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Thermodynamic descriptions of the phase diagram and thermodynamic properties of the Bi–K binary system

F. Dziri, E. Belbacha, Y. Djaballah and A. Belgacem Bouzida

Laboratory of Physical and Chemical Study of Materials (LEPCM), Batna 1 University Batna, 05000, Algeria

*Corresponding author, email:yassine.djaballah@univ-batna.dz

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Abstract

The Bi-K binary system is reassessed by coupling CALPHAD approach and first principles calculations. The calculated lattice parameters and enthalpies of formation have been obtained from density functional theory as implemented in the VASP (Vienna Ab-initio Simulation Package) code. The whole system is optimized by CALPHAD method, where the liquid solution is described by the associate model and the binary compounds are described as stoichiometric phases. A good agreement has been obtained between the experimental data, first principles calculation and the thermodynamic optimization.

Keywords: Bi-K alloy; phase diagram; First principle calculations; Calphad;

1. Introduction

The phase diagrams play an important role in fundamental aspects of material research and serve as a guide for material design. According to previous studies, binary system and intermetallic compounds based on Bi and alkali metals are of high interest for technology and industrial applications, Bismuth is usually used in the form of an alloy with other metals.

Bismuth has low melting points, which has increased properties of materials used in thermocouple devices, moreover and further to the small density difference between lead and bismuth, the bismuth can substitute lead in many ballistics and weighting applications [1, 2]. Especially Bi-Alkali alloys have attracted considerable attention over the last decade, due to their importance in superconductors and thermoelectric materials with great technological interest [3, 4]. Therefore many thermodynamic databases of Bi-Rare earth and Bi-Alkali systems are developed, which are important for the design of alloys.

In this work, we have determined the enthalpies of formation of the compounds: Bi_2K, Bi_4K_5, Bi_2K_3 and BiK_3 by (DFT) method (first-principles calculations) using VASP code[5, 6]. The assessment of the all thermodynamic functions of the system using the CALPHAD (CALculation of PHAse Diagrams) method [7,8] is supported by our first-principles calculations results.

2. Experimental information

The phase diagram of the Bi-K system has been studied by several authors. The different results are summarized by Pelton and Petric [9]. Four intermetallic compounds exist in this system Bi_2K, Bi_4K_5, Bi_2K_3, and BiK_3. The Bi_2K, Bi_2K_3 and BiK_3 melt congruently at 565 °C, 442 °C, and 671°C respectively [10]. The Bi_4K_5 compound was formed by peritectic reaction at 381°C. Three eutectic reactions are given in this diagram, the first with Bismuth and liquid at 265 °C, the second between Bi_2K and Bi_4K_5 compounds at 381°C and the third between Bi_2K_3 and BiK_3 at 442 °C. The BiK_3 compound has a polymorphic transformation at 280°C [10].

By X-ray diffraction, Gascoin and Sevov [11, 12] have determined the crystal structure of Bi_4K_5 and Bi_2K_3, with monoclinic structure (mS18) and(mS20) respectively. Bi_2K is examined by Emmerling et al. [13] with cubic structure. The crystallographic structure of the αBiK_3 has been determined by Kerber et al. [14] and the ß phase of this compound has been examined with cubic structure by [15].

Petric et al. [16] have determined the Gibbs energy, enthalpy, entropy and activity of the liquid phase by using the Electromotive force measurements method (EMF). Voronin et al. [17, 18] have determined the enthalpies and entropies of formation for the intermetallics compounds by using Vapor Pressure Measurements.

The Bi-K system has been optimized in 2012 by Niua et al. [19], using associate model for the liquid phase and it has been reoptimized in 2014 by Cao et al. [20] using the MQM model for liquid phases.

3. First- principles calculation

First-principles calculations, based on density functional theory (DFT), were performed using the projected augmented wave (PAW) pseudo-potentials as implemented in the VASP (Vienna Ab-initio Simulation Package) code [5, 6] with the generalized gradient approximation as implemented by Perdewetal. (GGAPBE) [21]. we have used also the local density approximation refined by Ceperley and Alder (LDA-CA) [22]. The atomic orbital's treated as valence states for Bi, K were respectively $5d^{10}6s^{2}$ $6p^{3}$, $4s^{1}$.

A plane wave cutoff energy of 410 eV is used for each elements and compounds. For the Brillion-zone integration, a gamma centered k-point grid is used for the pure elements, while an Auto calculation grid is chosen for the binary compounds. The energies of formation of the intermetallic compounds (Bi_2K, Bi_4K_5, Bi_2K_3 and BiK_3) were obtained through the following equation:

$$\Delta E(Bi_xK_y) = E(Bi_xK_y) - \left(\frac{x}{x+y}E(Bi) + \frac{y}{x+y}E(K)\right) \qquad (1)$$

Where $E(Bi_xK_y)$, $E(Bi)$ and $E(K)$ are the total energy for (Bi_xK_y), pure rhombohedral (rho_A7) (Bi), or pure body-centered cubic (bcc_A2), K() respectively at T=0 K, P=0 Pa.

