

## Calorimetric study of enthalpies of mixing in liquid gallium–germanium–yttrium alloys

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### Abstract

The yttrium partial enthalpies of mixing ( $\Delta_{\text{mix}}\bar{H}_Y$ ) and the integral enthalpies of mixing ( $\Delta_{\text{mix}}H$ ) of liquid Ga–Ge–Y alloys have been determined by high-temperature mixing calorimetry for five sections with constant ratios of Ga and Ge at 1760 K. Plots of concentration dependence of  $\Delta_{\text{mix}}\bar{H}_Y/(1-x_Y)^2$  show sharp inflections, which correspond to transition of the liquid alloys into heterogeneous state and can be used for determination of liquidus surface. Furthermore, the  $\Delta_{\text{mix}}H$  has been estimated in the ternary system using seven geometric models and the Bonnier model has been chosen as the most adequate one. The differences between the experimental and model integral enthalpies of mixing have been described by polynomial concentration dependence. The possible contribution of binary and ternary intermetallide compounds into the thermodynamics of the liquid Ga–Ge–Y alloys has been considered.

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### 1. Introduction

Multicomponent alloys of gallium and germanium with rare-earths are of high actuality due to possible application in production of novel magnetic materials. Molten gallium has been used as a solvent for the synthesis of rare-earth (RE) intermetallides containing germanium and transition metals, e.g.  $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5+n-x}\text{Ge}_x$  [1],  $\text{RE}_3\text{Ga}_9\text{Ge}$  [2],  $\text{REMGa}_3\text{Ge}$  ( $M = \text{Co}, \text{Ni}$ ) [3],  $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$  [3],  $\text{REGaGe}$  [4], and  $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$  [5]. Substitution of magnetic elements (i.e. rare-earth or transition metals) by non-magnetic dilutor such as yttrium, results in a change of magnetic properties of the compounds. Consequently, the Ga–Ge–Y is of considerable interest as a boundary ternary system of the quaternary

Ga–Ge–Y–TR ones (TR is rare-earth or transition metal). No systematic examinations on the thermodynamic properties of the Ga–Ge–Y system have been reported in the literature.

Crystal structures of intermetallide compounds, which are formed in the Ga–Ge–Y system, have been examined by X-ray powder diffraction using Rietveld refinement [6,7]. The isothermal sections have been studied at two temperatures: firstly at 1073 K in the region from 33.3 to 100 at.% Y [6] and later at 873 K in the region up to 37 at.% Y [7]. Four rare-earth intermetallide compounds have been found in the system at 1073 K [6], namely  $\text{YGe}_{0.6}\text{Ga}_{1.4}$  (I),  $\text{Y}(\text{Ge}_x\text{Ga}_{1-x})_{1.8}$  ( $0.2222 < x < 0.3889$ ) (II),  $\text{Y}(\text{Ge}_x\text{Ga}_{1-x})_{1.7}$  ( $0.5882 < x < 0.7647$ ) (III) and  $\text{Y}_2(\text{Ge}_x\text{Ga}_{1-x})_3$  ( $0.5667 < x < 0.7667$ ) (IV). Besides, continuous series of solid solution  $\text{YGa}_x\text{Ge}_{1-x}$  ( $0 < x < 1$ ) (V) form on the YGa–YGe section at 1073 K [6]. At least eight ternary compounds are registered in the system at 873 K, i.e. (I), (III),  $\text{Y}_2\text{Ge}_{6.66}\text{Ga}_{0.34}$  (VI),  $\text{Y}(\text{Ge}_x\text{Ga}_{1-x})_{3.34}$  ( $0.7425 < x < 0.8713$ ) (VII),  $\text{Y}_2(\text{Ge}_x$

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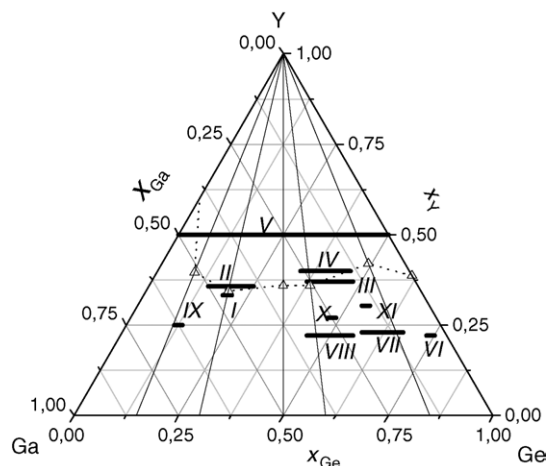


Fig. 1. Plot of intermetallides compositions in the Ga–Ge–Y system. (I)  $\text{YGe}_{0.6}\text{Ga}_{1.4}$ , (II)  $\text{Y}(\text{Ge}_x\text{Ga}_{1-x})_{1.8}$  ( $0.2222 < x < 0.3889$ ), (III)  $\text{Y}(\text{Ge}_x\text{Ga}_{1-x})_{1.7}$  ( $0.5882 < x < 0.7647$ ), (IV)  $\text{Y}_2(\text{Ge}_x\text{Ga}_{1-x})_3$  ( $0.5667 < x < 0.7667$ ), (V)  $\text{YGa}_x\text{Ge}_{1-x}$  ( $0 < x < 1$ ), (VI)  $\text{Y}_2\text{Ge}_{6.66}\text{Ga}_{0.34}$ , (VII)  $\text{Y}(\text{Ge}_x\text{Ga}_{1-x})_{3.34}$  ( $0.7425 < x < 0.8713$ ), (VIII)  $\text{Y}_2(\text{Ge}_x\text{Ga}_{1-x})_7$  ( $0.5714 < x < 0.7143$ ), (IX)  $\text{YGe}_{0.5}\text{Ga}_{2.5}$ , (X)  $\text{YGe}_{1.78}\text{Ga}_{0.92}$  and (XI)  $\text{YGe}_{1.8}\text{Ga}_{0.5}$ . Compounds (I)–(V) have been found at 1073 K [6], compounds (I), (III) and (VI)–(XI) have been determined at 873 K [7]. Dotted line bounds the region of liquid alloys examined by calorimetry in the present study. Triangles denote the concentrations corresponding to the transition into a two-phase region. Lines connecting the Y-corner of the Gibbs triangle and the Ga–Ge boundary denote the studied sections.

