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Thermodynamic properties of liquid germanium–yttrium alloys

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Abstract

Partial enthalpy of mixing of yttrium ($\Delta_{mix}\bar{H}_Y$) in the Ge–Y system was measured at 1770 K using a new high-temperature mixing calorimeter. Literature data on the enthalpies of mixing in the Ge–Y system and results of present examination were compared and discussed. Temperature dependence of $\Delta_{mix}\bar{H}_Y$ was estimated based on comparative analysis of the enthalpies of mixing, and corresponding heat capacity change at alloy formation was evaluated. Polynomial equations approximating thermodynamic functions ($\Delta_{mix}\bar{H}_Y$, $\Delta_{mix}H$, $\Delta_{mix}\bar{C}_{p,Y}$, and $\Delta_{mix}C_p$) versus yttrium mole fraction were determined. Some trends observed in the thermodynamic properties of the Ge–Y alloys were described.

Keywords: Ge–Y; Calorimetry; Thermodynamics; Mixing enthalpy; Liquid alloys

1. Introduction

Magnetic refrigeration, operating with solid magnetic materials as the cooling agents, makes freezing considerably more effective and environmentally safer compared to conventional vapor-cycle refrigeration, because no chlorofluorcarbones destroying ozonosphere are used. The principle of magnetic refrigeration is based on application of magnetocaloric effect (MCE), i.e. the ability of magnetic materials to change their entropy or temperature in the isothermal or adiabatic magnetising-demagnetising cycles, respectively [1]. The MCE can be increased considerably when it is coupled to a phase transition accompanied by the change of the magnetic properties of a material. In this case, significant contribution into the entropy change is achieved by the field-induced transformation [1]. Large MCE's have been reported recently, in particular for $MnFeP_{0.45}As_{0.55}$ [2], $LaFe_{11.7}Si_{1.3}$ [3] and $Gd_5Si_2Ge_2$ [4,5] alloys. The $Y_5Si_xGe_{4-x}$ ($x = 3.5$–4) alloys with the monoclinic $Gd_5Si_2Ge_2$-type structure were reported in [6]. Consequently, the temperature of the giant MCE in the $Gd_5Si_2Ge_2$ can be tuned through a partial substitution of the Gd by a nonmagnetic Y [6,7].

Therefore, the examination of quaternary Gd–Ge–Si–Y alloys as well as of the corresponding ternary and binary systems are of special interest for creation of new alloys with the MCE. Previously, the Gd–Si system was studied by calorimetry [8]. In the present work, we continue the examination of the binary boundaries of the Gd–Ge–Si–Y system and represent analysis of enthalpies of mixing in the Ge–Y alloys.

Phase diagram of the Ge–Y system is characterized by several refractory intermetallics. The germanides Y_5Ge_3, Y_5Ge_4 melt congruently at 2238 K and 2218 K, while the $Y_{11}Ge_{10}$ and YGe melt incongruently at 2173 K and 2003 K, respectively [9,10]. The refractory yttrium germanides make the liquid alloys examination too complicated for $0.4 < x_Y < 0.8$. Thus, a number of thermodynamic examinations have been performed by high temperature calorimetry only for $0.0 < x_Y < 0.46$ [11–14] and for $0.8 < x_Y < 1.0$ [12–14]. The data comparison is shown on Figs. 1 and 2. Nikolaenko and co-authors have measured the $\Delta_{mix}\bar{H}_Y$ for $0.0 < x_Y < 0.235$ at 1523 K [11] and for $0.0 < x_Y < 0.423$ at 1900 K [12,13]. The $\Delta_{mix}\bar{H}_{Ge}$ was also measured in

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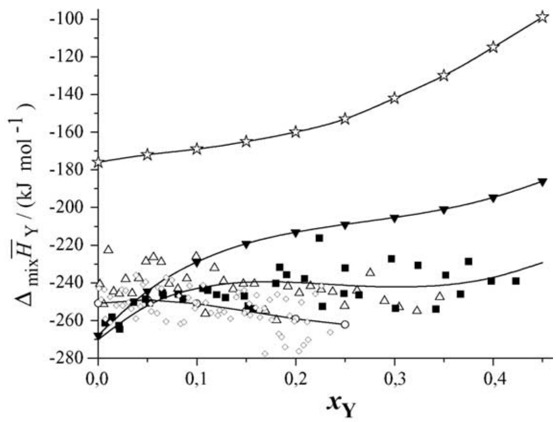

Fig. 1. Plot of partial enthalpy of mixing of yttrium against mole fraction of yttrium; literature data: (◊) data of [11] at 1523 K; (–○–) smoothed data of [11]; (–▼–) smoothed data of [12] at 1900 K; (■) data of [13] at 1900 K; (—) smoothed data of [13]; (–☆–) smoothed data of [14] at 1920 K; (△) our experimental data at 1770 K.

