Thermodynamic properties of Ga-Zn system. Experiment vs model

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ABSTRACT

This paper contains the results of the integral molar mixing enthalpy of Ga-Zn liquid alloys, measured calorimetrically at two temperatures: 722 K over the entire concentration range and 923 K for the concentration range of Zn lower than 0.5 at.%. Experimental values obtained in this range of temperatures indicate that the integral molar enthalpy of liquid alloys of this binary system is temperature independent. The available experimental values of the partial or molar Gibbs energies, together with the enthalpy of mixing, were used for the elaboration of the equation in the form proposed by Redlich and Kister, which describes the dependence of the excess Gibbs energy on the concentration and temperature. The experimental thermodynamic values of the excess Gibbs energy, mixing enthalpy change and activity were compared with those calculated with the use of the elaborated Redlich-Kister equation. Moreover, the partial structure factors and short-range order parameter were calculated and discussed in relation to the thermodynamic properties and the phase diagram of the Ga-Zn system.

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1. Introduction

Gallium alloys are crucial materials for manufacturing of semiconductor devices, and also promising materials for lead-free solders, because of their low melting point, good wetting properties, adhesion, and oxidation resistance [1–3].

The Ga-Zn phase diagram is a simple eutectic system with an eutectic point at 3.87 at.% of Zn and temperature of *ca.* 298 K. The *liquidus* of this system was investigated by Puschin et al. [4], Valenti and Fiorani [5], Heumann and Predel [6], Chart [7], Delcroix et al. [8], Shurai et al. [9], while the *solidus* was defined by Davis [10], using X-ray diffraction. The activities of Ga-Zn liquid alloys were extensively investigated electrochemically (by electromotive force method (EMF)) by many scientists such as Genta et al. [11], Kleppa and Thalmayer [12], Svirbely and Read [13], Gerasimenko et al. [14], Predel et al.[15], Ryabov and Sryvalin [16], Moser [17] and Girard et al. [18] in the entire composition range at different temperatures from 693 K to 1396 K. Picente et al. [19], also measured the thermodynamic activities of components in this liquid binary system with the use of the vapour pressure method at 916 K. The mixing enthalpy of the liquid Ga-Zn system was calorimetrically measured by Kleppa [20] at 723 K, and later, by Gambino et al. [21,22] at 723 K and 873 K, and finally by Bourkba

et al. [23] at 717 K. Kubaschewski et al. [24,25], Akhkubekov et al. [26] and Dutkiewicz et al. [27] calculated the phase diagram, based on available literature data. Moreover, some thermodynamic calculations were done by Ptak [28], Hajra and Mazumdar [29], Hultgren [30]. Later, Dutkiewicz et al. [27] presented the optimized and completed thermodynamic description of the Ga-Zn system. Finally, in 2003 Živković et al. [31] presented the thermodynamic study of Ga-Zn system with the use of quantitative differential thermal analysis.

The thermodynamic description of the liquid Ga-Zn solutions, given by Dutkiewicz et al. [27], shows the curve linear temperature dependence of excess free energy and the same temperature dependence of the mixing enthalpy change. The most of the studies concerning the mixing enthalpy were conducted only at one temperature, thus it is hard to deduce if the dependence cited above is correct since measurements were performed at different calorimeters, and the observed deviations or data consistency could be the result of experimental errors. Moreover, in the paper [27], a non-literature source has been cited in which the temperature dependence was experimentally confirmed. Hence, the idea emerged to measure the mixing enthalpy change of Ga-Zn liquid solutions at the temperature range wide enough to observe mentioned dependence and with the use of the same calorimeter with the same experimental error. Such studies could most likely decide if the Ga-Zn liquid solutions are characterized by the temperature dependence of the mixing enthalpy and they allow a new elaboration of the thermodynamics of Ga-Zn alloys.

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2. Materials and methods

The calorimetric measurements were performed with the use of an MHTC 96 drop calorimeter. The experimental procedure adopted in all experiments was previously described in [32]. The specifications of all chemicals used for determination of the integral mixing enthalpy are listed in Table 1. All calorimetric measurements were done in the protective argon atmosphere using the Al_2O_3 crucibles. At the beginning of each experiment, the calorimeter was evacuated with the vacuum pump several times and flushed with high purity argon (Table 1). After such procedure, the calorimeter was calibrated with the use of six pieces of gallium or zinc (depending on the measured side of Ga-Zn system).

2.1. Enthalpy of mixing

The integral enthalpies of mixing ($\Delta_{mix}H$) of the Ga-Zn liquid alloys can be calculated using the following equations:

$$H_{DISS-X} = (\Delta H_{Signal} \cdot K) - (\Delta H_X^{T_R \to T_M} \cdot n_X), \qquad (1)$$

$$K = \frac{\Delta H_X^{T_R \to T_M} \cdot n_X}{\Delta H_{Calibration}} \qquad (2)$$

$$\Delta_{mix}H = \frac{\sum H_{DISS-X}}{n_{Ga} + n_{Zn}} \qquad (3)$$

Here the ΔH_{Signal} is the heat effect of each dropped metal (Ga or Zn) which equalled the added drop enthalpy; K is the calorimeter constant; $\Delta H_X^{T_R \to T_M}$ is the molar enthalpy difference of gallium and zinc between room temperature (T_R = 298 K) and temperature of measurement (T_M), calculated using the Pandat 2013 (Pan SGTE database based on the original SGTE v4.4 database); n_x (n_{Ga}, n_{Zn}) are the number of moles of gallium and zinc, respectively; H_{DISS-X} represents the enthalpy of dissolution of pure gallium and zinc; $\Delta H_{Calibration}$ is the heat effect of dropped metal which was used for calibration.

