Coupled Phase Diagram Experiments and Thermodynamic Modeling of the CaO-SiO_2-Ga_2O_3 system for Ga recycling

W O Choe[1], *and I H Jung*[1,*]

1. Department of Materials Science and Engineering, Seoul National University, Seoul, South Korea, 08826. email: 6565oh@snu.ac.kr, * in-ho.jung@snu.ac.kr

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ABSTRACT

Gallium-containing compounds such as Gallium Arsenide (GaAs) and Gallium Nitride (GaN) are widely used in electronic devices due to their superior electro-optical properties, and their usages increase rapidly. For the sustainable supply of Ga to electronic industry, therefore, the recycling of Gallium becomes essential. Pyrometallurgical Ga recycling process involves the complex chemical reactions between slag, matte, liquid metal, gas, refractories, etc. Therefore, the accurate thermodynamic information and phase diagram data for the oxide system containing Ga_2O_3 is important. In the present study, new phase diagram experiments for binary SiO_2-Ga_2O_3 and ternary CaO-SiO_2-Ga_2O_3 system are carried out using DTA and quenching experiments followed by EPMA and XRD phase analysis. Based on new phase diagram data and available literature data, the thermodynamic modelling of the entire CaO-SiO_2-Ga_2O_3 system is performed for the first time.

INTRODUCTION

The consumption of Gallium (Ga), a constituent of GaAs and GaN materials with superior electro-optical properties, has increased steadily. More than 90% of Ga is currently produced as a by-product from the aluminium production and zinc smelting process, so the current mainstream production will not be sufficient to meet the demand in future. Therefore, recycling of Ga from electronic scrap becomes important for sustainable supply chain for Ga.

The CALPHAD (CALculation of PHAse Diagram) type thermodynamic database is very useful for new materials design and process optimization. Thermodynamic database allows to perform complex thermodynamic equilibrium calculations for pyrometallurgical process involving multi-component and multi-phases of solid, liquid and gas. In particular, electronic scrap containing Ga can be processed in Cu smelting, the thermodynamic database for molten slag, matte and liquid Cu containing Ga can be important for optimizing Ga recycling process.

In the present study, a coupled phase diagram experiment and thermodynamic modelling of the CaO-SiO_2-Ga_2O_3 system is conducted using the CALPHAD method. The CaO-Ga_2O_3 system can be modelled using the available phase diagram and thermodynamic property data in literature. Because the available data in the SiO_2-Ga_2O_3 system and the CaO-SiO_2-Ga_2O_3 system are inaccurate and insufficient, new phase diagram experiments are conducted in this study to assist the thermodynamic database development. All thermodynamic calculations are performed using the FactSage thermochemical computing program (Bale *et al*, 2016; Jung and Van Ende, 2020).

PHASE DIAGRAM EXPERIMENTS

- Starting materials

For the binary and ternary phase diagram study within CaO-SiO_2-Ga_2O_3 system, $CaCO_3$ (Sigma Aldrich; 99.95% purity), SiO_2 (Sigma Aldrich; 99.995% purity), and Ga_2O_3 (Alfa Aesar; 99.99% purity) powders were used to prepare starting sample materials. Due to the highly hygroscopic nature of

CaO, $CaCO_3$ was used intentionally. Starting materials with target compositions were prepared by grinding appropriate amount of each powders in an alumina mortar for 20 mins. In order to grind them well in a mortar, cyclohexane (Sigma Aldrich; 99.5% purity) liquid containing nearly zero H_2O was applied. Ground samples were dried in the vacuum oven at 70 °C. The powder mixtures were stored in sealed Ar-filled vials with cyclohexane to prevent any hydration, and were dried in the vacuum oven before usage. If necessary, $xCaO \cdot yGa_2O_3$ compounds were synthesised by heating the mixtures of $CaCO_3$ and Ga_2O_3 mixture at 1100 °C in a Pt cup and used as starting materials.

For main phase diagram experiments, the dried powder samples were put in sealed Platinum (Pt) capsules to prevent vaporization loss of Ga_2O_3 and the hydration of sample during quenching process. First, 20 ~ 40 mg of the powder mixtures were put in one-side welded Pt capsules, which were made from Pt tube (10mm length, 3 mm inner diameter, and 0.3 mm wall thickness). The powder-packed Pt capsules were put in the box furnace at 1000 °C for minimum 20 hours to decarbonise the $CaCO_3$ into CaO. The completion of decarbonization of the samples were confirmed by mass changes before and after the heating. After the decarbonization, the other side of the Pt capsule was welded to seal the Pt capsule. The sealed Pt capsules were sonicated in water for 5 mins to check any leakage by measuring their mass changes.

