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Thermodynamic Modeling of the Al-Ba and Ba-Ge Systems Supported by First-Principles Calculations

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Abstract The phase diagrams of Al-Ba and Ba-Ge systems are optimized by coupling the CALPHAD approach and first-principles calculations. The binary intermetallic compounds were treated as stoichiometric phases. The total energies of nine intermetallic compounds: Al_4Ba, $Al_{13}Ba_7$, Al_5Ba_3, Al_5Ba_4, Ba_2Ge, Ba_5Ge_3, BaGe, β-Ba_3Ge_4 and $BaGe_2$ were calculated by first-principles calculation using density functional theory approximation as implemented in the VASP (Vienna Ab-initio Simulation Package) code and used in the CALPHAD approach to assess the two systems. The liquid solutions are described by the Redlich–Kister polynomial model. A set of thermodynamic parameters were obtained for the Al-Ba and Ba-Ge systems. The calculated phase diagrams and thermodynamic properties are in good agreement with most of the accuracy available data.

Keywords Al-Ba alloys · Ba-Ge alloys · CALPHAD · first-principles calculation · phase diagram · thermodynamics

1 Introduction

Barium is a very reactive metal which quickly oxidizes in contact with air. For technology and industrial applications, barium is usually used in the form of an alloy with other metals. Alloyed with aluminum and germanium, barium is applied as a getter or unwanted gas remover for vacuum tubes in electronic industry and as an additive to steel and cast iron. These alloys can also show large glass forming ability (GFA) and recently suggested to safe storage of hydrogen for clean energy.[1–3] It is therefore important to know well the exact phase diagrams of the Al-Ba and Ba-Ge systems.

Since the experimental thermodynamic data of the two systems under study are very limited related to the high oxidability of barium and volatility of germanium which usually lead to metastable compounds and to many experimental errors, theoretical investigations are needed to obtain more accurate results.

The goals of the present work are the determination of the enthalpies of formation of the intermetallic compounds of the two systems Al-Ba and Ba-Ge using first-principles calculations, the assessment of the all thermodynamic functions of the systems using the CALPHAD approach supported by our first-principles results and then the establishment of the Al-Ba and Ba-Ge binary phase diagrams.

2 Literature Review

2.1 Al-Ba System

Alberti[4] investigated the phase diagram of the Al-Ba system in the composition region up to 10 at.% Ba using

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thermal and metallography analysis. The eutectic reaction between liquid, Fcc_A1 Al and Al_4Ba was detected at 0.4 at.% Ba and 924 K. Later, the structure of Al_4Ba was identified as a body centred tetragonal by Andress and Alberti.[5] The phase diagram between 44 to 100 at.% Ba was examined by Flanigen.[6] The eutectic point of Ba-rich side detected at 72.6 at.% Ba and 804 K. With thermal analysis and metallographic techniques, Iida[7] confirmed the existence of the Al_4Ba compound, which melts congruently at 1370 K.

The Al-Ba system evaluated by Elliot and Shunk[8] included three intermediate phases Al_4Ba, Al_2Ba and AlBa, based on the Bruzzone and Merlo[9] diagram and reported in the Massalski compilation.[10] Fornasini and Bruzzone[11,12] studied the system with the above techniques and showed that the formula of Al_2Ba and AlBa compounds are more appropriate as $Al_{13}Ba_7$ and Al_5Ba_4 respectively. Later, Fornasini[13] found a new compound in the system, Al_5Ba_3, which probably formed by a peritectic reaction at 1023 K as suggested by Flanigen.[6] The most recent information on this binary phase diagram was taken from the phase diagram evaluated by Itkin and Alcock[14] which included four intermetallic compounds: Al_4Ba melting congruently at 1377 K and $Al_{13}Ba_7$, Al_5Ba_3 and Al_5Ba_4 formed by peritectic reactions at 1187, 1023 and 1003 K, respectively. The position of the eutectic point at the Al-rich side was adopted as 932 K and 0.2 at.% Ba and the eutectic point at the Ba-rich region occurred at 71.5 at.% Ba and 811 K.

The crystal structures of the pure elements and the intermetallic compounds of the Al-Ba system determined by several authors are summarized in Table 1.[5,11–13,15,16]

The enthalpies of formation of different compounds of this system were measured by different authors and different methods. Kulichkina and Nikonov,[17] Burylev et al.[18] and Vigdorovich et al.[19] estimated the Gibbs energy of formation of Al_4Ba from the vapor pressure method measurements. Nepochatov et al.[20] have measured the enthalpy of formation using the calorimetry of dissolution method at 323 K, and calculated the enthalpy of formation of the compound Al_4Ba. Notin et al.[21] measured the partial enthalpy of mixing of Barium in Al-Ba alloys by the drop calorimetry method at 1215 K, and the enthalpy of formation of the solid compound Al_4Ba by its precipitation from the Al-Ba liquid bath. Srikanth and Jacob[22] measured the activity of barium in liquid Al-Ba alloys at 1373 K using the Knudsen effusion-mass loss technique and the associated solution model to describe the thermodynamic behavior of Al-Ba liquid alloys.

The phase diagram of the (Al-Ba) system has been optimized thermodynamically by Bao et al.,[23] based essentially on the discrepancy thermodynamic data of the researchers cited above. In addition, the compound Al_5Ba_3, proposed by Fornasini,[13] has not been taken into account in this optimization.

