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Thermodynamic description of the Gallium-Lanthanum binary system

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Abstract. Until now, no thermodynamic calculation has been done for the Ga-La system In the present work, it has been evaluated by means of the Calphad approach The solution phases (Liquid, (αLa), (βLa) and (γLa)) were modelled with the sublattice formalism and the excess term of the Gibbs energy with the Redlich-Kister equation. The intermetallic compound Ga_2La which has a homogeneity range, was treated as the formula (Ga)0.667 (Ga,La)0.333 by a two-sublattice model with Ga on the first sublattice and Ga and La on the second one. Ga_6La, Ga_4La, GaLa, Ga_3La_5, $GaLa_3$ have been treated as stoichiometric compounds. The calculated phase diagram and the thermodynamic properties of the system are in satisfactory agreement with the experimental data.

1 Introduction

The gallium-lanthanum system is a border of some ternary systems interesting for opto-electronics such as Ga-La-S [1]. A recent assessment of the Ga-La system by Palenzona and Cirafici [2] is based on the 31 original references. The same phase diagram was reproduced by Massalski et al [3], figure 1. The assessed phase diagram is essentially based on the work of [4-7]. The equilibrium phases are: (1) the liquid L; (2) the six intermetallic compounds Ga_6La, Ga_4La [8-10], Ga_2La with a homogeneity range (ε region), GaLa, Ga_3La_5 and $GaLa_3$; and (3) the four terminal solid solutions (Ga), (αLa), (βLa) and (γLa) with negligible solubilities. The crystals structure of the various phases of the Ga-La system are reported in Table 1

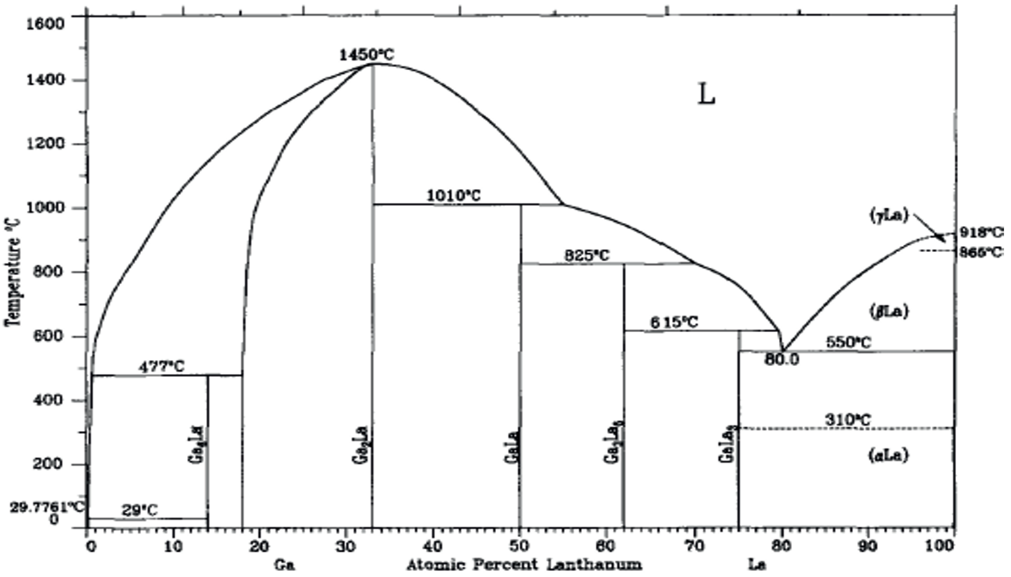

Fig. 1. The Ga-La phase diagram drawn by Palenzona and Cirafici [2].

