

Density of Ga₂O₃ Liquid

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The density of Ga₂O₃ liquid in equilibrium with air has been measured at 1800° to 1900°C using an Ir double-bob Archimedean method. The data yield the following description of the density of Ga₂O₃ liquid: $\rho = 4.8374(84) - 0.00065(12)(T - 1850^\circ\text{C})$. This density-temperature relationship is compared with the partial molar volume of Ga₂O₃ in glasses in the systems CaO-Ga₂O₃-SiO₂ and Na₂O-Ga₂O₃-SiO₂, corrected to the glass transition temperature using thermal expansivities. The comparison illustrates that a positive excess volume term is required in these systems at low temperature. This observation is similar to those deduced from studies of the partial molar volumes of Fe₂O₃ and Al₂O₃ in silicate melts. [Key words: gallium oxide, liquid phase, density, volume, glass.]

I. Introduction

LIQUID oxide components form the basis of complex silicate melts. As such, the densities of single-component liquids provide useful fix points for the construction of binary, ternary, and multicomponent melt density models. Although notable exceptions (such as B₂O₃, P₂O₅, and GeO₂) exist, the high melting temperature of most oxide components complicates direct measurement of the density of single-component, simple-oxide liquids. In this study the problem of high-melting-point liquids and the attendant problems of Mo- and W-based furnaces and crucibles (i.e., sample contamination and reduction) are circumvented with the use of an Ir- and ZrO₂-based measuring system operating in air.

Studies of the densities of Al₂O₃-, Fe₂O₃-, and TiO₂-bearing silicate melts have, in particular, yielded evidence for significant volumes of mixing in ternary silicate melts based on the alkali silicate binaries. Such data are some of the most direct determinations of the consequences of coordination shifts of cations on the density of silicate melts. These coordination shifts are, in turn, likely to be temperature- and pressure-dependent equilibria which complicate significantly the understanding of silicate liquid volumes at extrapolated temperatures and (especially important in the earth sciences) extrapolated pressures.

In the present study, results are reported for the determination of the liquid density of gallium oxide (Ga₂O₃). Ga₂O₃ is of particular interest in the study of silicate melts because Ga has been used as an analogue of Al in both the glass and geologic literatures. The molar volume of Ga₂O₃ is compared with partial molar volume data from silicate liquids for Fe₂O₃ and Al₂O₃ and from silicate glasses for Ga₂O₃.

II. Method

The starting material for the generation of Ga₂O₃ liquid was Ga₂O₃ powder (99.99%, Heraeus, GmbH, Karlsruhe, FRG).

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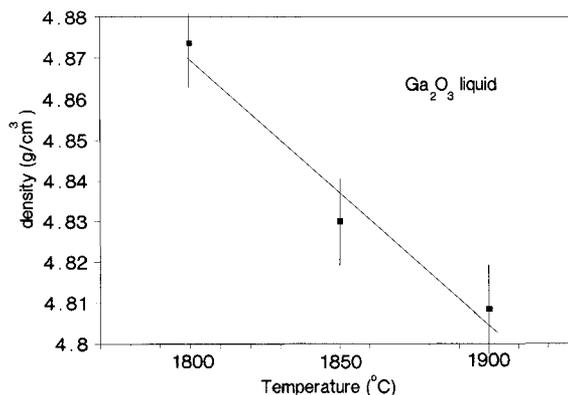


Fig. 1. Data for the temperature dependence of Ga₂O₃ density.

The powder was loaded directly into an Ir crucible (2.5-cm inner diameter, 5.1-cm height). The Ir crucible was then wrapped in ZrO₂ felt and placed in a tight-fitting MgO tube. This assembly was bottom loaded into the inner chamber of a high-temperature furnace.

The furnace is a commercially available (Model VHT 2100®, Linn HighTherm GmbH, Eschenfelden, FRG). Its special features are an inner chamber constructed from bubble-form ZrO₂ and two independent sets of heating elements. The outer set are MoSi₂ hairpin elements which preheat to 1700°C. These elements sit in wells within the bubble-form ZrO₂ walls. The other set of heating elements are ZrO₂ with (La,Sr)CrO₃ end pieces. These elements become sufficiently electrically conducting at 1250°C and are capable of heating to 2150°C in the present configuration.

The furnace is operated via electronic programmable temperature controllers. The preheating is controlled by a type-B thermocouple, and the main heating is controlled by an infrared pyrometer. The pyrometer has been calibrated against a type-B thermocouple at 1700°C.

The density measurements are based on the Archimedean buoyancy method. Two Ir bobs are used. The bobs have masses of approximately 14 and 24 g. Both are suspended from 0.5-mm Ir wire. The measuring balance (Model AE 100®, Mettler

Table I. Volumes of Gallium Silicate and Gallium Oxide Liquids Estimated at 773 K

Composition (mol%)			Density, ρ (g/cm ³)	Volume (cm ³ /mol)	
Na ₂ SiO ₃	CaSiO ₃	Ga ₂ O ₃		RT	773 K
0		100		32.80(96)*	
33.33		66.67	3.766	43.99	44.65
42.86		57.14	3.558	44.81	45.48
53.85		46.15	3.338	45.61	46.29
66.67		33.33	3.110	46.26	46.95
81.82		18.18	2.865	46.75	47.46
100		0	2.56	47.7	48.4
	66.67	33.33	3.533	39.61	40.20
	100	0	2.901	40.04	40.64

*Extrapolated from the liquid Ga₂O₃ data of this study. All other density data taken from Ref. 2. Number in parenthesis refers to 1 σ uncertainty.