- Quenching experiments

The quenching experiments were conducted in a vertical tube furnace equipped with $Pt_{87}Rh_{13}$-Pt (type R) thermocouples. The temperature was controlled using a PID controller and maintained within ± 3 °C at the target temperature. The sealed Pt capsules were hanged in an alumina tube using a Pt wire and equilibrated at target temperature between 1400 to 1600 °C for 2 to 20 hrs. After the equilibration, the samples were quenched in cold water by releasing Pt wire. The mass of the quenched samples was again checked to confirm no weight changes during the whole equilibration and quenching process.

- Differential Thermal Analysis (DTA) experiments

DTA experiments were carried out with the NETZSCH STA 449 F5 Jupiter equipment. Temperature was calibrated with several standard materials. The sealed Pt capsule containing starting materials was placed in DTA alumina crucible and DTA experiments were carried out up to 1500 °C with the heating and cooling rate of 10 K/min in an Ar atmosphere with 20 mL/min flow rate. At least two cycles of heating and cooling were conducted for each sample. Thermogravimetric analysis (TGA) was also performed simultaneously to ensure no weight loss by vaporization of Ga_2O_3.

- Characterizations

The phase characterizations for quenched samples and DTA samples were carried out using X-Ray Diffraction (XRD) and Electron Probe Micro-Analyser (EPMA). Bruker New D8 advance with Cu Kα radiation at Research Institute of Advanced Materials (RIAM) in Seoul National University (SNU) was used for XRD analysis. All peaks of the XRD patterns were identified with Powder Diffraction Files (PDF) from the International Centre for Diffraction Data (ICDD) using Bruker AXS DIFFRAC.EVA software. The compositional analysis was carried out using EPMA attached to JEOL JXA-8530F at National Centre for Inter-University Research Facilities (NCIRF) in SNU. The exact composition of each phase was measured using Wavelength Dispersive Spectroscopy (WDS) with a 15 kV accelerating voltage, 10 nA beam current, and 1 μm beam diameter. Raw data were reduced with the PRZ Armstrong algorithm employing standard samples of Gadolinium Gallium Garnet ($Gd_3Ga_5O_{12}$) and Wollastonite ($CaSiO_3$) provided by NCIRF.

THERMODYNAMIC MODEL

As shown in FIG 1, there are four stoichiometric compounds in the CaO-SiO_2 system, and four in the CaO-Ga_2O_3 system. No binary solid phase has been reported in the SiO_2-Ga_2O_3 system. Two ternary compounds, $Ca_2Ga_2SiO_7$ and $CaGa_2Si_2O_8$, are found in the CaO-SiO_2-Ga_2O_3 system. No solid solution phase has been reported in this ternary system.

The CaO-SiO_2 system was optimised previously, and the optimised data are stored in FactSage FToxid database (Bale *et al*, 2016). The Gibbs energy data of all solids and liquid phase for the system are adopted from FToxid database without any modification. Binary $CaO-Ga_2O_3$ system and $SiO_2-Ga_2O_3$ system, and ternary $CaO-SiO_2-Ga_2O_3$ system are newly optimised in the present study.

