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CALCULATION OF BINARY PHASE DIAGRAM CURVES IN THE $PbO—Ga_2O_3$ SYSTEM

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ABSTRACT

A model of the regular behaviour of binary solutions was employed for the calculation of the liquidus curves in the $PbO—Ga_2O_3$ system. The unknown thermodynamic data necessary for the calculation were determined experimentally and/or calculated from the equilibria at the invariant points, respectively. The calculated curves are compared with those determined experimentally.

INTRODUCTION

The direct experimental determination of the phase diagram is very exacting with regard to the requirements of laboratory equipment and time consumption. Therefore, the calculation of binary phase diagram curves, mainly in the high temperature region, can substantially simplify the phase diagram construction.

In the present work, the calculation procedure for the $PbO—Ga_2O_3$ system, experimentally determined in our previous work [1], is shown. For the calculation the procedure suggested by Holba [2] was employed. The procedure is based on a model of the regular behaviour of binary solutions, and on the presumption that the microscopic composition of a two-component system can be expressed by a single parameter equation derived from the macroscopic molar fraction.

CALCULATION PROCEDURE

As follows from the experimentally determined phase diagram (see Fig. 1), three different regions of the equilibrium coexistence of liquid and solid phases (PbO—melt, $PbGa_2O_4$—melt and Ga_2O_3—melt) exist in the $PbO—Ga_2O_3$ system.

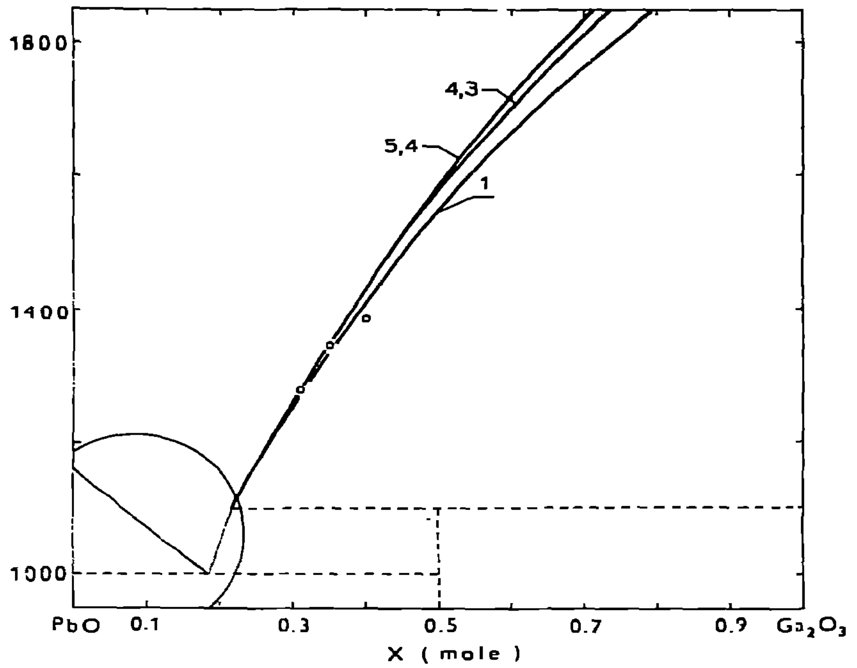

Fig. 1. Phase diagram of the PbO—Ga$_2$O$_3$ system (o, experimentally determined points; 1, 4, 3 and 5, 4, calculated curves).

These equilibria can be expressed by the following equations

$$\frac{\partial G_L^m}{\partial x_L} = \frac{G_L^m - G_A^m}{x_L - x_A} \tag{1}$$

$$\frac{\partial G_L^m}{\partial x_L} = \frac{G_L^m - G_B^m}{x_L - x_B} \tag{2}$$

$$\frac{\partial G_L^m}{\partial x_L} = \frac{G_L^m - G_C^m}{x_L - x_C} \tag{3}$$

where x_i are equilibrium compositions of the coexisting phases, G_i^m are molar Gibbs free energies of these phases and, A, B and C relate to PbO, PbGa$_2$O$_4$ and Ga$_2$O$_3$ compounds with transformed formulas, in order that the sum of cations is equal to unity, i.e., A = PbO, B = $Pb_{1/3}Ga_{2/3}O_{4/3}$ and C = $GaO_{3/2}$. For the molar Gibbs free energies of coexisting phases the following equations hold