2.2 Ba-Ge System

The Ba-Ge system has been studied by DTA, x-ray powder diffraction, metallography, chemical analysis and measurements of the electrical conductivity.[24–35] Three variants of Ba-Ge phase diagram exist:

The first one investigated by Andrianov et al.[24] between 0 and 66 at.% Ge and by Sokolov et al.[25] in the region 66-100 at.% Ge, and was reported in the Massalski

Table 1 The crystal structure data of Al-Ba system

Phase	Comp, at.% Ba	Pearson symbol and prototype	Space group	Lattice parameters, nm		References
				a, b	c	
(Al)	0	*cF4* (Cu)	$Fm\bar{3}m$ (225)	0.4049	…	15
				0.4049	…	This work
Al_4Ba	20	*tI*10 (Al_4Ba)	I4/mmm (139)	0.4539	1.1160	5
				0.4540	1.1186	This work
$Al_{13}Ba_7$	35	*hP*20 ($Al_{13}Ba_7$)	$P\bar{3}m1$ (164)	0.6099	1.7269	11
				0.6014	1.7223	This work
Al_5Ba_3	37,5	*hP*16 (Al_5Ba_3)	$P6_3/mmc$ (194)	0.6066	1.4611	13
				0.6066	1.4611	This work
Al_5Ba_4	44,5	*h*P18 (Al_5Sb_4)	$P6_3/mmc$ (194)	0.6092	1.7782	12
				0.6105	1.7807	This work
(Ba)	100	*cI*2 (W)	$Im\bar{3}m$ (229)	0.5013	…	16
				0.4991	…	This work

compilation.[10] This diagram presents four intermetallic compounds: BaGe melting congruently at 1428 K, while the Ba_2Ge, $BaGe_2$ and $BaGe_4$ are formed by peritectic reactions at 1228, 1323 and 1088 K successively. Two eutectic reactions occur at the compositions of 4 at.% Ge at 838 K and 84 at.% Ge at 1043 K.

Later Carrillo-Cabrera et al.[26,27] determined the partial phase diagram between 75 and 100 at.% Ge and confirmed the existence of two new compounds in the germanium-rich part: Ba_8Ge_{43} which is stable only between 1043 and 1083 K, where it formed peritectically, and $BaGe_5$ stable in the temperature range of 881 and 723 K. According to this study, there is an eutectic reaction at 1081 K and 82.5 at.% Ge and the compound $BaGe_4$ is designed as Ba_6Ge_{25}. Therefore the second binary phase diagram of the Ba-Ge system has been reported by Okamoto,[28] who combined the partial phase diagram of Carrillo-Cabrera et al.[26,27] and the Massalski compiled phase diagram.

The most recent experimental investigation of Ba-Ge system was carried by Pani and Palenzona.[29] The system has been revised in the composition part from 0 to 75 at.% Ge using differential thermal analysis. Two new compounds were observed: Ba_5Ge_3, peritectically formed at 1213 K and dimorphic Ba_3Ge_4, melting by peritectic reaction at 1188 K and transformed to low temperature form at about 613 K. Three congruently melting points were determined at 1273 K for Ba_2Ge, 1253 K for BaGe and 1378 K for $BaGe_2$. Four eutectics points occur at the compositions of about 7.5, 42.5, 56, 82.5 at.% Ge and temperatures of 913, 1168, 1178 and 1081 K respectively. Finally, Pani and Palenzona[29] presented the whole Ba-Ge phase diagram, taking into account the studies of Carrillo-Cabrera et al.[26,27] in the Ge-rich part.

Recently Prokofieva and Pavlova[30] used DTA, x-ray diffraction, metallographic and chemical analyses, measurements of the electrical conductivity and Czochralski pulling method to study the Ba-Ge phase diagram over the composition of 50-100 at.% Ge. The main result of this study is that many metastable phases can appear during the crystallization process like the clathrate compounds

Table 2 The crystal structure data of the Ba-Ge system

Phase	Comp, at.% Ge	Pearson symbol and prototype	Space group	Lattice parameters, nm			References
				a	b	c	
(Ba)	100	*cI*2 (W)	Im$\bar{3}$m (229)	0.5013	0.5013	0.5013	16
				0.49908	0.49908	0.49908	This work
Ba_2Ge	33.3	*oP*12 (Co_2Si)	Pnma (62)	0.838	0.5480	1.0040	31
				0.8419	0.5444	1.0068	29
				0.8429	0.5495	1.0110	This work
Ba_5Ge_3	37.5	*tP*32 (Ba_5Si_3)	P4/ncc (130)	0.8538	0.8538	1.6495	29
				0.8519	0.8519	1.6554	32
				0.8539	0.8539	1.6563	This work
BaGe	50.0	*oC*8 (CrB)	Cmcm (63)	0.5057	1.1942	0.4299	33
				0.5062	1.1954	0.4301	29
				0.507	1.1995	0.4310	This work
α- Ba_3Ge_4	57.1	*oC*56 (Ba_3Ge_4)	Cmmm (65)	1.1789	1.2197	1.2090	29
				1.1799	1.2210	1.2097	34
β- Ba_3Ge_4	57.1	*tP*28 (Ba_3Si_4)	P4_2/mnm (136)	0.8621	0.8621	1.2031	34
				0.8550	0.855	1.2137	This work
$BaGe_2$	66.7	*oP*24 ($BaSi_2$)	Pnma (62)	0.9050	0.6830	1.1650	35
				0.9076	0.6812	1.1642	29
				0.9150	0.6870	1.1730	This work
Ba_6Ge_{25}	80.6	*cP*124 (Ba_6Ge_{25})	P$4_1$32 (213)	1.4560	1.4560	1.4560	29
				1.45635	1.45635	1.4563	36
				1.45564	1.45564	1.4556	37
$BaGe_5$	83.3	*oP*60 ($BaGe_5$)	Pmna (53)	1.0727	9.2844	1.4794	38
Ba_8Ge_{43}	84.3	*cI*408 (Ba_8Ge_{43})	Ia$\bar{3}$d (230)	2.1312	2.1312	2.1312	26
				2.1303	2.1303	2.1303	29
(Ge)	100	*cF*8 C (diamond)	Fd$\bar{3}$m (227)	0.5656	0.5656	0.5656	39
				0.5690	0.5690	0.5690	This work