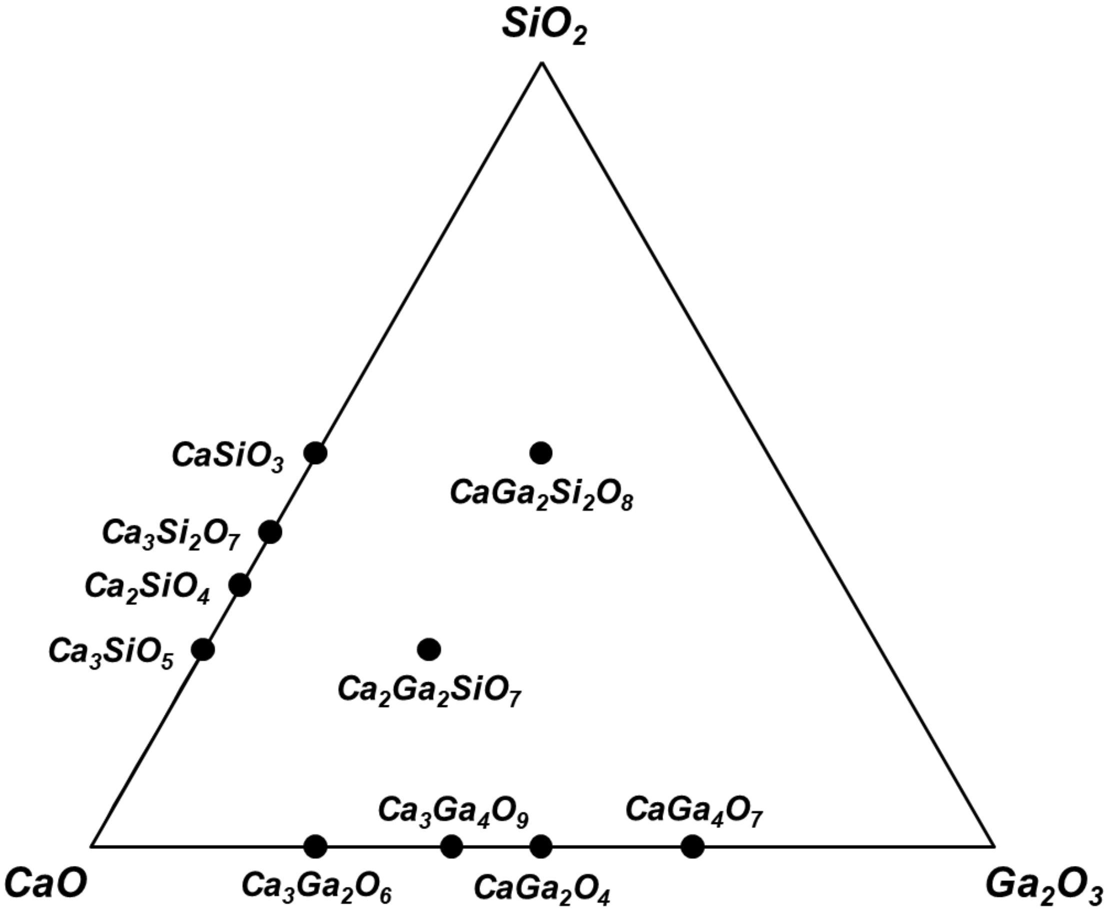

FIG 1 – Schematic diagram of the $CaO-SiO_2-Ga_2O_3$ system with all the stoichiometric compounds.

- Stoichiometric compounds

The Gibbs energies of stoichiometric compounds can be expressed as follows:

$$G_T^o = H_T^o - TS_T^o \quad (1)$$

$$H_T^o = \Delta H_{298.15K}^o + \int_{298.15K}^{T} C_p \, dT \quad (2)$$

$$S_T^o = S_{298.15K}^o + \int_{298.15K}^{T} \frac{C_p}{T} dT \quad (3)$$

where $\Delta H_{298.15K}^o$ and $S_{298.15K}^o$ are the standard formation enthalpy and standard entropy at 298.15 K, respectively, and C_p is the heat capacity which is a function of temperature.

- Liquid solution (Slag)

The Gibbs energy of liquid solution phase in the $CaO-SiO_2-Ga_2O_3$ system is described by the Modified Quasichemical Model (MQM) (Pelton *et al*, 2000; Pelton and Chartrand, 2001). In the MQM, a quasi-chemical pair exchange reaction between A and B cations in oxide melt can be expressed as:

$$(\mathrm{A}-\mathrm{A}) + (\mathrm{B}-\mathrm{B}) = 2(A-B) : \Delta g_{AB} \quad (4)$$

where A and B are cations in the solution and $(A-A)$, $(B-B)$, and $(A-B)$ represent each pair containing O^{2-} anion between the cations. In the present study, the cation species are Ca^{2+}, Si^{4+}, and Ga^{3+}. Δg_{AB} represents the Gibbs energy of pair exchange reaction. Then, the Gibbs energy of the solution phase is expressed in MQM as following:

$$G_{sol} = \sum_i n_i g_i^o - T\Delta S^{config} + \sum_{i<j} \left(\frac{n_{ij}}{2}\right) \Delta g_{ij} \quad (5)$$

where n_i and g_i^o are the number of moles and molar Gibbs energy of solution component i, and n_{ij} is the number of moles of $(i-j)$ pair at equilibrium. ΔS^{config} is the configurational entropy for the random distribution of the cation pairs, and Δg_{ij} can be expressed a function of composition and temperature. In the binary solution, Δg_{AB} can be expressed by the pair fraction X_{ij}:

$$\Delta g_{AB} = \Delta g_{AB}^o + \sum_{i\geq 1} g_{AB}^{io} X_{AA}^i + \sum_{i\geq 1} g_{AB}^{oj} X_{BB}^j \quad (6)$$

where Δg_{AB}^o, g_{AB}^{io}, and g_{AB}^{oj}, which are model parameter of MQM, can be optimised as a function of temperature.

