



Thermodynamic evaluation of the germanium-lutetium and dysprosium-germanium binary systems

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ABSTRACT

The Ge-Lu and Dy-Ge binary systems have been optimized using the available experimental data on phase diagrams and thermodynamic functions by means of the CALPHAD approach. The Ge-Lu system contains seven phases based on six intermetallic compounds: $\text{Ge}_{1.8}\text{Lu}$, Ge_3Lu_2 , Ge_5Lu_4 , $\text{Ge}_{10}\text{Lu}_{11}$, Ge_4Lu_5 , and Ge_3Lu_5 , which were all treated as stoichiometric compounds. For the Dy-Ge system seven intermetallic compounds were found: Dy_5Ge_3 , Dy_5Ge_4 , DyGe , Dy_2Ge_3 , Dy_3Ge_5 , DyGe_2 and DyGe_3 . These phases were stoichiometric except Dy_5Ge_3 that has a homogeneity range, was treated by a two-sublattice model with substitution in each sublattice. A solution model has been used for the description of the excess term of the Gibbs energy for the liquid phase and the solid solution for the Dy-Ge system. The Ge-Lu system was examined using two different descriptions of the liquid phase: exponential dependence of temperature (Kaptay model) and linear dependence (Redlich-Kister model). The calculations based on the thermodynamic modeling are in good agreement with the phase diagram data and experimental thermodynamic values available in the literature. The process of modeling allows us to calculate the phase equilibria and thermodynamic properties of the liquid phase and intermetallic compounds for the first time. The results obtained are reported in a series of figures and tables in this manuscript.

1. Introduction

Compounds of rare earth elements (REEs) with germanium are amongst several alloys that have attracted considerable attention in recent years. These alloys are indispensable in different engineering applications due to their unique properties and their wealth of structures that individually pertain to covalent, ion, or metal crystals. They are especially attractive candidates for the chemical industry, metallurgy, optical engineering, and microelectronics [1]. It is also known that Germanium and its alloys have super- and semiconducting properties and can be used as resistive and magnetic materials [2,3].

On the other hand the (REEs) and their alloys and compounds with other elements provide inexhaustible sources of new materials. In general, there are two industries reliant on REEs: mature sectors like catalysts, glassmaking, lighting, and metallurgy; and secondly, emerging sectors including battery alloys, ceramics, and permanent magnets.

In order to satisfy the ever increasing needs for reliable thermodynamic data for this class of materials, to refine the REE-Ge phase diagrams and to improve germanium alloy production methods, it is important to investigate the phase diagrams and develop a thermodynamic database of these systems based on the CALPHAD method.

The current work is a continuation of similar studies of REE-Ge (REE = Y [4], Ho [5], Yb [6], Er [7] and Tm [8]) already calculated in our laboratory, and the first in thermodynamic modeling of Ge-Lu and Dy-Ge binary systems. The objectives of the present work are to calculate the phase diagram and the values of thermodynamic functions of REE-Ge (REE = Lu, Dy) systems in standard conditions, to compile the experimental information, and to study its consistency in comparison with the calculated results obtained by using the Redlich-Kister [9] and Kaptay [10–12] models.

2. Bibliographic description of the binary systems

2.1. Equilibrium diagram

2.1.1. The Ge-Lu system

The germanium-lutetium equilibrium phase diagram was established experimentally by Eremenko et al. [13] over the whole composition range. They used X-ray diffraction, metallography, and differential thermal analysis techniques. From there information Moffatt [14] and Massalski [15] construct the phase diagram in Fig. 1.

According to these authors [13] the Ge-Lu system is characterized

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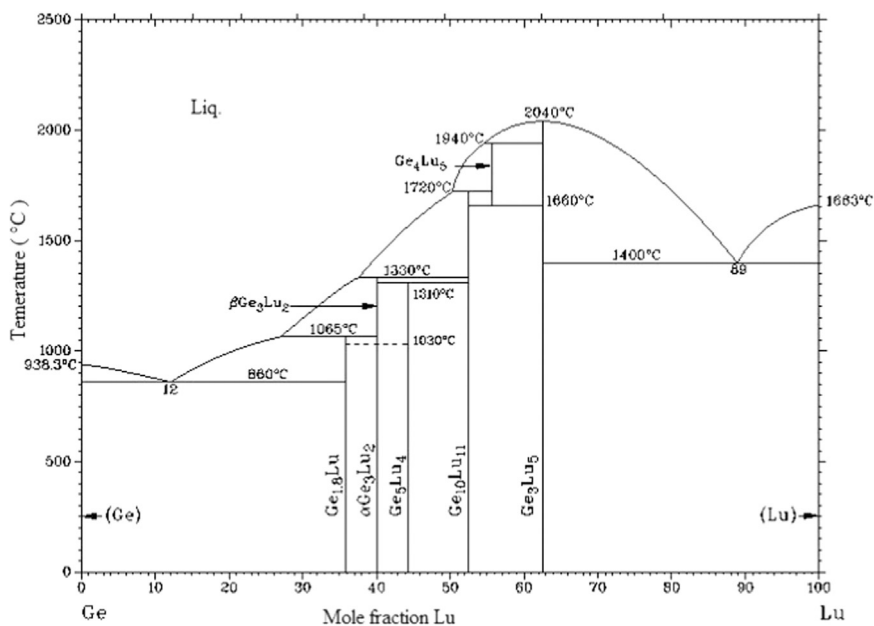