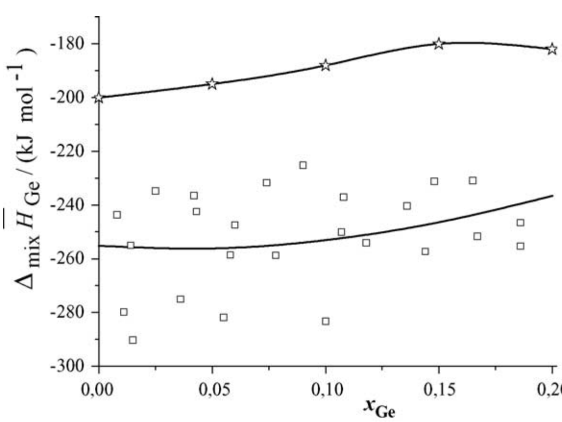

Fig. 2. Plot of partial enthalpy of mixing of germanium against mole fraction of germanium: (□) data of [12,13] at 1900 K; (—) smoothed data of [12,13]; (–☆–) smoothed data of [14] at 1920 K.

[12,13] for $0.0 < x_{Ge} < 0.186$ at 1900 K. Esin et al. have measured the $\Delta_{mix}\overline{H}_Y$ for $0.0 < x_Y < 0.46$ and the $\Delta_{mix}\overline{H}_{Ge}$ for $0.0 < x_{Ge} < 0.2$ at 1920 K [14]. The data of [14] are significantly less negative than those of [11–13]. Moreover, the $\Delta_{mix}\overline{H}_Y$ data reported in [12] and [13] for $T = 1900$ K are different. The present examination has been performed to critically analyze the literature data on the enthalpies of mixing and to determine temperature dependence of the $\Delta_{mix}H$.

2. Experimental

2.1. Materials

The germanium, yttrium and tungsten, which was used as a reference material, are applied in calorimetric studies. The germanium (Alfa-Aesar, 99.9999%), yttrium distillate (Dahuachem, 99.97%) and reference material, i.e. tungsten

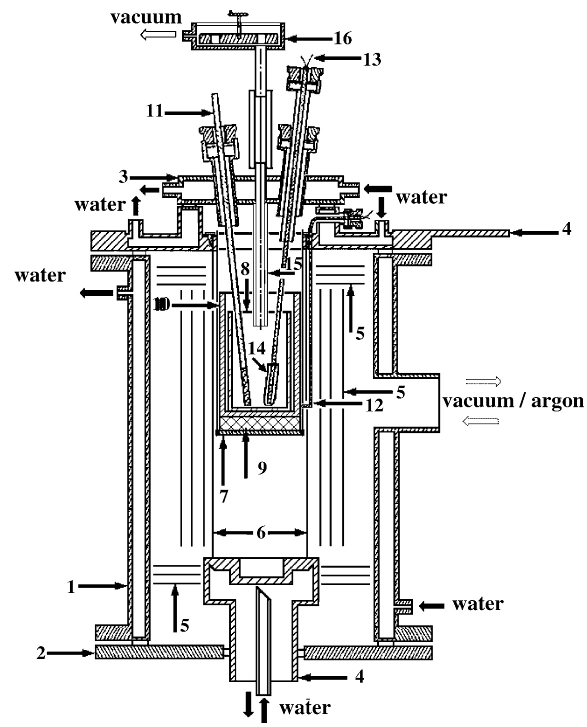

Fig. 3. The schematic of the calorimeter's principal part: (1) water-cooled jacket, (2) lower cover, (3) upper water-cooled cover, (4) water-cooled current leads, (5) reflecting shields, (6) tungsten heater, (7) niobium hanger, (8) alumina crucible, (9) boron–aluminum nitride gasket, (10) molybdenum block, (11) stirrer, (12) controlling W–Re 5/20 type thermocouple, (13) measuring W–Re 5/20 type thermocouple, (14) zirconia protector, (15) alumina tube, (16) revolving container.

(Alfa-Aesar, 99.96%) were used for the experiments. High-purity argon (NII KM Ltd., Russia, Moscow, 99.997 vol.%) was used as inert atmosphere in the calorimeter's internal volume.

2.2. Apparatus

The apparatus construction is similar to the high-temperature mixing calorimeter for determination of the enthalpies of mixing at temperatures up to 1900 K briefly discussed in [15]. The schematic of the calorimeter's principal part is drawn in Fig. 3.

The calorimeter is based on a vacuum resistant furnace providing 5–10 kW output powered through a reducing transformer (OSU-40/0.5 of Elecar Ltd., Russia). The transformer primary coil voltage is applied through thyristor converter (RNTO-190-250 of Electroproject Ltd., Russia). High temperature in the calorimeter is maintained by a cylindrical tungsten heater (6) constructed of Ø = 2 mm rods. The heater (h = 310 mm, Ø = 90 mm) is mounted on a copper water-cooled current leads (4). The block of coaxial molybdenum shields (5), made of 0.5 mm foil, surrounds the heater to minimize radiative heat losses. A massive molybdenum crucible-like block (10) hangs in the central part of the heater. High thermal conductivity and mass of the block smooth-out tem-