The experimental measurements for the Ga-Zn system were performed at two different temperatures (722 K and 923 K). The results obtained were compared with literature data and calculated with the use of the Miedema model [33,34].

3. Results and discussion

The experimental values of the integral mixing enthalpy of Ga-Zn liquid alloys measured in this study, together with the standard errors and other information concerning the calorimetric experiment are presented in Table 2.

The experimental values of liquid Ga-Zn solutions were elaborated by the Redlich and Kister [35] equation which describes the dependence of the excess Gibbs energy on the temperature and concentration of components in the form given below:

$$\Delta_{mix}G^E = X_{Ga} \cdot X_{Zn} \cdot \sum_{i=0}^{i=n} (A_i + B_i \cdot T) * (X_{Ga} - X_{Zn})^i \quad i = 1, 2, 3 \ldots \quad (4)$$

Table 1
Provenance and mass fraction purity of the applied materials.

Chemical name	Source	Mass fraction purity	Purification method	Analysis method
Gallium	Alfa Aesar	0.99999	None	Certified purity
Zinc	Alfa Aesar	0.99999	None	Certified purity
Argon	Air Products	0.999999	None	Certified purity

where A_i, B_i are adjustable parameters, i is the exponent, X_{Ga} and X_{Zn} are the mole fraction of gallium and zinc in solution and T is the temperature.

The mixing enthalpy, excess entropy and the partial excess Gibbs energy of Zn and Ga are calculated with the use of Eq. (4) according to the following relations:

$$\Delta_{mix}H = X_{Ga} \cdot X_{Zn} \cdot \sum_{i=0}^{i=n} A_i * (X_{Ga} - X_{Zn})^i \qquad (5)$$

$$\Delta_{mix}S^E = -X_{Ga} \cdot X_{Zn} \cdot \sum_{i=0}^{i=n} B * (X_{Ga} - X_{Zn})^i \qquad (6)$$

$$\Delta G_{Ga}^E = \Delta_{mix}G^E - X_{Zn} \left(\frac{d(\Delta_{mix}G^E)}{dX_{Zn}} \right)_{T,p} \qquad (7)$$

$$\Delta G_{Zn}^E = \Delta_{mix}G^E + (1 - X_{Zn}) \left(\frac{d(\Delta_{mix}G^E)}{dX_{Zn}} \right)_{T,p} \qquad (8)$$

Inserting in Eqs. (7) and (8) $\Delta_{mix}H$ (Eq. (5)) or $\Delta_{mix}S^E$ (Eq. (6)) instead of $\Delta_{mix}G^E$, one can calculate partial enthalpy and partial excess entropy of Ga and Zn. Moreover, other thermodynamic quantities such as molar mixing Gibbs energy and entropy ($\Delta_{mix}G$, $\Delta_{mix}S$), partial Gibbs energy, activity and activity coefficient of Ga and Zn ($\Delta G_{Ga}, \Delta G_{Zn}, a_{Ga}, a_{Zn}, \gamma_{Ga}, \gamma_{Zn}$) are calculated using following equations:

$$\Delta G_i = R \cdot T \cdot \ln X_i + \Delta G_i^E \qquad (9)$$

$$\Delta S_i = -R \cdot \ln X_i + \Delta S_i^E \qquad (10)$$

$$a_i = exp\left(\frac{\Delta G_i}{R \cdot T} \right) \quad \gamma_i = exp\left(\frac{\Delta G_i^E}{R \cdot T} \right) \qquad (11)$$

where R is the universal gas constant, and i symbolizes gallium (Ga) or zinc (Zn).

Calculations of A_i and B_i parameters in Eq. (4) were conducted by the least squares method. It means that using different values of mentioned parameters, the values of partial excess Gibbs energy of Zn and molar mixing enthalpy change were calculated, and next the sum of square differences between the experimental and calculated values cited thermodynamic functions was counted. Finally, the A_i and B_i parameters in Eq. (4) were accepted (chosen) for which the mentioned sum was the lowest. The calculated standard error of estimation of Eq. (4) was calculated as the square root of the sum of square differences divided by the number of experimental data points. In the determination of the A_i and B_i parameters, the following values were applied (in the case of ΔG_{Zn}^E: Genta et al. [11] (761.4 K), Kleppa, and Thalmayer [12] (978 K), Svirbely, and Read [13] (743 K), Gerasimenko et al. [14] (773 K), Predel et al. [15] (978 K), Ryabov, and Sryvalin [16] (933 K), Moser [17] (714 K, 757 K, 805 K, 843 K, 877 K), Girard et al. [18] (850 K, 9733 K), Piacente et al. [19] (916 K), and in the case of $\Delta_{mix}H$: this study (722 K, 923 K), Kleppa [20] (723 K), Bourkba et al. [23] (717 K) and Živković et al. [31] (723 K)). The results of $\Delta_{mix}H$ obtained by Valenti and Fiorani [5] were not used in calculations, since they are calculated using this parameter based on the Ga-Zn phase diagram and made an assumption that $\Delta_{mix}S^E = 0$, similar to the ΔG_{Zn}^E given by Živković et al. [31] only based on the calorimetric investigations. The temperature given in parenthesis in the case of ΔG_{Zn}^E is that at which authors gave explicitly the measured values in their works. In the case of $\Delta_{mix}H$, the temperature in brackets correspond to the measured temperatures.