In this study, the Gibbs energies of liquid solution in binary CaO-Ga_2O_3 system and SiO_2-Ga_2O_3 system were optimised based on all phase diagram data and thermodynamic data available in each system.

The Gibbs energy of ternary liquid solution can be predicted from the binary Gibbs energy expression using the so-called geometric interpolation model. There are several geometric interpolations to be used in the prediction for the Gibbs energy of ternary system. Depending on the nature of constituents in ternary system, a proper interpolation method should be determined. In this ternary CaO-SiO_2-Ga_2O_3 system, Kohler-Toop type interpolation method with SiO_2 as an asymmetric component was used for the prediction. It should be noted that the same interpolation method was used for the CaO-SiO_2-Al_2O_3 solution (Eriksson and Pelton, 1993). The detailed explanation regarding the Gibbs energy for ternary solution can be found elsewhere (Pelton and Chartrand, 2001).

RESULTS AND DISCUSSIONS

- The CaO-Ga_2O_3 system

Jeevaratnam (1961) conducted quenching experiments using Mercury (Hg) as a quenching media, and reported three stoichiometric compounds in the binary CaO-Ga_2O_3 system: $Ca_3Ga_2O_6$, $CaGa_2O_4$, and $CaGa_4O_7$. However, their experimental results are less reliable because the number of phases in equilibrated sample sometimes disobeyed the Gibbs phase rule. Later, Young (1979) reported a new stoichiometric compound $Ca_3Ga_4O_9$, located between $Ca_3Ga_2O_6$ and $CaGa_2O_4$. Daminova (1997) observed the solid-state phase transition of $CaGa_2O_4$ at 1300 °C using DTA experiment. Based on all available literature data, it can be confirmed that total four solid intermediate compounds are stable in this binary system: $Ca_3Ga_2O_6$, $Ca_3Ga_4O_9$, $CaGa_2O_4$ (low- and high temperature polymorphs) and $CaGa_4O_7$. The melting point of each compound was measured using quenching method (Jeevaratnam, 1961) or DTA (Young, 1979; Kovba, Lykova and Kalinina, 1980; Scolis *et al*, 1981). The melting points reported by Jeevaratnam (1961) are quite different from other DTA results, but it is hard to tell exactly why such discrepancies among existing experimental data. When the samples are less well quenched, solid crystals can form during quenching, and lead misinterpretation of the experimental liquidus temperature. Considering that liquid CaO-Ga_2O_3 solution is not very viscous like silicate melt, DTA results can be considered to be reliable in this system. All phase diagram results from DTA experiments are plotted in FIG 2 (a).

Scolis (1981) performed the electromotive force (EMF) experiments using electrochemical cells with CaF_2 electrolyte to determine the Gibbs energies of four stoichiometric compounds at 800 ~ 1100 °C. CaO-stabilised zirconia ($0.17CaO\cdot 0.83ZrO_2$)+$CaZrO_3$ was used as a reference electrode for the determination of the activity of CaO in working electrodes by EMF measurement. In the EMF experiments, Scolis (1981) also confirmed the existence of all four compounds. The enthalpies and entropies of formation of the compounds from CaO and Ga_2O_3 were obtained from the EMF data and the reported data are plotted in FIG 2 (b) and (c).