$$G_L^m = RT[x \ln x + (1-x)\ln(1-x)] + x(1-x)\Omega(1+kx) \tag{4}$$

$$G_A^m = \Delta H_A^{melt}(1 - T/T_A^{melt}) \tag{5}$$

$$G_B^m = \Delta H_B^{melt}(1 - T/T_B^{melt}) + G_L^m(x_B) \tag{6}$$

$$G_C^m = \Delta_C^{melt}(1 - T/T_C^{melt}) \tag{7}$$

where ΔH_A^{melt}, ΔH_B^{melt}, ΔH_C^{melt} are the heats, and T_A^{melt}, T_B^{melt}, T_C^{melt} are the temperatures of the congruent melting of the individual compounds, having in the case of $Pb_{1/3}Ga_{2/3}O_{4/3}$($PbGa_2O_4$), which, in fact, melts incongruently, only hypothetical sense, Ω and k parameters cover the regular behaviour of the melt (the contribution of the additional mixing enthalpy). From the whole set of thermodynamic data, the ΔH_B^{melt}, T_B^{melt}, Ω and k are not experimentally accessible; nevertheless, these data can be calculated by the use of equations describing the equilibria at the invariant points (eutectic or peritectic), where the following relations are valid

$$\frac{\partial G_L^m(x_E)}{\partial x} = \frac{G_B^m - G_A^m}{x_B - x_A} \qquad (8)$$

$$\text{for } T = T_E$$

$$\frac{\partial G_L^m(x_E)}{\partial x} = \frac{G_B^m - G_L^m}{x_B - x_L} \qquad (9)$$

$$\frac{\partial G_L^m(x_P)}{\partial x} = \frac{G_C^m - G_B^m}{x_C - x_B} \qquad (10)$$

$$\text{for } T = T_P$$

$$\frac{\partial G_L^m(x_P)}{\partial x} = \frac{G_B^m - G_L^m}{x_B - x_L} \qquad (11)$$

T_E, T_P, x_E and x_P are the temperatures and compositions of eutectic and/or peritectic, respectively.

These relations can be completed by the expression for the enthalpy change connected with the eutectic melting [3]

$$\Delta H_E^{melt} = x_E(1 - x_E)\Omega(1 + kx_E) - (x_B - x_E)\Delta H_A^{melt}/x_B$$
$$- [\Delta H_B^{melt} + x_B(1 - x_B)\Omega(1 + kx_B)]x_E/x_B \qquad (12)$$

The experimental thermodynamic data used for the calculation of unknown data are listed in Table 1.

TABLE 1

Experimental data used for the calculation of unknown data

	T^{melt} (K)	ΔH^{melt} (J × 10^3 $mole^{-1}$)	Composition	
			Molar fraction	Ionic fraction
PbO	1158 [a]	26.1 [a]	0.000	0.000
Ga_2O_3	1998 [b]	91.7 [b]	1.000	1.000
$PbGa_2O_4$			0.500	0.666
Eutectic	1001 [c]	29.8 [d]	0.185 [c]	0.312
Peritectic	1098 [c]		0.215	0.354

[a] L. Barin and O. Knacke, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin, Heidelberg, New York, 1973.

[b] Thermodynamiccheskie Svoystva Neorg, Veschcchestv, Spravocchnik, Atomizdat, Moscow, 1965.

[c] Experimentally determined [1].

[d] Determined by DTA commercial apparatus "O2" from VEB Laborelectronik Halle, D.D.R. The temperature difference ΔT was indicated with a sensitivity of 4 $\mu V\ cm^{-1}$ at a heating rate 10 K min^{-1}. The apparatus constant $K = 11.6 \pm 1.0$ mcal deg^{-1} sec at 1001 K was determined by calibration on ICTA standards (K_2SO_4, $BaCO_3$, $SrCO_3$).

TABLE 2

Thermodynamic data calculated by using the equilibria at invariant points

Equations used for the calculation of unknown data	Calculated data						Curve
	T_B^{melt} (K)	ΔH_B^{melt} (J × 10^3 mole^{-1})	Ω	k	ΔH_C^{melt} (J × 10^3 mole^{-1})	ΔH_E^{melt} (J × 10^3 mole^{-1})	
9, 11	1595	−17.5					1
8, 11; 9, 10; 8, 10	1316	−33.0					2
8, 9, 11	1553	−23.3	−4.6				3
8—11	1624	−35.1	−12.4	1.66			4
8—12	1624	−35.1	−12.4	1.66		−25.5	4
8—12	1664	−17.8	−20.6	1.09	−136.1		5

RESULTS AND DISCUSSION

The thermodynamic data calculated by using the equilibria at invariant points (from eqns. (S—12)) are given in Table 2.