4. Thermodynamic modeling:

4.1. Pure elements

The function of the Gibbs energy ${}^{0}G_i^{\varphi}(T) = G_i^{\varphi} - H_i^{SER}$ (298.15 K) for the elements i = (Bi, K) is described by an equation of the following form:

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

where the coefficients a, b, c, d, e, f, g and h are taken from the Scientific Group Thermodata (SGTE) database compiled by Dinsdale. [25]. H_i^{SER} (298.15 K) is the molar enthalpy of the element i at 298.15 K in its standard element reference (SER), ${}^{0}G_i^{\varphi}$ and G_i^{φ} are the absolute and the relative Gibbs energy of the element i in the φ state, and T is the absolute temperature.

4.2. Intermetallic compounds

All the intermetallic compounds in the Bi-K system are treated as stoichiometric phases, the Gibbs energy of each compound is given by the following expression:

$$G^{Bi_XK_Y} = \frac{X}{X+Y}G_{Bi}^{SER} + \frac{Y}{X+Y}G_K^{SER} + \Delta H_f^{Bi_XK_Y} - T\Delta S_f^{Bi_XK_Y} \qquad (3)$$

where $\Delta H_f^{Bi_X K_Y}$ and $\Delta S_f^{Bi_X K_Y}$ is the enthalpy and entropy of formation for the intermetallic compounds.

Table 1: The crystal structure data of the Bi-K system.

Phase	Pearson symbol and prototype	Space group	Lattice parameters, (nm)			References
			a	b	c	
Bi	hR 6(As)	R̄m (166)	0.4544 0.4565 0.4488	0.4544 0.4565 0.4488	1.1859 1.1918 1.1537	[23] GGA LDA
K	cI2(W)	Im-3m (229)	0.5247 0.5309 0.5069	0.5247 0.5309 0.5069	0.5247 0.5309 0.5069	[24] GGA LDA
Bi_2K	cF24 ($MgCu_2$)	Fd-3m (227)	0.9520 0.9602 0.9333	0.9520 0.9602 0.9333	0.9520 0.9602 0.9333	[13] GGA LDA
Bi_4K_5	mS18 (Bi_4K_5)	c12/m1 (12)	1.2517 1.278 1.2222	0.5541 0.56713 0.54359	1.162 1.172 1.12799	[11] GGA LDA
Bi_2K_3	mS20 (Eu_3Ga_2)	C2/2 (15)	0.9381 0.9458 0.9064	0.9794 0.9962 0.9064	0.9284 0.94704 0.90737	[12] GGA LDA
αBiK_3	Cu_3P (hP24)	$P6_3cm$ (185)	1.0649 1.0818 1.0360	1.0649 1.0818 1.03606	1.0939 1.1092 1.0584	[14] GGA LDA
βBiK_3	BiF_3 (cF16)	Fm-3m (225)	0.8805 0.8721 0.8333	0.8805 0.8721 0.8333	0.8805 0.8721 0.8333	[15] GGA LDA

4.3. Liquid phase

For the liquid phase, we chose in the present work the associated liquid model [26] with the constituent species Bi, Bi_2K, BiK_3 and K.

The Gibbs energy of the liquid is expressed by the following equation:

$$G^{Liq} = RT\left[x_{Bi}Ln(x_{Bi}) + x_K Ln(x_K) + x_{Bi2K}Ln(x_{Bi2K}) + x_{BiK_3}\,Ln\left(x_{BiK_3}\right)\right] + G^{exc}_{Liq} + x_{Bi}\,{}^0G^{Liq}_{Bi} + x_K\,{}^0G^{Liq}_K + x_{Bi2K}\,{}^0G^{Liq}_{Bi2K} + x_{BiK_3}\,{}^0G^{Liq}_{BiK_3} \quad (4)$$

with G^{exc}_{Liq} the excess Gibbs energy. x_i which shows the mole fraction of each species i (i = Bi, Bi_2K, BiK_3 and K) in the liquid is expressed as follows:

$$G^{exc}_{Liq} = \sum_i \sum_{j\neq i} x_i x_j \sum_{\vartheta=0}^{n} {}^{\vartheta}L^{Liq}_{i,j}\left(x_i - x_j\right)^{\vartheta} \quad (5)$$

Where i and j correspond to the species Bi, Bi_2K, BiK_3 and K. The interaction parameters varies as linear functions of temperature ${}^{\vartheta}L^{Liq}_{i,j} = {}^{\vartheta}A_{i,j} + {}^{\vartheta}B_{i,j}T$

5. Results

Crystallographic parameters of the intermetallic compounds are reported in Table 1. The calculated lattice parameters are in good agreement with experimental data a maximum difference about 2 %, for the GGA calculation, and the LDA results underestimate the experimental values.