2 Review of experimental data

Table 1. Symbols and crystal structures of the solid phases in the La-Ga alloys

Diagram Symbol	Composition at %La	Symbol used in Thermo-Calc Data File	Pearson symbol	Space group	Struktur-bericht Designation	Prototype
αGa	0	ORTHORHOMBIC_GA	*oC8*	*Cmca*	All	αGa
Ga_6La	14.29	Ga6La	*tP14*	*P4/nbm*		Ga_6Pu
Ga_4La	20	Ga4La	*oP20*	*Pmmm*		
Ga_2La	18 to 33.3	Ga2La	*hP3*	*P6/mmm*	*C32*	AlB_2
GaLa	50	GaLa	*oC8*	*Cmcm*	*Bf*	CrB
Ga_3La_5	62.5	Ga3La5	*tI32*	*I4/mcm*	*D8 r*	Cr_5B_3
$GaLa_3$	75	GaLa3	*cP4*	$Pm\bar{3}m$	Ll_2	$AuCu_3$
γLa	100	BCC	*cI2*	$Im\bar{3}m$	*A2*	W
βLa	100	FCC	*cF4*	$Fm\bar{3}m$	*A1*	Cu
αLa	100	DHCP	*hP4*	*P63/mmc*	*A3′*	αLa

Yatsenko [4] and Yatsenko et al [5] investigated the Ga-La equilibrium phase diagram by means of thermal analysis, microscopy, and X-ray diffraction. The resulting phase diagram showed four intermetallic phases Ga_2La (congruent melting at 1450°C), GaLa, Ga_3La_5, and $GaLa_3$ (peritectic formation at 1010°C, 825°C, and 615°C respectively). There were also two eutectics Liq$\Leftrightarrow$$Ga_6La$+(Ga) at 30°C and Liq$\Leftrightarrow$$GaLa_3$+(βLa) at 550°C and about 80 at.% La. To describe the eutectic on the Ga-rich side, [4] and [5] used the term "degenerate," presumably because the solidus temperature does not differ significantly from the melting temperature of Ga. [4] reported an accuracy in the temperature determination of ± 5°C. No appreciable solid solubility of La in (Ga) or Ga in (La) was observed by [4] and [5], and all the intermediate phases (except Ga_2La) appeared to be line compounds. Pelleg et al [6] investigated the Ga-rich side of the Ga-RE systems, finding the Ga_6La compound. This Ga-rich compound, called η phase, is formed by a peritectic reaction $Ga_6La$$\Leftrightarrow$Liq+$Ga_2La$ at T=477°C. Dayan et al [7], using interdiffusion studies of lanthanum with gallium, carried out with diffusion couples formed by annealing La metal in liquid Ga at various temperatures, determined the homogeneity range of Ga_2La and found it extends on the Ga-rich side from 18 to 33.3 at.% La. Their study excluded also the possible existence of Ga_3La as no layer of this composition is present in this system. Lu et al [11] studied the Ga-rich side of the Ga-La system. They reported that Ga_2La has an homogeneity range extending from 28.4 to 33.3 at.% La, which occurs when one La atom is replaced randomly by a pair of Ga atoms. These authors also fixed the peritectic reaction of formation for Ga_6La (Liq + Ga_2La $\Leftrightarrow$ Ga_6La) at 477°C. A critical evaluation of the data available in the literature for the Ga-La system has been reported by Palenzona and Cirafici [2]. They made the assessment of the phase diagram principally on the basis of the experimental investigation carried out by [4-7]. In their work, Dayan et al [7], studied samples prepared at 600°C and around 80 at. Ga content. By differential thermal analysis a phase transformation was observed in the ε region and by scanning electron micrographs a phase with about 80 at. % Ga was detected but its crystal structure was not identified. Later on, an analysis of the structure of Ga_4La was given by Zevin et al [8]. The structure is ordered orthorhombic. Ga pairs assumed ordering positions within the lattice and orientation ordering of the pairs of Ga depends on the Ga concentration. More recently, a new type of phase transformation was proposed by [9, 10]. The Ga_4La (ε’) phase was described as a long-range ordered structure with a stoichiometric concentration of 80 at. % Ga. Due to its definition by the orientation of pairs of gallium atoms the nature of the ordering transition is unique. The ordering temperature is 480°C. In order to obtain equilibrium state, samples were arc-cast and then vacuum annealed and homogenized at 600°C for 72 hours, finally at 480°C for 72 hours. As in the earlier works, the homogenization treatments of the samples were carried out at or above 600°C, and the ε’ phase was not detected. The enthalpies of formation of the intermetallic compounds of the Ga–La system have been determined by several authors [12-15]. Vnuchkova et al [12] have measured the standard enthalpies of formation of Ga_2La by e.m.f, in the 675-975K temperature range. De Boer et al. [13] calculated by a semi-empirical model the enthalpies of formation of Ga_3La_5, GaLa, Ga_2La and $Ga_{0.81}La_{0.19}$. In 2000, Meschel and Kleppa [14] have measured the standard enthalpies of formation of Ga_2La by high-temperature direct synthesis calorimetry at 1373 K. Recently, Babu et al [15] measured the standard enthalpies of formation of Ga_3La_5, GaLa and Ga_2La by high temperature liquid gallium solution calorimetry. The same authors determined the integral enthalpies of formation of GaLa alloys at 1125 K by using precipitation calorimetry and the partial enthalpy of solution of lanthanum in liquid gallium at infinite dilution at 1099K .Babu et al [1(] confirmed the result of Meschel and Kleppa [14].

