). In this structure, Ga and Se atoms occupy different sites, and a third of the metal sites are unoccupied.\(^4,5\) Based on this structure, the α-Ga₂Se₃ phase is described by the sublattice model developed by Hillert,\(^6\) and Sundman\(^7\) with two sublattices after the formula:

\[
\text{(Ga, Va)}_2(\text{Se, Va})_3
\]

where Va represents vacancy. The formation of vacancy in the sublattice occupied by Se is considered mathematically for the modeling of the Gibbs energy. This does not mean that the Se sublattice should necessarily contain considerable vacancies. From the assessment results of this work, it will be found that the vacancy in the Se sublattice is very small, which is in good agreement with the structural information.

The Gibbs energy of α-Ga₂Se₃ can also be expressed by Equation 29 (where I should be replaced by α) with,

\[
\alpha \text{G}^\circ = \gamma_{Ga} \gamma_{Se} \text{G}^\circ_{Ga:Se} + \gamma_{Ga} \gamma_{Va} \text{G}^\circ_{Ga:Va} + \gamma_{Va} \gamma_{Se} \text{G}^\circ_{Va:Se} \quad [34]
\]

\[
\Delta \text{G}^\circ = RT[2(\gamma_{Ga} \ln \gamma_{Ga} + \gamma_{Va} \ln \gamma_{Va}) + 3(\gamma_{Se} \ln \gamma_{Se} + \gamma_{Va} \ln \gamma_{Va})] \quad [35]
\]

\[
\text{E} \text{G}^\circ = \gamma_{Ga} \gamma_{Va} \left[ \gamma_{0L}^{\alpha}(1 + \frac{a}{1L_{Ga:Va:Se}} + \frac{1}{1L_{Ga:Va:Se}}(\gamma_{Ga} - \gamma_{Va})) + \gamma_{0L}^{\alpha}(1 + \frac{b}{1L_{Ga:Va:Se}})(\gamma_{Ga} - \gamma_{Va})) \right] + \gamma_{0L}^{\alpha}(1 + \frac{1}{1L_{Ga:Va:Se}}(\gamma_{Va} - \gamma_{Va})) + \gamma_{0L}^{\alpha}(1 + \frac{1}{1L_{Ga:Va:Se}}(\gamma_{Va} - \gamma_{Va})) \quad [36]
\]

where \( \gamma_{0L}^{\alpha} \) and \( \gamma_{i}^{\alpha} \) refer to the site fractions of the component i in the first and second sublattice, respectively. \( \text{G}^\circ_{Ga:Se} \) is the standard Gibbs energy of the stoichiometric α-Ga₂Se₃. \( \text{G}^\circ_{Ga:Va} \) and \( \text{G}^\circ_{Va:Se} \) are expressed as:

\[
\text{G}^\circ_{Ga:Va} = 2\text{G}^\circ_{Ga} + a_1 + b_1 T \quad [37]
\]

\[
\text{G}^\circ_{Va:Se} = 3\text{G}^\circ_{Se} + a_2 + b_2 T \quad [38]
\]

where \( \text{G}^\circ_{Ga} \) is the standard Gibbs energy of pure Ga in orthorhombic phase; \( \text{G}^\circ_{Se} \) is the standard Gibbs energy of pure Se in trigonal phase. The \( a_1 \) and \( b_1 \) are the parameters to be optimized. To reduce the number of parameters, the following formulations\(^5\) are used in the optimization:

\[
\text{L}^\circ_{Ga:Va:Se} = 0 \text{L}^\circ_{Ga:Va:Se} = 0 \text{L}^\circ_{Ga:Va} \quad [39]
\]

\[
\text{L}^\circ_{Ga:Se:Va} = 0 \text{L}^\circ_{Va:Se:Va} = 0 \text{L}^\circ_{Va:Se} \quad [39]
\]

\[
\text{L}^\circ_{Ga:Va:Se} = 0 \text{L}^\circ_{Ga:Va} \quad [39]
\]

\[
\text{L}^\circ_{Ga:Se} = 1 \text{L}^\circ_{Ga:Se} \quad [39]
\]

Results and Discussion

A selected set of thermodynamic and phase diagram data resources which is used in modeling and calculations is listed in Table V. Those data from the list are used for the optimization of thermodynamic model parameters of all phases in this system. The optimization procedure is performed by using the PARROT module of the Thermo-Calc program package.\(^34\)

### Table V. Data sources used during the optimization.

<table>
<thead>
<tr>
<th>Equilibrium/Function</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase equilibrium data</td>
<td>7, 6, 4, 3, 13, 5</td>
</tr>
<tr>
<td>Vapor pressure data</td>
<td>20</td>
</tr>
<tr>
<td>Standard Gibbs energies of pure substances</td>
<td>49, 46, 45, 47</td>
</tr>
<tr>
<td>Enthalpy of melting</td>
<td>5</td>
</tr>
</tbody>
</table>

First, the Gibbs energy coefficients of the stoichiometric α-Ga₂Se₃, liquid Ga₂Se₃, and liquid GaSe are deduced based on enthalpy of transition, transition temperature, melting enthalpy, and melting point data. Then, assuming that α-Ga₂Se₃ is a stoichiometric phase and there is no interaction between the pure elements in the liquid phase, a rough optimization of the liquid coefficients is performed based on the activities of selenium, miscibility gap, and three-phase equilibrium. Third, the coefficients of the ordered nonstoichiometric α-Ga₂Se₃ phase are roughly optimized while fixing the coefficients of the liquid phase. Finally, all parameters of the phases are optimized to fit closely to the experimental data taken from the list in Table V.