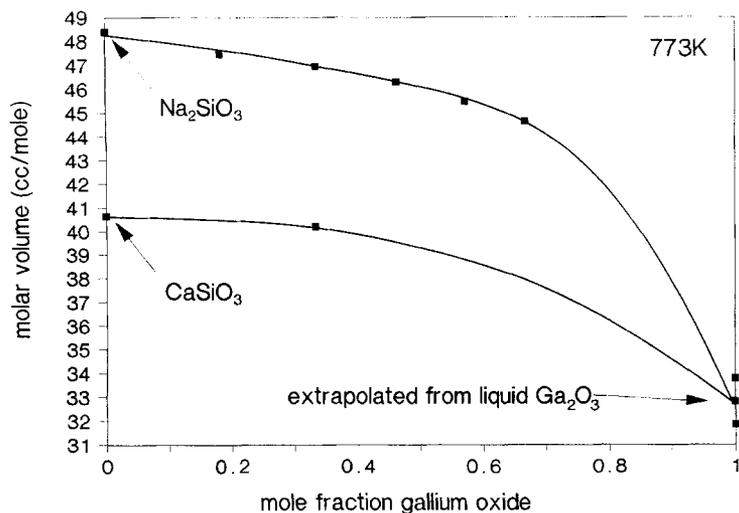


Fig. 2. Comparison of the computed volumes of liquids on the $\text{Na}_2\text{SiO}_3\text{-Ga}_2\text{O}_3$ and $\text{CaSiO}_3\text{-Ga}_2\text{O}_3$ joins with the extrapolated volume of Ga_2O_3 liquid.

Instrument Corp., Hightstown, NJ) is interfaced to a personal computer for data gathering using a data interface module (Model 012, Mettler Instrument Corp.). The data logging of buoyancy is performed at a 1- to 2-s interval, and the results are computer averaged over time.

The procedure for density measurement is to bring the sample to temperature, then load the Ir bob into the furnace from above, wait for thermal equilibrium, tare the balance, submerge the bob to a known depth in the liquid, and computer record the buoyancy. This procedure is repeated for the second bob, and the difference on buoyancy force, divided by the difference in submerged volume of Ir, yields the liquid density, e.g.,

$$\rho = (B_1 - B_2)/(V_1 - V_2) \quad (1)$$

where ρ is the liquid density, B_1 and B_2 are the buoyancies, and V_1 and V_2 are the submerged volumes of the first and second bobs, respectively. The volume-temperature relationship of Ir is taken from Wimber:¹

$$\begin{aligned} V_t = & 4.4601 \times 10^{-4}(100 + 1.994 \times 10^{-3}T \\ & - 8.07 \times 10^{-8}T^2 + 4.599 \times 10^{-10}T^3 \\ & - 1.052 \times 10^{-13}T^4) \end{aligned} \quad (2)$$

Buoyancy determinations have a precision of $\pm 0.1\%$ at 1σ (σ is standard deviation) and the density determinations are reported with a precision of $\pm 0.2\%$ at 1σ .

III. Results

The density of Ga_2O_3 liquid was determined at 1800°, 1850°, and 1900°C using the Ir double-bob Archimedean method. The densities determined (Fig. 1) were 4.8736, 4.8305, and 4.8082 g/cm³ at 1800°, 1850°, and 1900°C, respectively. The temperature dependence of density is given by

$$\rho = 4.8374(84) - 0.00065(12)(T - 1850^\circ\text{C}) \quad (3)$$

The density data and fitted expansivity curve are illustrated in Fig. 1.

The partial molar volume of Ga_2O_3 in silicate liquids is estimated from the densities of glasses by correcting room-temperature densities to the fictive temperatures with glassy expansivity data. Limited glass density data exist for the $\text{Na}_2\text{O-Ga}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-Ga}_2\text{O}_3\text{-SiO}_2$ systems.^{2,3} The volume composition data for the $\text{Na}_2\text{SiO}_3\text{-Ga}_2\text{O}_3$ and $\text{CaSiO}_3\text{-Ga}_2\text{O}_3$ joins taken from the literature sources and

corrected using literature expansivities to 500°C are tabulated in Table I and illustrated in Fig. 2. The partial molar volume exhibited by Ga_2O_3 in the $\text{Na}_2\text{O-Ga}_2\text{O}_3\text{-SiO}_2$ system at low temperature (corrected to 500°C) is 43.1(2) cm³/mol compared with a value of 32.80(97) cm³/mol from Eq. (3), indicating that a large positive excess volume of mixing exists in the $\text{Na}_2\text{O-Ga}_2\text{O}_3\text{-SiO}_2$ system. A similar conclusion has been reached by Hanada *et al.*² The case is less clear for the $\text{CaO-Ga}_2\text{O}_3\text{-SiO}_2$ system because of the limited glass data. If an excess volume exists, it is much smaller than that in the Na_2SiO_3 system. Similarly, larger excess volumes exist in the $\text{Na}_2\text{O-Fe}_2\text{O}_3\text{-SiO}_2$ and $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ systems than in the $\text{CaO-Fe}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-TiO}_2\text{-SiO}_2$ systems.^{6,7}

The molar volume of Ga_2O_3 is comparable to that estimated for Fe_2O_3 .⁴⁻⁶ Additionally, the presence of positive volumes of mixing in $\text{Na}_2\text{O-Fe}_2\text{O}_3\text{-SiO}_2$ required by the mismatch between the partial molar volume of Fe_2O_3 in the $\text{Na}_2\text{O-Fe}_2\text{O}_3\text{-SiO}_2$ and that estimated from very Fe-rich compositions and Fe-O liquids⁴⁻⁶ is similar to the behavior of Ga_2O_3 deduced above. Similarly, positive volumes of mixing have been proposed for the $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ system⁸ by comparison with the density of liquid Al_2O_3 .⁹

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