Thermodynamic modelling of the CaO-Ga_2O_3 system is performed based on the DTA results of Young (1979) and Kovba (1980), and the thermodynamic properties of compounds from EMF measurements of Scolis (1981). The Gibbs energies of liquid solution and four stoichiometric compounds are optimised in the present study to reproduce the experimental data. The calculated phase diagram and thermodynamic properties from the present optimised model parameters are shown in FIG 2 in comparison to the experimental data. As shown in FIG 2 (a), the phase diagram data are well reproduced except the liquidus points at X_{CaO} > 0.7. It is known that CaO-rich oxide melt, especially when it is saturated with solid CaO, can readily dissolve gas species like N_2 and CO_2 from atmosphere during the equilibrium experiment and be easily stabilised and show lower liquidus than real equilibrium liquidus. The enthalpy and entropy of solid stoichiometric compounds are also well reproduced within experimental error range. In the thermodynamic description, the heat capacities of solid compounds are estimated from constituent oxides, CaO and Ga_2O_3, using the Neumann-Kopp rule. It should be noted that the phase diagram of the CaO-Ga_2O_3 system is quite similar to that of the CaO-Al_2O_3 system.

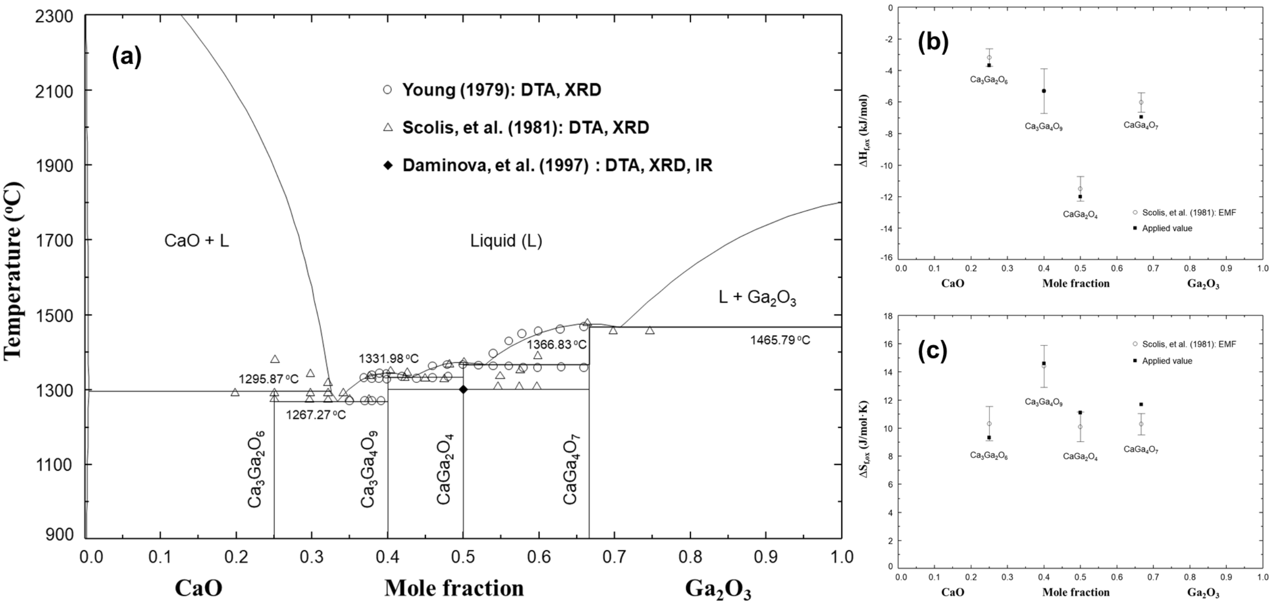

FIG 2 – Optimised results of the CaO-Ga_2O_3 system along with experimental data. (a) Phase diagram, (b) enthalpy of formation, (c) entropy of formation of stoichiometric compounds.

- The SiO_2-Ga_2O_3 system

Glasser (1959) and Toropov (1960a) performed the phase diagram study of the SiO_2-Ga_2O_3 system using quenching method. In both studies, no binary intermediate phase was found, but the phase diagrams proposed by two studies are completely different each other. Glasser (1959) reported the possibility of a large miscibility gap with a monotectic reaction L1 → L2 + Ga_2O_3 at about 1650 °C, and a eutectic reaction of L → SiO_2 + Ga_2O_3 in the SiO_2-rich region at about 1635 °C. On the other hand, Toropov (1960a) reported a simple eutectic reaction of L → SiO_2 + Ga_2O_3 in the SiO_2-rich region at about 1560 °C. The SiO_2-Ga_2O_3 melt should be very viscous so it requires a long equilibration time. However, the equilibrium experiments of Glasser were held for only several minutes most probably due to the evaporation of Ga_2O_3, and the experiments of Toropov (1960a) lasted also 1 hr to several hrs. Therefore, both results might be less reliable. Therefore, new phase diagram experiments are conducted in the present study.