3 Thermodynamic Models

1.1. Pure elements

The Gibbs energy function (298.15K) for the element i (i=La, Ga) in the ϕ phase (ϕ = Liquid, αLa (hP4), βLa (cF4), γLa (cI2), Ga (oS8)) is described by an equation of the following form:

$$G_i^{\phi} = a + bT + cT\ln T + dT + eT^{3} + fT^{7} + gT^{-1} + hT^{-9} \quad (1)$$

The coefficients *a-h* of the power series of the Gibbs energy of the different phases ϕ are taken from the SGTE data set [16].In this paper, the Gibbs energy functions are taken from the SGTE compilation of Dinsdale [16]. These functions are valid up to T=4000 K for La and Ga.

1.2. Solution phase

The liquid phase was modelled as a substitutional solution according to the polynomial Redlich-Kister [17] model. The Gibbs energy of one mole of formula unit of phase is expressed as the sum of the reference part ${}^{ref}G$, the ideal part ${}^{id}G$ and the excess part ${}^{ex}G$:

$$G^{liq} - H^{SER} = {}^{ref}G^{liq} + {}^{id}G^{liq} + {}^{ex}G^{liq} \quad (2)$$

$${}^{ref}G_{liq} = x_{Ga}\left[{}^{0}G_{Ga}^{liq} - H_{Ga}^{SER}\right] + x_{La}\left[{}^{0}G_{La}^{liq} - H_{La}^{SER}\right] \quad (3)$$

where H_i^{SER} (298.15K) is the molar enthalpy of the *i* element at 298.15K in its Standard Element Reference (SER) state, orthorhombic for Ga and hexagonal for La:

$${}^{id}G_{liq} = RT(y_{Ga}\ln y_{Ga} + y_{La}\ln y_{La}) \quad (4)$$

where *R* is the ideal gas constant; *T* is the temperature, in Kelvin; x_{Ga} and x_{La} are the mole fraction of the elements Ga and La, respectively.

The ${}^{ex}G_{liq}$ energy part in Eq. (2) is given by the Redlich–Kister polynomial [17]

$${}^{ex}G_{liq} = y_i\, y_j \sum_{\lambda=0}^{\lambda} {}^{\lambda}L_{i,j}^{Liq}\,(y_i - y_j)^{\lambda} \quad (5)$$

with the *i* and *j* indices which correspond to the two species Ga and La.

The binary interaction parameters of the ${}^{\lambda}L_{i,j}^{Liq}$ type, assessed in the present work, were temperature dependent as follows:

$${}^{\lambda}L_{i,j}^{Liq} = a_{\lambda} + b_{\lambda}T \quad (6)$$

a_{λ} and b_{λ} are the coefficients to be optimized.

The Ga (oS8), αLa (hP4), βLa (cF4) and γLa (cI2), phases were respectively modelled as pure Ga and La because of the unknown and certainly very low solubility of La in Ga and Ga in La.

1.3. Stoichiometric compounds:

The Gibbs energy of the stoichiometric compounds is expressed as follows**:**

$$G_{A_pB_q} = \frac{p}{p+q}\,{}^{0}G_A + \frac{q}{p+q}\,{}^{0}G_B + a + bT \quad (7)$$

where ${}^{0}G_A$ and ${}^{0}G_B$ are the Gibbs energy of the pure elements Ga and La respectively; *a* and *b* are parameters to be determined.