The fact that five equations were at our disposal for the calculation of four unknown quantities (T_B^{melt}, ΔH_B^{melt}, Ω, k) made it possible to compare the experimentally determined and calculated enthalpy change ΔH_E^{melt}. The discrepancy found between these two values equals 17 rel. %. Although this

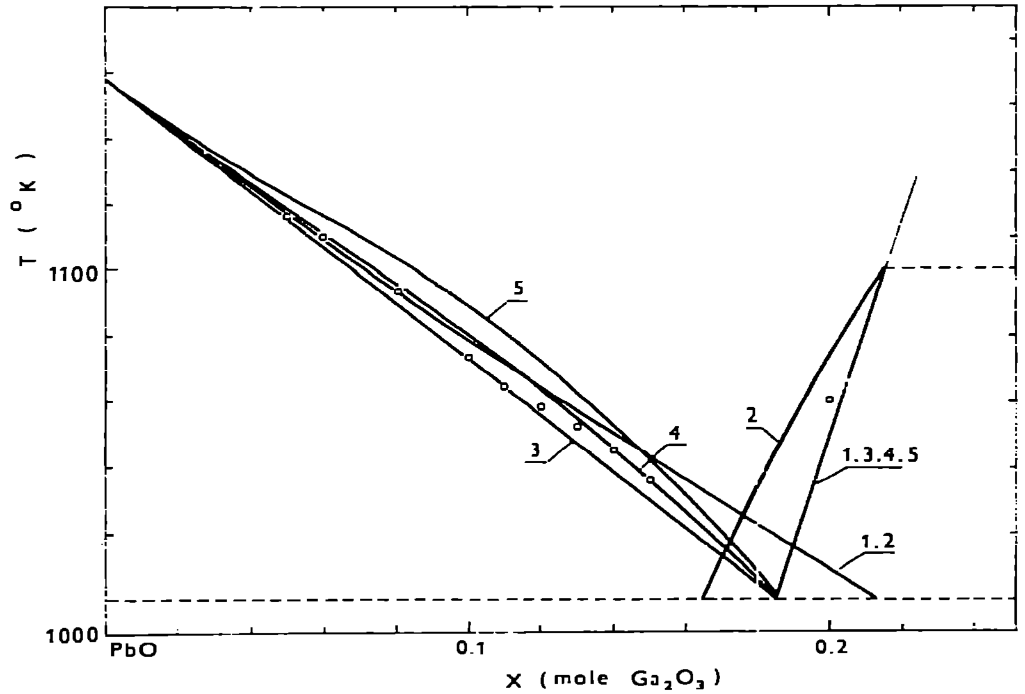

Fig. 2. The liquidus curves for the concentration range 0—0.22 mole Ga_2O_3 in detail (o, experimentally determined points; 1, 2, 3, 4 and 5, calculated curves).

is in the limit of the experimental errors of the DTA method used for the calorimetric measurement, it leads to the following deviations of the other calculated quantities: $T_{\mathrm{B}}^{\mathrm{melt}} \sim 2.5$ rel. %, $\Delta H_{\mathrm{B}}^{\mathrm{melt}} \sim 36$ rel. %, $\Omega \sim 66$ rel. %, $k \sim 26$ rel. % and $\Delta H_{\mathrm{C}}^{\mathrm{melt}} \sim 48$ rel. % (see also Table 2).

The liquidus curves (T—x dependence) were determined by the solution of eqns. (1—3), where the experimental and calculated data (see Tables 1 and 2) were employed. The calculated curves 1—5 are compared to the experimental one (see Figs. 1 and 2).

The best agreement between the experimental and the calculated liquidus curves was attained for curve 4 in the regions of melt—PbO and melt—$PbGa_2O_4$ and for curves 4 and 5 in the melt—Ga_2O_3 region, i.e. where both Ω and k parameters were used during the calculation. In the last case the comparison is more difficult, with regard to the lack of experimental points, which cannot be obtained due to high volatility of PbO at high temperatures. On the other hand, the assumption of the ideal behaviour of the melt (i.e. neglecting Ω and k) leads to curves 1 and 2, which differ significantly from the experimental situation.

The results obtained permit the conclusion to be made that the use of the model anticipating the regular behaviour of the melt is justified.

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