Ba_8Ge_{43} and Ba_6Ge_{25} or Zintl phases like $BaGe_4$ and $BaGe_5$, nevertheless Ba_6Ge_{25} were grown, using Czochralski technique at the conditions close to equilibrium. Table 2 reports the crystallographic data and lattice parameters of the intermetallic compounds observed in the Ba-Ge system.[29,31–39]

Up to now there are neither experimental thermodynamic data obtained nor thermodynamic assessment conducted for the Ba-Ge system.

3 First-Principles Calculations

In order to have a reliable description for the thermodynamic parameters, the first-principles method was used to calculate the enthalpies of formation of the binary compounds in the Al-Ba and Ba-Ge systems. A structure of minimization at the ground state (0 K) has been carried out using density functional theory (DFT)[40] as implemented in the Vienna Ab-initio Simulation Package (VASP)[41,42] with plane wave basis sets. The calculations are performed using the Project Augmented Wave (PAW) pseudo-potential[43,44] and employed the Generalized Gradient Approximation (GGA) of Perdew, Burke and Ernzerhof (PBE).[45] A plane wave cutoff energy of 650 eV is used for all compounds and K-points meshes are compiled using the fully automatic scheme.[46] Convergence on the number of K-points in the irreducible wedge of the first Brillouin zone is checked for each structure.

The energy of formation at 0 K of the Ba_xM_y compounds (M = Al, Ge) is calculated by the following formula:

Table 3 The standard enthalpies and entropies of formation of the intermetallic compounds in the Al-Ba and Ba-Ge systems

Compound	$\Delta_f H$, kJ/mol	$\Delta_f S$, J/K mol	Method	References
Al_4Ba	− 23.576	…	Ab-initio	This work
	− 23.474	− 2.251	CALPHAD	This work
	− 24.800	…	Vapor pressure	19
	− 50.630	…	Calorimetry	20
	− 22.700	…	Vapor pressure	17
	− 37.100	…	Drop calorimetry	21
	− 37.100	…	Vapor pressure	22
	− 46.649	− 17.46	CALPHAD	23
$Al_{13}Ba_7$	− 21.795	…	Ab-initio	This work
	− 23.896	− 0.291	CALPHAD	This work
	− 45.930	…	Vapor pressure	22
	− 53.874	− 22.49	CALPHAD	23
Al_5Ba_3	− 23.356	…	Ab-initio	This work
	− 23.954	− 0.746	CALPHAD	This work
Al_5Ba_4	− 22.927	…	Ab-initio	This work
	− 22.928	− 1.032	CALPHAD	This work
	− 44.470	…	Vapor pressure	22
	− 48.160	− 19.88	CALPHAD	23
Ba_2Ge	− 50.129	…	Ab-initio	This work
	− 51.130	− 1.362	CALPHAD	This work
Ba_5Ge_3	− 56.880	…	Ab-initio	This work
	− 56.880	− 4.319	CALPHAD	This work
BaGe	− 60.314	…	Ab-initio	This work
	− 60.062	− 2.606	CALPHAD	This work
α- Ba_3Ge_4	− 59.090	− 3.8419	CALPHAD	This work
β- Ba_3Ge_4	− 58.317	…	Ab-initio	This work
	− 58.599	− 3.041	CALPHAD	This work
$BaGe_2$	− 54.015	…	Ab-initio	This work
	− 54.015	− 1.626	CALPHAD	This work
Ba_6Ge_{25}	− 31.819	− 0.939	CALPHAD	This work
Ba_8Ge_{43}	− 21.198	+3.553	CALPHAD	This work

Table 4 Thermodynamic parameters obtained in this work for the Al-Ba system

Phase	Thermodynamic parameters
Liquid	${}^{0}L^{liq} = -49725 - 8.505T$
	${}^{1}L^{Liq} = -43500 + 18.286T$
	${}^{2}L^{Liq} = -14330 + 28.461T$
Al_4Ba	$G^{Al_4Ba}_{Al:Ba} - 0.200G^{SER}_{Ba} - 0.800G^{SER}_{Al} = -23474 + 2.251T$
$Al_{13}Ba_7$	$G^{Al_{13}Ba_7}_{Al:Ba} - 0.350G^{SER}_{Ba} - 0.650G^{SER}_{Al} = -23896 + 0.291T$
Al_5Ba_3	$G^{Al_5Ba_3}_{Al:Ba} - 0.375G^{SER}_{Ba} - 0.625G^{SER}_{Al} = -23954 + 0.746T$
Al_5Ba_4	$G^{Al_5Ba_4}_{Al:Ba} - 0.445G^{SER}_{Ba} - 0.555G^{SER}_{Al} = -22928 + 1.032T$