1.3.1 Ga_2La Phase

The Ga_2La phase is a C32 Laves phase, isotypic with AlB2. The homogeneity range of Ga_2La extends between Ga_2La and the Ga-rich side in the range 18.0 to 33.3 at. % La [2] and more recently in the 14.3 to 33.3 at % La [10]. The ε and η designations for Ga_2La and Ga_6La from [6] were omitted by Palenzona and Cirafici [2]. The Ga_2La intermetallic compounds was treated as (Ga)0.667(Ga,La%)0.333 by a two sublattice model. The symbol % denotes the major component in the corresponding sublattice.The Gibbs energy function per mole (m) of the formula unit (Ga)0.667(Ga,La%)0.333 is the following:

$$G_m^{Ga2La} = y_{Ga}^1 y_{Ga}^2 G^{Ga2La} + y_{Ga}^1 y_{La}^2 G^{Ga2La} + RT\left[0.333(y_{Ga}^2\ln(y_{Ga}^2) + y_{La}^2\ln(y_{La}^2))\right] + {}^{ex}G_m^{\phi} \quad (8)$$

where $y_{Ga}^1 = 1$ denotes the site fraction of gallium in the first sublattice, y_{Ga}^2 and y_{La}^2 the site fractions of gallium and lanthanum in the second sublattice, ${}^{0}G^{Ga0.667Ga0.333}$ is the Gibbs energy of the hypothetical compounds $Ga_{0.667}Ga_{0.333}$. ${}^{0}G^{Ga0.667La0.333}$ is the Gibbs energy of the stoichiometric compound $Ga_{0.667}La_{0.333}$.

$$H^{SER}_{(Ga)0.667(La\%,Ga)0.333} = (0.667\,y_{Ga}^1 + 0.333\,y_{Ga}^2)H_{Ga}^{SER} + (0.333\,y_{La}^2)H_{La}^{SER}) \quad (9)$$

${}^{ex}G_m^{\phi}$ is the excess Gibbs energy expressed by the following expression:

$$ {}^{ex}G_m^{\phi} = y_{Ga}^2 y_{La}^2 (L_{Ga:Ga,La}^{\lambda}) \tag{10}$$

where $L_{Ga:Ga,La}^{\lambda}$ represent the interaction parameters between the elements Ga and La in the second sublattice; the first sublattice being only occupied by the element Ga. These excess parameters are temperature dependent as:

$$L_{Ga:Ga,La}^{\lambda} = a_{\lambda} + b_{\lambda}T \tag{11}$$

In order to avoid the occurrence of the hypothetical compound Ga0.6667Ga0.3333, during the phase diagram calculation, the value +5000 J/mol of atoms was added to GHSERGa, see Table 2.

Most of the experimental data mentioned in Section 2 were used for the optimization of the thermodynamic parameters. As the first step, the thermodynamic parameters for liquid were optimized based on the integral enthalpies of mixing of the liquid alloys determined by Babu et al [15], using the Thermo-Calc program [18]. The data of the single phase domain (La-Ga) were used while the ones of the two-phase domain (La-Ga+LaGa$_{2+x}$) were discarded. The compositions of the phases involved in the invariant reactions are mainly based on the phase diagram of the Ga-La system evaluated by Palenzona and Cirafici [2]. For the Ga$_2$La phase, the interaction parameters Eq. ((8)–(11)), were adjusted according to the enthalpies of formation measured by Meschel and Kleppa [14] and Babu et al [15]. For the stoichiometric compounds, the interaction parameters Eq. (6) were adjusted according to the enthalpies of formation measured by Babu et al. [15]. All the optimized parameters are given in Table 2.