Fig. 1. Germanium-Lutetium phase diagram according to Eremenko et al. [13].

by:

- Ge_3Lu_5 , the richest in Lu, is the most refractory compound in the Lu-Ge system and the only in this system that melts congruently at 2040 °C.
- Four compounds form peritectically Ge_4Lu_5 at 1940 °C, $\text{Ge}_{10}\text{Lu}_{11}$ at 1720 °C, $\beta\text{Ge}_3\text{Lu}_2$ at 1330 °C, and $\text{Ge}_{1.8}\text{Lu}$ at 1065 °C.
- Ge_3Lu_4 decomposes peritectoidally at 1310 °C.
- Ge_3Lu_2 exhibits an allotropic transformation at 1030 °C; the crystal structure of the low temperature form is hexagonal, and the high-temperature modification is unknown
- Two eutectic reactions occur between (Ge) and $\text{Ge}_{1.8}\text{Lu}$ at 860 °C and 12 at% Lu and between Lu and Ge_3Lu_5 at 1400 °C and 89 at% Lu.
- The mutual terminal solid solubility of the pure elements appears to be very small.
- All the intermediate phases are stoichiometric.

2.1.2. The Dy-Ge system

The dysprosium-germanium phase equilibria have been determined by Eremenko et al. [16] Fig. 2 includes the following phases: liquid; pure elements (αDy), (βDy), and (Ge); and seven intermediate compounds.

- Dy_5Ge_3 melts congruently at 1825 °C and show a homogeneity region at about 1 at%.
- $\text{DyGe}_{1.63}$ forms during the peritectoid reaction and disintegrates into two solid phases $\beta\text{Dy}_2\text{Ge}_3$ and DyGe_2 at 935 °C.
- Dy_5Ge_4 , DyGe , $\gamma\text{Dy}_2\text{Ge}_3$, DyGe_2 , and $\text{DyGe}_{2.84}$ formed by peritectic reactions at 1575, 1530, 1405, 965, and 885 °C, respectively.
- The addition of germanium to dysprosium results in eutectic reaction among liquid, (αDy) and Dy_5Ge_3 at 1215 °C about 11 at% Ge in Dy rich part.
- The addition of dysprosium to germanium results in a eutectic reaction among liquid, $\text{DyGe}_{2.84}$ and (Ge) at 860 °C and about 85 at% Ge.
- The mutual solid-state solubility of dysprosium and germanium is lower than 1 at%.
- The Ge_3Lu_2 exhibits two allotropic transformations $\alpha\text{Dy}_2\text{Ge}_3 \leftrightarrow \beta\text{Dy}_2\text{Ge}_3 \leftrightarrow \gamma\text{Dy}_2\text{Ge}_3$ at 890 and 1300 °C, respectively.

2.2. Thermodynamic data

2.2.1. The Ge-Lu system

Meshel and Kleppa determined the standard enthalpies of formation of Ge_3Lu_5 by the mean of direct synthesis calorimetry at 1473 ± 2 K in two separate works [17,18]. The experimental values are -73.5 ± 1.5 kJ mol⁻¹ at⁻¹ [17] and -93.1 ± 2.2 kJ mol⁻¹ at⁻¹ [18]. In this work we take into account the recent one [18] because it seem to correlate with the data of the germanides of the earlier REE, contrarily to the value given in ref [17] which was significantly less exothermic. Gorbachuk and Bolgar [19] and Gorbachuk et al. [20] give the measured enthalpies H-H298 of Lu_5Ge_3 and Lu_2Ge_3 , respectively. For Lu_5Ge_3 these quantities are measured by the method of mixtures with an error of 1.5% in the range 300–1300 K by means of a high-temperature differential calorimeter [21], while above 1300 K, it was measured with a high-temperature vacuum calorimeter [22]. Concerning Lu_2Ge_3 the experimental data [20] were corrected to allow for the impurity phase and fitted with the Meier–Kelly equation over a range from 442 to 1576 K: $H^\circ(T) - H^\circ(298.15 \text{ K}) = AT^2 + BT + CT^{-1} + D$. The coefficients of this equation were calculated with the least-squares method. Nikolaenko et al. [23] measured the integral enthalpy of mixing of liquid alloy for $x(\text{Lu}) = 0.16$ at 1275 K, the experimental value is -29 kJ mol⁻¹.

2.2.2. The Dy-Ge system

Based on their calorimetric measurement at 1473 ± 2 K, Meshel and Kleppa [24] obtained the standard enthalpy of formation of Dy_5Ge_3 and equal to -92.4 ± 2.3 kJ mol⁻¹ at⁻¹. Gorbachuk and Bolgar [25] determined the enthalpies of three dysprosium germanides Dy_5Ge_3 , DyGe , and DyGe_2 between room temperature and the melting point. The enthalpies were examined by the method of mixtures with an error of not more than 1.5% with a high temperature differential calorimeter (DC) at 300–1200 K and with a high-temperature vacuum calorimeter (VC) above 1200 K [22,26].

2.3. Crystallographic data

The crystallographic data for the intermediate phases formed in these systems are reported in Tables 1 and 2.

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