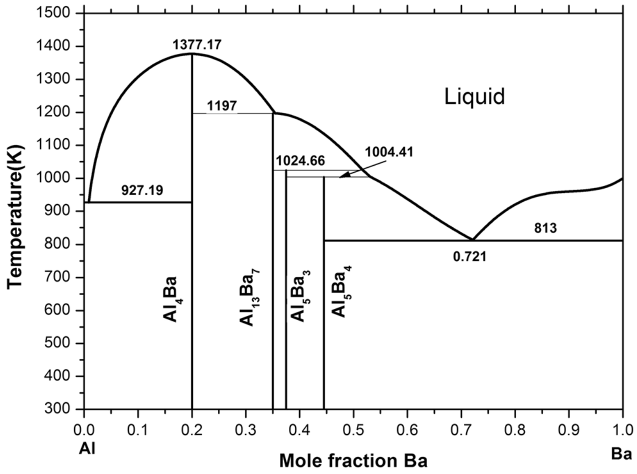

Fig. 1 Calculated phase diagram of the Al-Ba system

$$\Delta E\left(Ba_xM_y\right) = E\left(Ba_xM_y\right) - \frac{1}{x+y}\left(x\ E(Ba) + y\ E(M)\right) \qquad \text{(Eq 1)}$$

where $E\left(Ba_xM_y\right)$, $E(Ba)$ and $E(M)$ are the total energies for the Ba_xM_y compound, pure Bcc_A2 Ba, pure Fcc_A1 Al and pure diamond_A4 Ge at 0 Kelvin respectively. This energy of formation corresponds to the enthalpy of formation of the compound at 0 K.[47]

4 Thermodynamic Models

The Ba-M (M = Al, Ge) systems are modeled according to the CALPHAD approach.[48,49] The calculations are based on the determination of the Gibbs energy of the different phases of the system as a function of temperature and concentration.

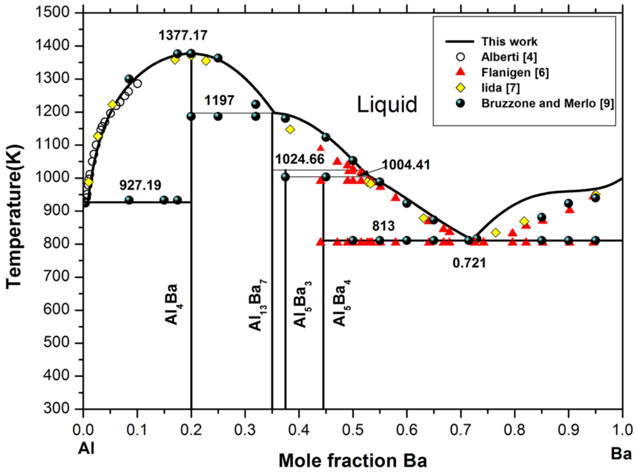

Fig. 2 Comparison between calculated and experimental phase diagram of the Al-Ba system

4.1 Pure Elements

The Gibbs energy function $G_i^{\varphi}(T)$ for the i element $(i = Al, Ba, Ge)$ in phase φ is described by an equation of the following form:

$$G_i^{\varphi}(T) = {}^{0}G_i^{\varphi}(T) - H_i^{SER}(298.15\,K) \qquad \text{(Eq 2)}$$

$$G_i^{\varphi}(T) = a + bT + cTlnT + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \qquad \text{(Eq 3)}$$

where $H_i^{SER}(298.15\,K)$ is the stable element reference (SER) state, that refers to the enthalpies of Fcc_A1 for Al, Bcc_A2 for Ba and diamond_A4 for Ge at 298.15 K. $G_i^{\varphi}(T)$and ${}^{0}G_i^{\varphi}(T)$ are the relative and the absolute Gibbs energy of the i element in the φ phase and T is the absolute temperature. The values of the coefficients a, b, c, d, e, f, g and h are taken from the Scientific Group Thermodata (SGTE) database compiled by Dinsdale.[50]

4.2 Solution Phases

The substitutional model was used to describe the liquid phase of the two systems Ba-Ge and Ba-Al. The Gibbs energy of this phase G^{Liq} consists of three terms: the standard, the ideal and the excess term:

$$G^{Liq} = {}^{ref}G^{Liq} + {}^{id}G^{Liq} + {}^{exc}G^{Liq} \qquad \text{(Eq 4)}$$

$$G^{Liq} = x_{Ba}{}^{0}G^{Liq}_{Ba} + x_M{}^{0}G^{Liq}_{M} + RT(x_{Ba}lnx_{Ba} + x_Mlnx_M) + {}^{exc}G^{Liq} \qquad \text{(Eq 5)}$$

where R is the gas constant, x_i is the mole fraction of specie i in the liquid phase and T is the temperature. The excess Gibbs energy of the liquid phase is described using the

Table 5 The invariant reactions in the Al-Ba system including calculated and experimental results