4 Assessment procedure

Table 2. The optimized thermodynamic parameters of the Ga-La system

Phase	Thermodynamic model	Parameters (units in J/mol.at and J/mol at.K)
Liquid	(Ga ,La)	${}^{0}L_{Ga,La}^{Liq}$ = - 236395.138 + 39.8826274T ${}^{1}L_{Ga,La}^{Liq}$ = - 64504.2950 + 0. 137122278T
BCC_A2	(Ga,La)$_1$(Va)$^*_3$	No excess term
FCC_A1	(Ga,La)$_1$ (Va)$_1$	No excess term
DHCP	(La)	No excess term
ORTHORHOMBIC_GA	(Ga)	No excess term
Ga$_6$La	(Ga)$_{0.857}$: (La)$_{0.143}$	$G_{Ga:La}^{Ga6La}$ -0.857 ${}^{298}H_{Ga}^{\text{ORTHORHOMBIC\_GA}}$ -0.143 ${}^{298}H_{La}^{DHCP}$ = - 41945.1358 + 1.05T
Ga$_4$La	(Ga)$_{0.8}$: (La)$_{0.2}$	$G_{Ga:La}^{Ga4La}$ -0.8 ${}^{298}H_{Ga}^{\text{ORTHORHOMBIC\_GA}}$ -0.2 ${}^{298}H_{La}^{DHCP}$ = - 55029.1060 + 3.07T
Ga$_2$La	(Ga)$_{0.667}$: (La)$_{0.333}$	$G_{Ga:La}^{Ga2La}$ - ${}^{298}H_{Ga}^{\text{ORTHORHOMBIC\_GA}} = GHSERGa + 5000$ $G_{Ga:La}^{Ga2La}$ -0.6667 ${}^{298}H_{Ga}^{\text{ORTHORHOMBIC\_GA}}$ -0.333 ${}^{298}H_{La}^{DHCP}$ = - 77450.7437 + 3.78135826T ${}^{0}L_{Ga:La,La}^{Ga2La}$ = - 32254.0822 + 1.24949858T ${}^{1}L_{Ga:La,La}^{Ga2La}$ = 10031.1315
GaLa	(Ga)$_{0.5}$: (La)$_{0.5}$	$G_{Ga:La}^{GaLa}$ -0.5 ${}^{298}H_{Ga}^{\text{ORTHORHOMBIC\_GA}}$ -0.5 ${}^{298}H_{La}^{DHCP}$ = - 77742.0789 + 10.7444362T
Ga$_3$La$_5$	(Ga)$_{0.375}$: (La)$_{0.625}$	$G_{Ga:La}^{Ga3La5}$ -0.375 ${}^{298}H_{Ga}^{\text{ORTHORHOMBIC\_GA}}$ -0.625 ${}^{298}H_{La}^{DHCP}$ = - 58509.0726 + 5.015T
GaLa$_3$	(Ga)$_{0.25}$: (La)$_{0.75}$	$G_{Ga:La}^{GaLa3}$ -0.25 ${}^{298}H_{Ga}^{\text{ORTHORHOMBIC\_GA}}$ -0.75 ${}^{298}H_{La}^{DHCP}$ = - 38632 + 1.8T

* (Va) for vacancy

Table 3. Invariant reactions in the Ga-La System

Reaction	Palenzona and Cirafici [2]		This work	
	T (K)	x(La).at.	T (K)	x(La) at.
Liq⇔ αGa + Ga_6La	302	Liq <0.001	301.7	Liq 0.005
Liq +Ga_4La ⇔ Ga_6La	750	Liq 0.005	748.6	Liq 0.092 Ga_2La 0.234
Liq +Ga_2La⇔ Ga_4La			752.3	Liq 0.093
Liq⇔ Ga_2La	1723	Liq 0.333	1727	Liq 0.333
Liq + Ga_2La ⇔ GaLa	1283	Liq 0.55	1295	Liq 0.508
Liq + GaLa ⇔ Ga_3La_5	1098	Liq 0.70	1095	Liq 0.655
Liq + Ga_3La_5 ⇔ $GaLa_3$	888	Liq 0.79	885.8	Liq 0.777
Liq ⇔ $GaLa_3$+βLa	823	Liq 0.80	826	Liq 0.830
Liq+ βLa ⇔γLa	1138	Liq 0.94	1134	Liq 0.9679