The optimized parameters of the liquid and α-Ga₂Se₃ phases in the Ga-Se system are listed in Table VI. The phase diagram and thermodynamic properties of this system have been calculated by using the optimized parameters, which were performed with the Poly3 module of the Thermo-Calc program package.

The calculated regions given in Figure 8 and Figure 9 show the comparison between the calculated phase diagram and literature data. The calculated phase diagram agrees with most of the measured data.

### Table VI. Optimized parameters according to the analytical description of the phases*.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>( \alpha \text{G}^\circ_{Ga:Se} = \alpha \text{G}^\circ_{Ga:Se} + 101190 - 78.8567T )</td>
</tr>
<tr>
<td>( \alpha \text{Ga}_2 \text{Se}_3 )</td>
<td>( \alpha \text{G}^\circ_{Ga:Se} = \alpha \text{G}^\circ_{Ga:Se} + 56000 - 45.2592T )</td>
</tr>
<tr>
<td>( \alpha \text{Ga}_2 \text{Se}_3 )</td>
<td>( \alpha \text{G}^\circ_{Ga:Se} = 113628 - 76.4409T )</td>
</tr>
<tr>
<td>( \delta \text{Ga}_2 \text{Se}_3 )</td>
<td>( \delta \text{G}^\circ_{Ga:Se} = 7654 )</td>
</tr>
<tr>
<td>( \delta \text{Ga}_2 \text{Se}_3 )</td>
<td>( \delta \text{G}^\circ_{Ga:Se} = -1151 )</td>
</tr>
<tr>
<td>( \delta \text{Ga}_2 \text{Se}_3 )</td>
<td>( \delta \text{G}^\circ_{Ga:Se} = 42407 - 35T )</td>
</tr>
<tr>
<td>( \delta \text{Ga}_2 \text{Se}_3 )</td>
<td>( \delta \text{G}^\circ_{Ga:Se} = -14239 )</td>
</tr>
</tbody>
</table>

\*Temperature (T) is in Kelvin. The Gibbs energy of the liquid phase is in J/mole of atoms. The Gibbs energy of \( \alpha \text{Ga}_2 \text{Se}_3 \) is in J/mole of \( \text{Ga}_2 \text{Se}_3 \). The symbol \( \alpha \) refers to Ga, Se or Va. The term tri is the abbreviation of trigonal, and ort is that of orthorhombic.

**Figure 8.** Comparison between the calculated Ga-Se phase diagram and various experimental data from 0.35 to 0.65 mole fraction of Se.
but the Se-rich liquidus data measured by Ref. 4 are much higher than the calculated and other measured ones. The thermal effects below the melting temperature of Se at the Se-rich side may correspond to the glass transition or crystallization of Se.4,3 These transitions have been considered in this optimization. Table III presents the experimental and calculated temperatures and compositions of the invariant reactions in this system. The calculated values agree well with the measured and other calculated ones. The thermodynamic data and phase diagram of the GaSe system were adopted.

![Figure 9. Calculated phase diagram section of Ga-Se in the vicinity of α-Ga2Se3, β-Ga2Se3 monotectic reactions.](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$-\Delta H_{1298}$</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaSe</td>
<td>143.5</td>
<td>Unknown</td>
<td>11</td>
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<tr>
<td></td>
<td>159.0</td>
<td>Evaluation</td>
<td>48, This work</td>
</tr>
<tr>
<td>Ga2Se3</td>
<td>439.3</td>
<td>Combustion</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>460.2</td>
<td>Combustion</td>
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<td>368.6</td>
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<td></td>
<td>405.9</td>
<td>Evaluation</td>
<td>49, This work</td>
</tr>
</tbody>
</table>

Table VII. Experimental and calculated standard enthalpies of formation ($\Delta H_{1298}$) of the intermediate phases, GaSe and β-Ga2Se3 at 298.15 K in the Ga-Se system (kJ/mol).

Conclusions

The thermodynamic data and phase diagram of GaSe system were critically investigated. Solid oxide electrochemical cells were used to measure the liquid phase $a_{\text{se}}$ along Ga-rich liquidus line. The chemical potential of selenium in liquid phase was calculated in the temperature range 800 to 1000 K. Invariant phase transition temperatures were measured and transition enthalpies were calculated from the Emiss measurements. From structural data, phase transition measurements and XRD results along with third law analysis, a self consistent thermodynamic data set was obtained by the optimization of the available phase equilibrium and thermodynamic data. The associated and sub-lattice models are used to represent the Gibbs energy of the liquid and α-Ga2Se3, β-Ga2Se3 phases, respectively. The phase diagram and thermodynamic properties of this system have been calculated based on the optimized model parameters. A reasonable agreement between the model-calculated values and the phase equilibria and thermodynamic data available in the literature was achieved.

References