Key samples are prepared to determine the phase diagram of the SiO_2-Ga_2O_3 system. The temperature range of the quenching experiments is 1530 to 1650 °C. The equilibrations of key samples are conducted for minimum 4 hrs and maximum 20 hrs. The present experimental results are summarised in FIG 3 (a). The back-scattered electron (BSE) images of two key samples are shown in FIG 3 (b) and (c). The microstructure of the quenched sample of 0.6SiO_2-0.4Ga_2O_3 in mol fraction equilibrated at 1580 °C (FIG 3 (b)) shows 2 phases of pure Ga_2O_3 and liquid phase with 0.954SiO_2-0.046Ga_2O_3. Two distinctive liquid phases in term of composition are observed in the sample of 0.8SiO_2-0.2Ga_2O_3 equilibrated at 1650 °C (FIG 3 (c)). That is, the liquid miscibility gap is found in this binary system as reported by Glasser (1959). The monotectic reaction of L1 → L2 + Ga_2O_3 at about 1620~1630 °C and the eutectic reaction of L → SiO_2 + Ga_2O_3 at about 1560 ~ 1575 °C are determined from the present quenching experiment. No noticeable mutual solubility between SiO_2 and Ga_2O_3 are found.

Based on the new phase diagram results in the present study, thermodynamic modelling of the SiO_2-Ga_2O_3 system is carried out. The Gibbs energy of the liquid solution is optimised to reproduce the present experimental data, and the phase diagram calculated from the present modelling results is plotted in FIG 3 (a). As can be seen, the phase diagram with liquid miscibility gap is well reproduced in the modelling study.

The liquid composition in the condition of FIG 3 (b) is calculated as 0.941SiO_2-0.059Ga_2O_3, which shows small error of 0.013Ga_2O_3 with experimental value. This can be caused by the sluggish kinetics due to viscous nature in SiO_2-rich region, and it requires much longer equilibration time to measure the exact composition of liquid. However, the closed Pt capsule can't endure the high vapour pressure of Ga_2O_3 at high temperature near 1600 °C for a long time. Considering these experimental challenges, that small error is actually negligible in terms of thermodynamic optimization.