5 Results and discussion

The thermodynamic optimization of the Gibbs energy parameters is an application of the CALPHAD [19] technique with the PARROT module of the Thermo Calc software [18]. All of the experimental information mentioned in the Section 2 (phase diagram information and thermodynamics) was used for the optimization of the thermodynamic parameters of the different modelled phases. In order to avoid the formation of a unwanted inverted miscibility gap in the liquid phase, additional constraints ΔH_f versus x(La) ranging from 0 to 1 (every Δx(La)=0.1 at.) and at different temperatures up to 5000 K (every ΔT=50K) were therefore imposed on the thermodynamic parameters. All the parameters for the Ga-La system obtained by means of the optimization procedure are listed in Table 2. The resulting binary Ga-La phase diagram, based on the assessment is shown figure 2 together with the data from the literature. The calculated phase boundaries are in good agreement with the experimental data. Table 3 indicates that the temperatures and compositions for all the invariant equilibria in the system are well reproduced. A very good agreement is observed for the temperatures. The agreement is less good for the compositions of the liquid phase. The Ga-rich region of the Ga–La phase diagram is plotted in figure 3. The assessed integral enthalpies of mixing of liquid Ga-La alloys referring to liquid components at T=1125 K are plotted in figure 4. Also shown in this figure are the data by [15]. A good agreement is noted. The enthalpies of formation of the Ga–La intermetallic compounds measured and calculated ones are presented in figure 5 and in Table 4. The optimized enthalpy of formation of Ga_4La (ΔH_f = -55033 J/mol) is higher than the one determined in [13, 15] (-42700 J/mol and -37500 J/mol)..

Table 4. Standard enthalpies of formation of the Ga-La alloys

Compound	$-\Delta Hf_{298.15}$ kJ/mol.at	Method	Ref.	This work J/mol.at
$Ga_{0.79}La_{0.21}$	37.5±3.7 42.7	Precipit. Calori. T=1125K Miedema's model	[15] [13]	- 41945.1358
Ga_4La				- 55033
Ga_2La	69±3.7 69.2±2.4 92.0±0.1 67.5	Ga. Soln. Calori. T=1099K Dir. Syn. Calori. T=1373K EMF: 675-975K Miedema's model	[15] [14] [12] [13]	- 72882 for x(La)=0.3 - 53226 for x(La)=0.202 - 50227 for x(La)=0.19
GaLa	74.8±3.7 73.5	Ga. Soln. Calori. T=1102K Miedema's model	[15] [14]	- 77746
Ga_3La_5	62.6±4.5 61.8	Ga. Soln. Calori. T=1102K Miedema's model	[15] [13]	- 58513
$GaLa_3$				- 38636

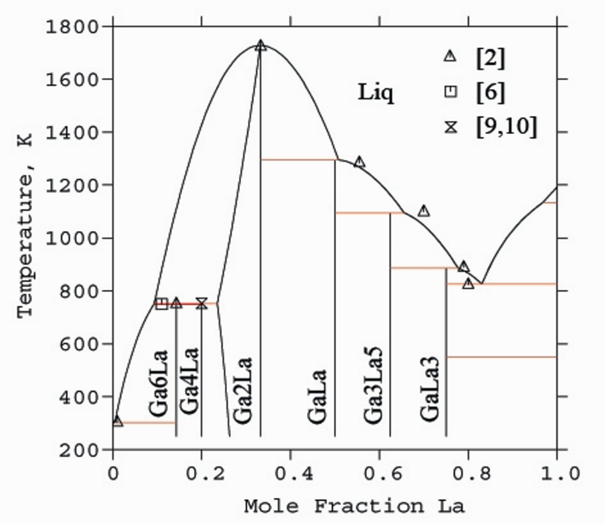

Fig. 2. Calculated Ga-La phase diagram with data from [2]

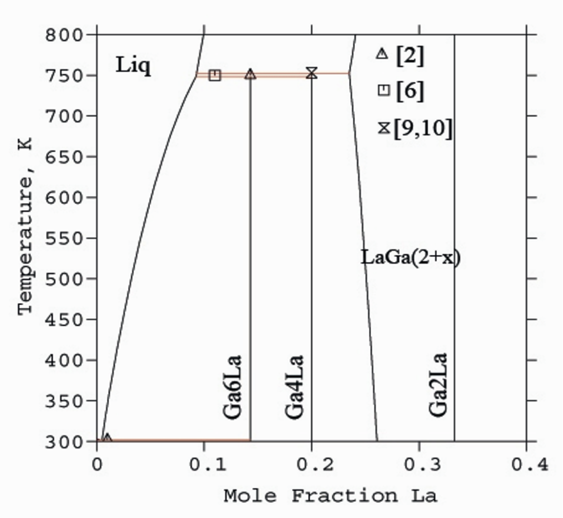

Fig. 3. Ga-rich region of the Ga–La phase diagram.