Reaction	Type of reaction	T(K)	Compositions of the respective phases, at.% Ba			References
Liq ↔ Al + Al_4Ba	Eutectic	924	0.4	0	20	4
		924	0.45	0	20	7
		933	…	0	20	9
		932	0.2	0	20	14,23
		933	…	0	20	22
		927.17	0.857	0	20	This work
Liq ↔ Al_4Ba	Congruent	1370	20	20	…	7
		1377	20	20	…	9,14,22
		1379	20	20	…	23
		1377	20	20	…	This work
Liq + Al_4Ba ↔ $Al_{13}Ba_7$	Peritectic	1187	37	20	35	9,14,22
		1186	38.3	20	35	23
		1197	35.44	20	35	This work
Liq + $Al_{13}Ba_7$ ↔ Al_5Ba_3	Peritectic	1018	…	35	37.5	6
		1023	51	35	37.5	14
		1024	51.73	35	37.5	This work
Liq + Al_5Ba_3 ↔ Al_5Ba_4	Peritectic	991	…	37.5	44.5	6
		1003	…	37.5	44.5	9
		1003	52.3	37.5	44.5	14
		1003	52.3	37.5	44.5	22
		995	57.2	37.5	44.5	23
		1004.41	53	37.5	44.5	This work
Liq ↔ Ba + Al_5Ba_4	Eutectic	804	72.6	100	44.5	6
		801	70	100	44.5	7
		811	71.5	100	44.5	9
		811	71.5	100	44.5	14
		801	72	100	44.5	22
		799	75.5	100	44.5	23
		813	72	100	44.5	This work

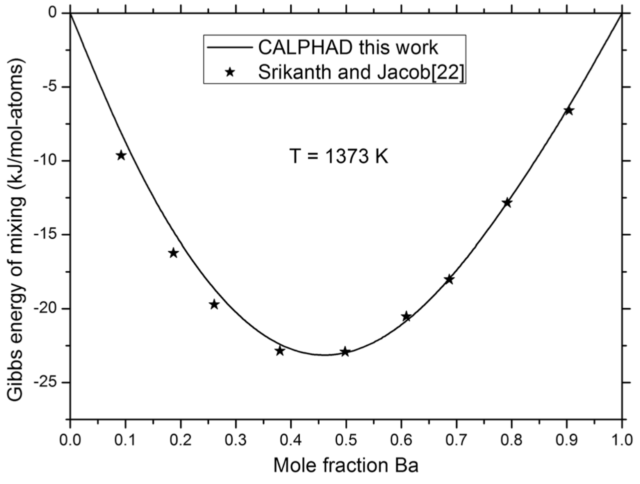

Fig. 3 Calculated Gibbs excess energy of mixing of liquid at 1373 K, compared with experimental data[22]

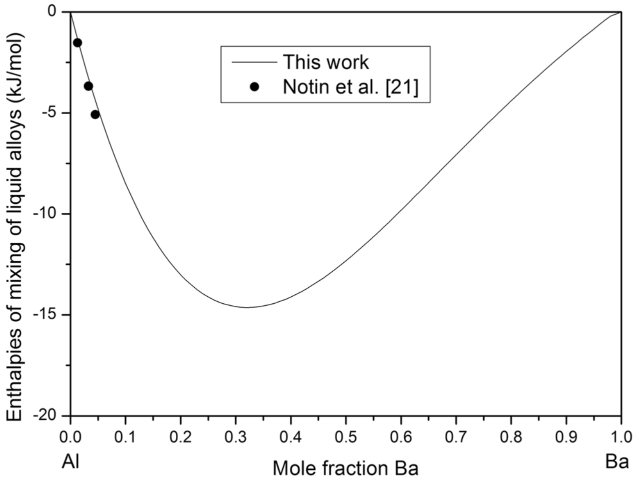

Fig. 4 Calculated enthalpies of mixing of liquid, compared with experimental data[21]

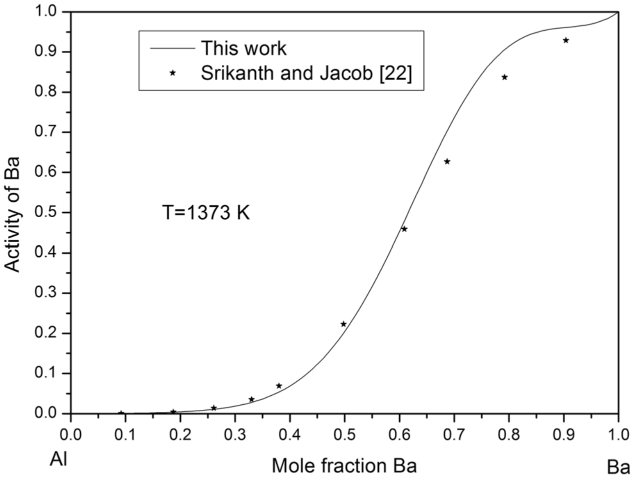

Fig. 5 Calculated activity of Ba in liquid phase at 1373 K, compared with experimental data[22]

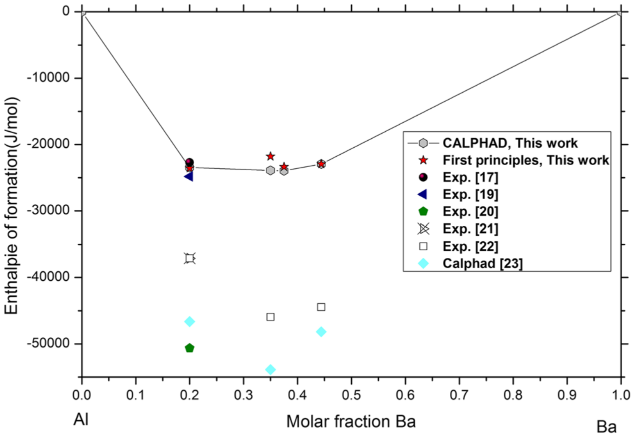

Fig. 6 Standard enthalpies of formation of intermetallic compounds in Al-Ba system

Redlich–Kister polynomial model[51] and given by the following expression:

$$^{exc}G^{Liq} = x_{Ba}x_M \sum_{\vartheta=0}^{n} {}^{\vartheta}L^{Liq}_{Ba,M}(x_{Ba} - x_M)^{\vartheta} \qquad \text{(Eq 6)}$$

where ${}^{\vartheta}L^{Liq}_{Ba,M}$ is the interaction energy of the ϑ-th order between elements Ba and M in the solution and takes the form:

$${}^{\vartheta}L^{liq}_{Ba,M} = a_{\vartheta} + b_{\vartheta}T \qquad \text{(Eq 7)}$$

with a_{ϑ} and b_{ϑ} are the adjusted parameters being evaluated in the present work.