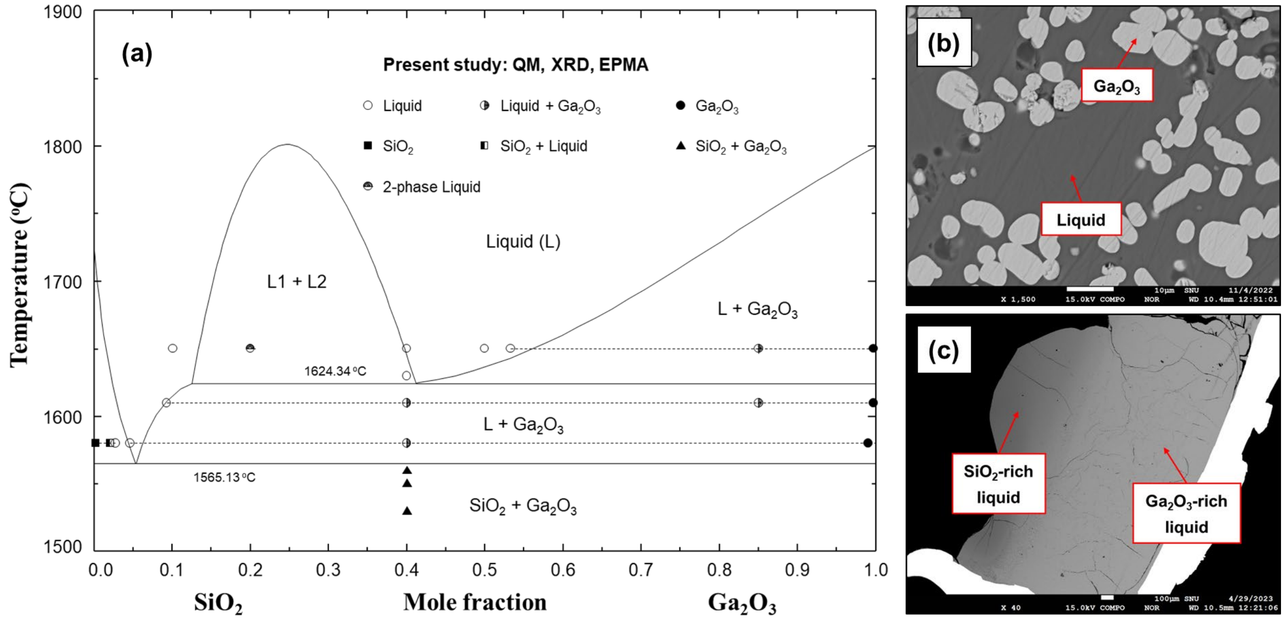

FIG 3 – Phase diagram experimental data and optimization results of binary SiO_2-Ga_2O_3 system. (a) Phase diagram along with all experimental data. BSE images of quenched samples of (b) 0.6SiO_2-0.4Ga_2O_3 equilibrated at 1580 °C and (c) 0.8SiO_2-0.2Ga_2O_3 at 1650 °C.

- The CaO-SiO_2-Ga_2O_3 system

Two ternary stoichiometric compounds are reported in the ternary CaO-SiO_2-Ga_2O_3 system: $Ca_2Ga_2SiO_7$ and $CaGa_2Si_2O_8$. These two compounds are almost identical to the ternary compounds, gehlenite $Ca_2Al_2SiO_7$ and anorthite $CaAl_2Si_2O_8$, in the CaO-SiO_2-Al_2O_3 system.

$Ca_2Ga_2SiO_7$ was first synthesised by Toropov (1960b), as part of continuous solid solution between $Ca_2Al_2SiO_7$ and $Ca_2Ga_2SiO_7$. Melting point of $Ca_2Ga_2SiO_7$ was first determined to be 1465 °C by Toropov (1960b). On the other hand, Korczak (1967) reported the melting point as 1485 °C by observing crystal growth from oxide melt during solidification process. In order to resolve this discrepancy, phase diagram experiments are conducted in this study to determine the melting temperature using classical quenching method. Eitel (1930) synthesised $CaGa_2Si_2O_8$ phase for the first time. The melting point of $CaGa_2Si_2O_8$ has not been reported yet. Therefore, the melting temperature of $CaGa_2Si_2O_8$ is also studied in the present study.

In general, no phase diagram study has been conducted for the ternary CaO-SiO_2-Ga_2O_3 system so far. In the present study, the preliminary phase diagram is predicted from the thermodynamic models with optimised model parameters of three binary systems. Then, based on the preliminary phase diagram, key sample compositions are chosen for three-phase equilibria or two-phase equilibria including liquid phase. Both quenching experiments and DTA experiments are performed for the ternary CaO-SiO_2-Ga_2O_3 system.

The melting points of $Ca_2Ga_2SiO_7$ and $CaGa_2Si_2O_8$ are determined from several quenching experiments. It is found that $Ca_2Ga_2SiO_7$ melts congruently at 1485 °C and $Ca_2Ga_2SiO_7$ melts incongruently at 1225 °C to liquid and Ga_2O_3. Isothermal phase diagrams at 1400 °C and 1500 °C are studied using quenching experiments. Several invariant reactions in the ternary system are determined using DTA. The examples of quenching and DTA experiment are presented in FIG 4 (a) and (b). The composition of liquid phase in FIG 4 (a) is measured as $0.41CaO\text{-}0.16SiO_2\text{-}0.43Ga_2O_3$. The onset temperature of 2nd and 3rd heating peak in FIG 4 (b) is 1374.4 °C.

Experimental results of the present study are used for the thermodynamic optimization of the ternary $CaO\text{-}SiO_2\text{-}Ga_2O_3$ system. The Gibbs energy of the liquid solution and two ternary compounds are optimised in the present study. The heat capacities of two ternary compounds $Ca_2Ga_2SiO_7$ and $CaGa_2Si_2O_8$ are estimated from CaO, tridymite SiO_2, and Ga_2O_3 using the Neumann-Kopp rule. The formation entropy of two ternary compounds are set to be the same value as those of ternary compounds $Ca_2Al_2SiO_7$ and $CaAl_2Si_2O_8$ in the $CaO\text{-}SiO_2\text{-}Al_2O_3$ system. Then, the standard enthalpy of formation of ternary compounds are optimised to reproduce their melting points. The Gibbs energy of liquid solution is optimised to reproduce entire phase diagram data in the present study.