$\text{Ga}_{1-x})_7$  ( $0.5714 < x < 0.7143$ ) (VIII),  $\text{YGe}_{0.5}\text{Ga}_{2.5}$  (IX),  $\text{YGe}_{1.78}\text{Ga}_{0.92}$  (X) and  $\text{YGe}_{1.8}\text{Ga}_{0.5}$  (XI) [7]. Fig. 1 demonstrates concentration regions of the intermetallide compounds existence reported in [6,7].

However, for assessment of the phase equilibria it is necessary to know the thermodynamic properties of the system in particular in the liquid state. Therefore, the present work is directed on calorimetric measurements of the enthalpies of mixing in the liquid Ga–Ge–Y alloys.

## 2. Experimental

### 2.1. Materials

Gallium (Alfa, 99.9999%), germanium (Alfa, 99.9999%), yttrium distillate (Dahuachem, 99.97%) and tungsten (Alfa, 99.96%) were used for the calorimetric experiments. High-purity argon (99.997 vol.%) was utilized for filling of the calorimeter's internal volume to prevent the alloys chemical reactions with air constituents.

### 2.2. Calorimetric procedure and data treatment

The heats of mixing have been measured using a high-temperature mixing calorimeter [8] at 1760 K. The mixing experiments have been performed under the argon at atmospheric pressure. The measurements have been

done along five sections of the Ga–Ge–Y system with Ga–Ge basis. The molar ratios of  $x_{\text{Ga}}:x_{\text{Ge}}$  are 0.15:0.85, 0.4:0.6, 0.5:0.5, 0.7:0.3 and 0.85:0.15 for  $0.0 < x_{\text{Y}} < 0.65$ . The calorimetric measurements routine has been previously reported in [9]. The initial calorimetric data are listed in Tables 1–5.

The heat-exchange coefficient of the calorimeter is calculated by the formula

$$k_i = \Delta H_{298}^T n_i / S_i, \quad (1)$$

where  $\Delta H_{298}^T$  is the enthalpy of 1 mol of reference component (Ge or W) heating from  $T = 298$  K up to experimental temperature [10],  $i$  is the dropped sample number,  $n_i$  is the mole quantity of the dropped sample, and  $S_i$  is the area of heat-exchange peak. The  $k_i$  values are treated by the least square regression (l.s.r.) for the linear model

$$k = a + b m_{\text{alloy}}, \quad (2)$$

where  $m_{\text{alloy}}$  is the alloy mass, and  $a$  and  $b$  are the l.s.r. coefficients. The partial enthalpy of mixing is calculated from the experimental heat-exchange curve by the formula

$$\Delta_{\text{mix}} \bar{H}_{\text{Y}} = -\Delta H_{298}^T + k_i S_i / n_i, \quad (3)$$

where  $\Delta H_{298}^T$  is the standard enthalpy of Y [10]. The values of the  $\Delta_{\text{mix}} \bar{H}_{\text{Y}}$  are assigned to the middle point of the composition range before and after sample addition. The experimental partial enthalpy of mixing is expressed via an alpha function

$$\alpha_{\text{Y}} = \Delta_{\text{mix}} \bar{H}_{\text{Y}} / (1 - x_{\text{Y}})^2. \quad (4)$$

The alpha function is smoothed using l.s.r. for the polynomial model. Respectively, concentration dependence of the  $\Delta_{\text{mix}} \bar{H}_{\text{Y}}$  is represented via the equation

$$\Delta_{\text{mix}} \bar{H}_{\text{Y}} = (1 - x_{\text{Y}})^2 \sum_{j=0}^l Q_j x_{\text{Y}}^j, \quad (5)$$

where  $Q_i$  are the polynomial coefficients and  $l$  is the polynomial degree determined by the Fisher's exact test [11]. The Darken's integration of Eq. (5) leads to

$$\Delta_{\text{mix}} H = (1 - x_{\text{Y}}) \left[ \Delta_{\text{mix}} H^\circ + \sum_{j=0}^l (j+1)^{-1} Q_j x_{\text{Y}}^{j+1} \right], \quad (6)$$

where  $\Delta_{\text{mix}} H^\circ$  is the integral enthalpy of mixing in the binary Ga–Ge alloy. The deviations of integral enthalpies of mixing have been determined as proposed in [9]

$$\sigma(\Delta_{\text{mix}} H) = (1 - x_{\text{Y}}) \times \left\{ D(\Delta_{\text{mix}} H^\circ) + x_{\text{Y}} \int_0^{x_{\text{Y}}} D(\alpha_{\text{Y}}) dx_{\text{Y}} \right\}^{1/2}, \quad (7)$$

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