4.3 Stoichiometric Compounds

Table 6 The optimized thermodynamic parameters of the Ba-Ge system

Phase	Parameters
Liquid	${}^{0}L^{liq} = -244749 + 41.779T$
	${}^{1}L^{Liq} = 67593 - 48.969T$
	${}^{2}L^{Liq} = 65211 - 9.686T$
Ba_2Ge	$G^{Ba_2Ge}_{Ba:Ge} - 0.333G^{SER}_{Ge} - 0.667G^{SER}_{Ba} = -51130 + 1.362T$
Ba_5Ba_3	$G^{Ba_5Ge_3}_{Ba:Ge} - 0.375G^{SER}_{Ge} - 0.625G^{SER}_{Ba} = -56880 + 4.319T$
BaGe	$G^{BaGe}_{Ba:Ge} - 0.5G^{SER}_{Ge} - 0.5G^{SER}_{Ba} = -60062 + 2.606T$
α-Ba_3Ge4	$G^{\alpha Ba_3Ge_4}_{Ba:Ge} - 0.571G^{SER}_{Ge} - 0.429G^{SER}_{Ba} = -59090 + 3.8419T$
β-Ba_3Ge4	$G^{\beta Ba_3Ge_4}_{Ba:Ge} - 0.571G^{SER}_{Ge} - 0.429G^{SER}_{Ba} = -58599 + 3.041T$
$BaGe_2$	$G^{BaGe_2}_{Ba:Ge} - 0.667G^{SER}_{Ge} - 0.333G^{SER}_{Ba} = -54015 + 1.626T$
Ba_6Ge_{25}	$G^{Ba_6Ge_{15}}_{Ba:Ge} - 0.806G^{SER}_{Ge} - 0.194G^{SER}_{Ba} = -31819 + 0.939T$
Ba_8Ge_{43}	$G^{Ba_8Ge_{43}}_{Ba:Ge} - 0.843G^{SER}_{Ge} - 0.157G^{SER}_{Ba} = -21198 - 3.553T$

In this work, all the intermetallic compounds Al_4Ba, $Al_{13}Ba_7$, Al_5Ba_3, Al_5Ba_4, Ba_2Ge, Ba_5Ge_3, BaGe, α-Ba_4Ge_3, ß-Ba_4Ge_3, $BaGe_2$, Ba_6Ge_{25} and Ba_8Ge_{43} are treated as stoichiometric phases. The Gibbs energy of each compound is given by the following expression:

$$G^{Ba_xM_y} = \Delta_f G^{Ba_xM_y} + \left[\frac{x}{x+y}G^{SER}_{Ba} + \frac{y}{x+y}G^{SER}_{M}\right] \qquad \text{(Eq 8)}$$

with

$$\Delta_f G^{Ba_xM_y} = \Delta_f H^{Ba_xM_y} - T\Delta_f S^{Ba_xM_y} \qquad \text{(Eq 9)}$$

where x and y are the number of Ba and M atoms in the compound Ba_xM_y, G^{SER}_{i} is the molar Gibbs energy of pure element i (i = Al, Ba, Ge) and $\Delta_f G^{Ba_xM_y}$ is the Gibbs energy of the formation of the stoichiometric compound. The parameters $\Delta_f H^{Ba_xM_y}$(enthalpy of formation) and $\Delta_f S^{Ba_xM_y}$.(entropy of formation), are determined for each compound in the present work.

5 Optimization Procedure

The thermodynamic optimization of the Gibbs energy parameters is an application of the CALPHAD approach.[48,49] It was carried out by means of our computer program,[52,53] using the experimental phase diagrams data,[14,29] the enthalpies of formation of the compounds, determined by the first-principles calculations in this work, and the enthalpies of mixing of the Al-Ba liquid, measured by calorimetry.[21] Appropriate weight factors are associated with the experimental phase diagram and thermodynamic data. To obtain the best description of the system, higher weight factors are usually given to the thermodynamic data than those given to the invariant