The assessed enthalpy of formation of Ga_2La (ΔH_f = -72882 J/mol) is in reasonable agreement with the experimental data (ΔH_f = -67500 J/mol, ΔH_f = -69200 J/mol and ΔH_f = -69000 J/mol) determined in [13], [12] and [15]. The computed value of enthalpy of formation of GaLa (ΔH_f = -77746 J/mol) is in good agreement with the values determined by [13, 15] (ΔH_f = -73500 J/mol and ΔH_f = -74800 J/mol). For Ga_3La_5, the computed value is -58513 J/mol, in reasonable agreement with the experimental data (ΔH_f = -62600±4500 J/mol and ΔH_f= -61800 J/mol) determined in [15] and [13]. As mentioned in [20], in order to check that the optimized thermodynamic parameters of the intermetallic compounds are satisfactory, we verified that, when the liquid phase is suspended during the calculation of the Ga–La phase diagram, the stoichiometric phases disappear at high temperatures and only the bcc_A2 solid solution is calculated on the whole La composition range and not the αGa one in the Ga-rich region. This is due to the power series in terms of temperature for the Ga element in the bcc A2 state which becomes metastable compared to the αGa state for higher temperatures [16].

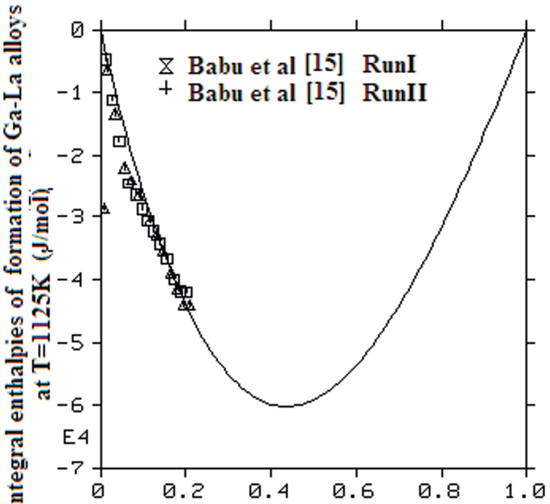

Fig. 4. Comparison of the calculated and measured integral enthalpy of formation of Ga-La alloys at T = 1125 K. The reference states were Ga and La liquid at T = 1125 K.

6 Conclusion

A thermodynamic assessment of the Ga-La system has been carried out. A consistent set of thermodynamic parameters has been derived. The computed values are in good agreement with the experimental thermodynamic and phase diagram data and we verified that no unwanted inverted miscibility gap was calculated for the solution phases up to 5000 K.

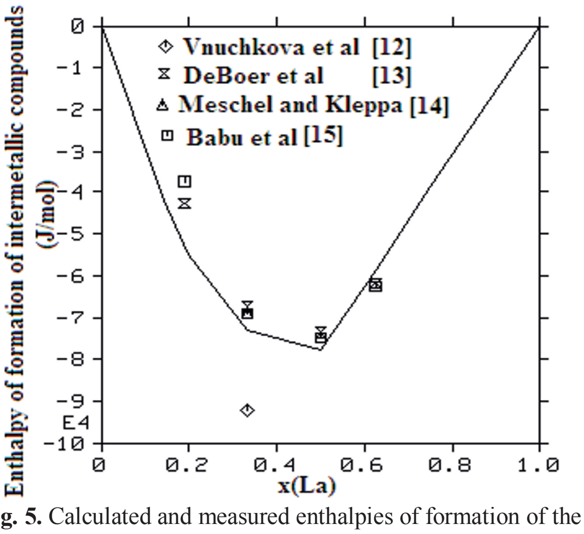

Fig. 5. Calculated and measured enthalpies of formation of the intermetallic compounds.

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