The calculated value of liquid composition in FIG 4 (a) is $0.415CaO\text{-}0.153SiO_2\text{-}0.432Ga_2O_3$. This matches well with the experimental value within the small error range less than 0.01. The invariant point expressing the reaction in FIG 4 (b) is the point number 5 at 1374.21 °C in FIG 4 (c). This also matches very well with the present experimental data.

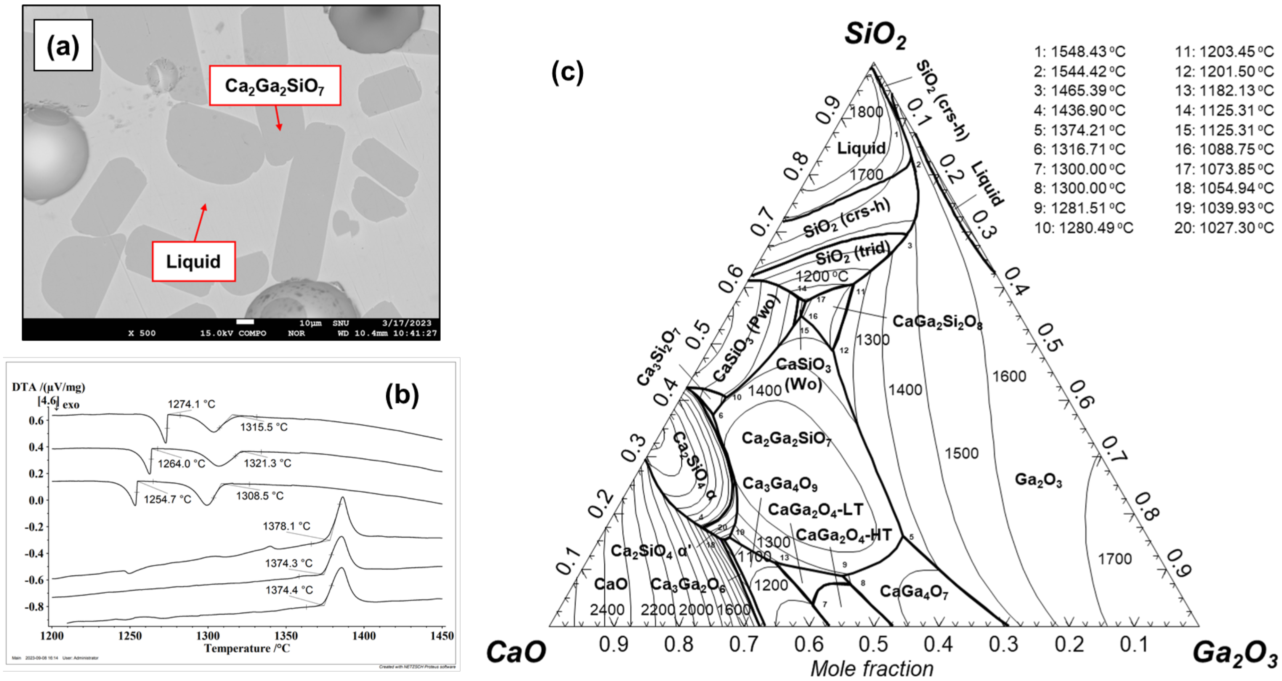

FIG 4 – Phase diagram experiments and calculated phase diagram of ternary $CaO\text{-}SiO_2\text{-}Ga_2O_3$ system. (a) BSE image for the quenched sample of $0.44CaO\text{-}0.19SiO_2\text{-}0.37Ga_2O_3$ equilibrated at 1400 °C, (b) DTA results of sample of $0.35CaO\text{-}0.17SiO_2\text{-}0.48Ga_2O_3$, and (c) calculated liquidus projection of ternary system.

CONCLUSIONS

Phase diagrams of the binary $SiO_2\text{-}Ga_2O_3$ and ternary $CaO\text{-}SiO_2\text{-}Ga_2O_3$ system are investigated using quenching experiments and DTA experiments, and accurate phase diagrams are determined for the first time. Based on reliable phase diagram data and thermodynamic data in literature and the present study, the CALPHAD-type thermodynamic modellings of binary $CaO\text{-}Ga_2O_3$, $SiO_2\text{-}Ga_2O_3$ and ternary $CaO\text{-}SiO_2\text{-}Ga_2O_3$ system are carried out. The optimised thermodynamic database can be integrated to the commercial FactSage thermodynamic database to calculate complex chemical reaction in pyrometallurgical Ga recycling process.

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