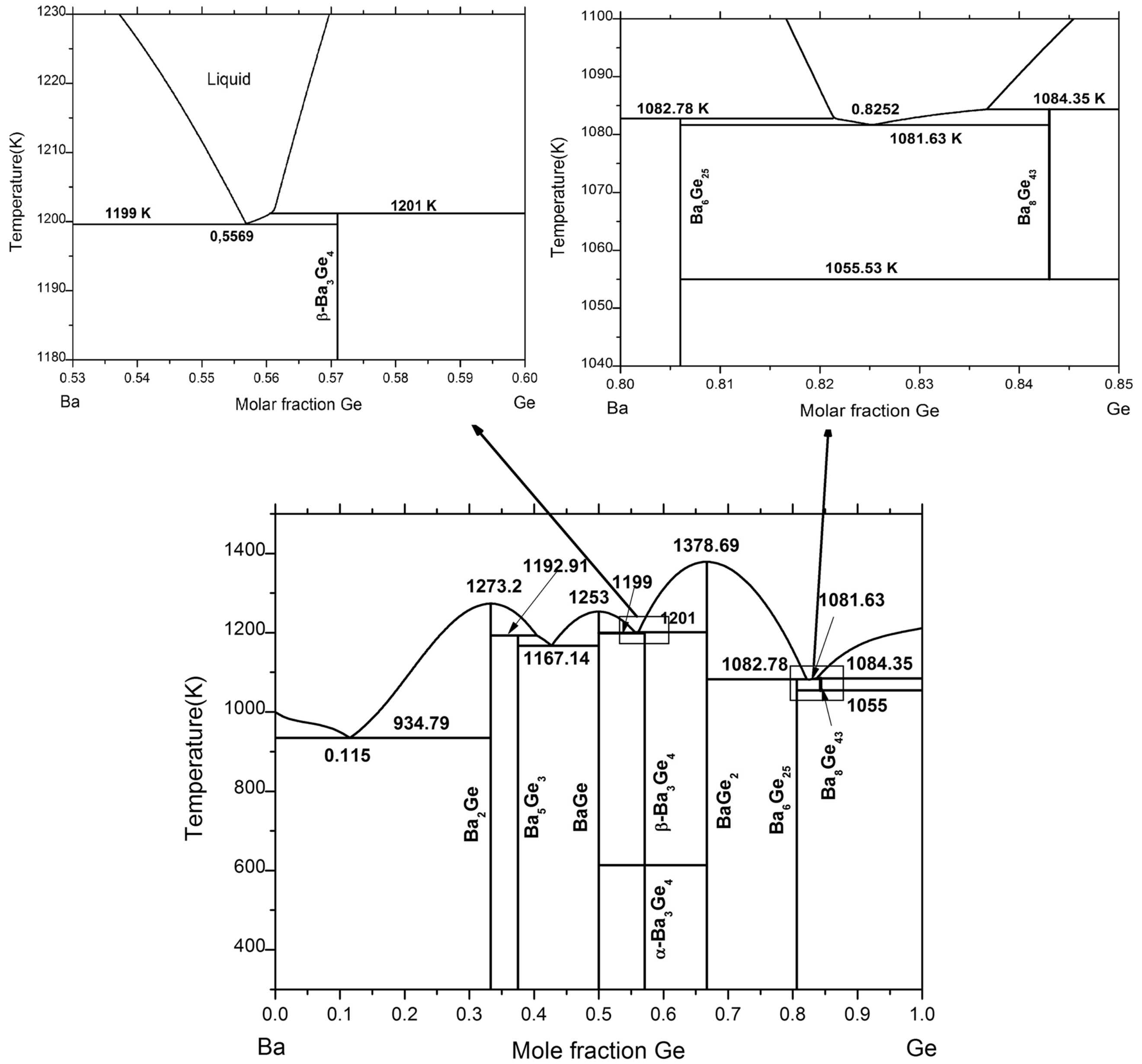

Fig. 7 Calculated phase diagram of the Ba-Ge system

reactions by considering their credibility. The factors are changed by trial and error during the assessment, reaching a good agreement with the selected experimental data within the expected uncertainly limits. A set of optimized model parameters is finally obtained which lead to establishing the phase diagram of the system under study.

6 Results and Discussion

DFT calculations were performed, using the GGA-PAW approach, for the standard pressure structures of the nine intermetallic compounds of the Al-Ba and Ba-Ge systems and for Al, Ba and Ge elements in the fcc, bcc and diamond ground state structure, respectively.[15,16,39] Lattice parameters and enthalpies of formation obtained are reported in Tables 1, 2, and 3. The calculated lattice parameters are in good agreement with the experimental data, with a difference less than 1.5%.

The parameters of the thermodynamic description of the Al-Ba system were obtained in the present assessment. The best optimization was obtained with three excess terms (six parameters) for the liquid phase. These parameters and those defining the Gibbs energies of formation of the four stoichiometric compounds are reported in Table 4. The calculated phase diagram of the Al-Ba system is shown in

Fig. 1 and compared with the experimental data[4,6,7,9] in Fig. 2. All invariant reactions are calculated and compared with the experimental data, as listed in Table 5. As can be seen from this figure the calculated liquidus and invariant points are in good agreement with the experimental data presented in the evaluation of Itkin and Alcock,[14] while the peritectic temperature of the invariant reaction: Liquid + Al_4Ba ↔ $Al_{13}Ba_7$ determined in this work at 1197 K was higher than the experimental one at 1187 K. This optimization confirms the existence of the Al_5Ba_3 compound proposed for the first time by Fornasini[13] formed by a peritectic reaction at 1023 K.

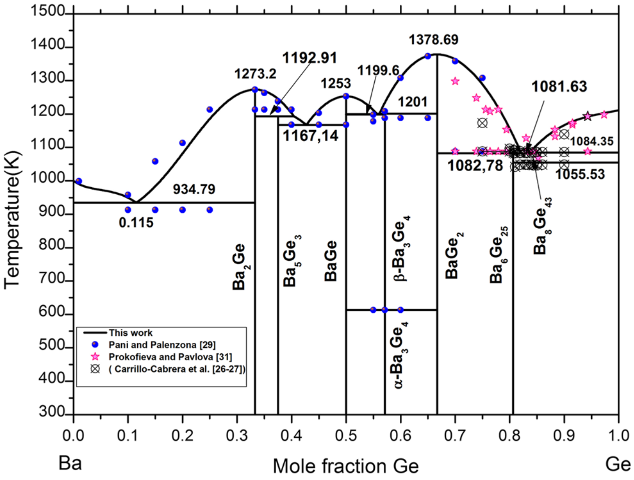

Fig. 8 Comparison between calculated and experimental phase diagram of the Ba-Ge system

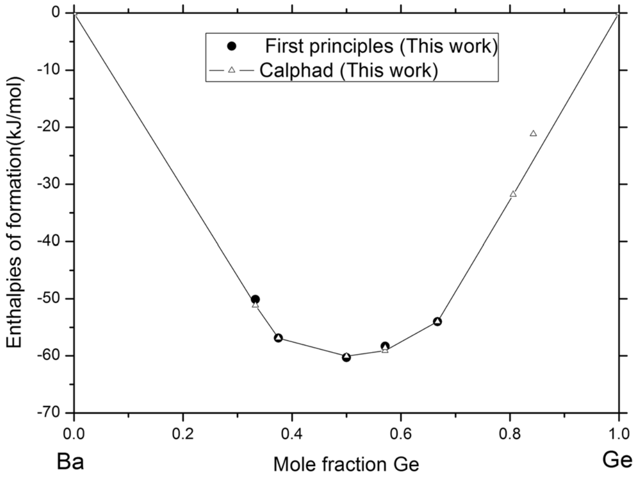

Fig. 9 Enthalpies of formation of intermetallic compounds of the Ba-Ge system

Table 7 The invariant reactions in the Ba-Ge system including calculated and experimental results

Reaction	Type of reaction	T°(K)	Compositions of the respective phases, at.% Ba			Reference
Liq → Ba + Ba_2Ge	Eutectic	818	4	0	33.3	24
		913	7.5	0	33.3	29
		934.79	11.5	0	33.3	This work
Liq → Ba_2Ge	Congruent	1273	33.3	33.3	…	29
		1273.20	33.3	33.3	…	This work
Liq + Ba_2Ge → Ba_5Ge_3	Peritectic	1213	40	33.3	37.5	29
		1192.91	40.42	33.3	37.5	This work
Liq → Ba_5Ge_3 + BaGe	Eutectic	1167	42.5	37.5	50	29
		1168	42.7	37.5	50	This work
Liq → BaGe	Congruent	1428	50	50	…	10
		1253	50	50		29
		1253	50	50	…	This work
Liq → βBa_3Ge_4 + BaGe	Eutectic	1178	56	57.1	50	29
		1199	55.69	57.1	50	This work
Liq + $BaGe_2$ → Ba_3Ge_4	Peritectic	1188	56.9	66.7	57.1	29
		1201	56.11	66.7	57.1	Thiswork
Liq → $BaGe_2$	Congruent	1378	66.7	66.7	…	29
		1378.69	66.7	66.7	…	This work
Liq + $BaGe_2$ → Ba_6Ge_{25}	Peritectic	1088	81.5	66.7	80.6	26,27,37
		1082.78	82.1	66.7	80.6	This work
Liq → Ba_6Ge_{25} + Ba_8Ge_{43}	Eutectic	1081	82.6	80.6	84.3	26,27,37
		1081.63	82.52	80.6	84.3	This work

Figure 3 shows the comparison between our calculated Gibbs excess energy and the experimental data [22] of the Al-Ba liquid alloys at 1373 K, while Fig. 4 presents the calculated enthalpies of mixing of the liquid phase with the experimental data obtained by Notin et al.[21] From these figures, we conclude that our results are very close to the experimental data. Figure 5 shows the calculated activities of Ba in liquid Al-Ba alloys compared with experimental measurements of Srikanth and Jacob[22] at 1373 K. The calculated data are slightly larger than the experimental data in the Ba-rich region.

Figure 6 shows that the optimised formation enthalpies of the intermetallic compounds are very close to the those obtained by first-principles calculations and the experimental results of Vigdorovich et al.[19]

The best optimization of the second system Ba-Ge was obtained with three excess terms for the liquid phase. The optimized parameters of the different phases are reported in Table 6. The calculated phase diagram of the Ba-Ge system is shown in Fig. 7 and compared with the experimental data[26,27,29] in Fig. 8. A comparison between the experimental and calculated invariant equilibrium is presented in Table 7. Our results agree well with those of Carrillo-Cabrera et al.[26,27] in the Ge rich part and differ not more than 2% with Pani and Palenzona[29] results.

Figure 9 shows the enthalpies of formation of the intermetallic compounds of the Ba-Ge system referred to solid Ba and solid Ge optimized by Calphad method and calculated by first principles calculations. These results show that the compound Ba_8Ge_{43} is not stable at low temperature, which agree with the calculated phase diagram. This compound only appears at 1055.53 K following the entropic effect.

7 Conclusion

Due to the lack of credible experimental thermodynamic data for the two binary systems Al-Ba and Ba-Ge, first-principles calculations were performed to remediate this deficiency. Thus the Al-Ba system has been reassessed and the Ba-Ge system has been assessed for the first time using the experimental phase diagrams data and enthalpies of formation of the intermetallic phases of the two systems obtained by first-principles calculations. A set of self-consistent thermodynamic parameters for each system has been obtained. The calculated phase diagrams, the temperatures and compositions of the invariant reactions, the congruent melting temperatures and enthalpies of the intermetallic compounds of the two systems show a good agreement with the experimental phase diagrams and first-principles calculations.

All our thermodynamic information obtained concerning the Al-Ba and Ba-Ge will be used soon in an optimized calculation of the Al-Ba-Ge ternary system.

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