The enthalpies of formation for Bi–K compounds, obtained from first principles calculations, are reported in Tables 2. Table 3 lists the optimized thermodynamic parameters of each phase in the Bi–K system. The calculated phase diagram of the Bi-K system is shown in Figure 1 and compared with the experimental data [9, 10, 16] and calculated ones [19, 20] in Figure 2.

The liquidus curve agrees well with the experimental data of [16]. The comparison of the calculated invariant reactions with the experimental data in this system is listed in Table 4. All calculated temperatures and compositions of the reactions are well reproduced within the experimental uncertainties except the melting congruent of the Bi_2K_3 compound determined by Petric et al. [16] at 718□5 K, evaluated by [9] at 718□5 K and calculated by [19, 20] at 715.1 K and 715 K respectively, in this work we have obtained this reaction at 739.45K.

Figure 4 shows the evaluated enthalpies of formation of the intermetallic phases determined by Calphad method and calculated by first principles calculations, together with the experimental data obtained by electromotive force method (EMF) [16], and calculated by Calphad technique [19, 20]. All the intermetallic compounds are stable at 0K except the Bi_2K_3 compound does not stabilize until 100 K.

Table 2: The standard enthalpies and entropies of formation of the intermetallic compounds in the Bi-K system.

phase	$\Delta_f H$ (KJ/mol)	$\Delta_f S$ (J/K.mol)	Reference
Bi_2K	-28.7 ± 2.2	-3.4 ± 6.3	[17]
	-41.0 ± 4.2	-17.2 ± 4.2	[18]
	-40.8	-16.9	[16]
	-34.211^{a}	-2.9^{a}	[19]
	-42.5^{b}	-19^{b}	[19]
	-33.394	-57.56	[20]
	-30.865^{c}	-0.433^{c}	This work
	-30.737^{d}		This work
	-34.151^{e}		This work
Bi_4K_5	-38.1 ± 2.2	-8.4 ± 5.0	[17]
	-50.2 ± 12.6	-23.4 ± 6.3	[18]
	-42.095^{a}	-6.1^{a}	[19]
	-48.4^{b}	-19.2^{b}	[19]
	-40.888	-57.111	[20]
	-39.873^{c}	-3.544^{c}	This work
	-35.998^{d}		This work
	-38.744^{e}		This work
Bi_2K_3	-39.5 ± 2.2	-8.4 ± 4.6	[17]
	-43.169^{a}	-6.52^{a}	[19]
	-43.2^{b}	-6.52^{b}	[19]
	-42.235	-56.667	[20]
	-41.000^{c}	-3.7^{c}	This work
	-34.115^{d}		This work
	-37.949^{e}		This work
αBiK_3	-45.1 ± 2.1	-19.7 ± 3.8	[17]
	-49.2	-19.9	[16]
	-46.712^{a}	-12^{a}	[19]
	-51.3^{b}	-22.4^{b}	[19]
	-46.712	+61.597	[20]
	-42.7475^{c}	-7.4975^{c}	This work
	-37.556^{d}		This work
	-42.472^{e}		This work
βBiK_3	-46.297^{a} -	$+11.25^{a}$	[19]
	41.030	+63.285	[20]
	-43.025^{c}	-8.00^{c}	This work
	-35.151^{d}		This work
	-41.892^{e}		This work

^{a}Calculated at 523 K ^{b}Calculated at 838 K

^{c} CALPHAD ^{d}GGA ^{e}LDA

The optimized enthalpies of formation are in good agreement with LDA approximation, better than the calculated ones by using the GGA. The comparisons between the measured and the calculated Gibbs energies and

Enthalpy of the liquid phase are shown in Figure 5(a) and (b), respectively. The difference between our results and the experimental data is acceptable

Table 3: Thermodynamic parameters in the **Bi–K** system.

System Phases	Thermodynamic parameters
Bi-K Liquid phase, formula (Bi,Bi₂K,BiK₃,K)	${}^{0}G^{Liq}_{Bi2K} = {}^{0}G^{Liq}_{Bi} + {}^{0}G^{Liq}_{K} - 79000+16T$ ${}^{0}G^{Liq}_{BiK3} = {}^{0}G^{Liq}_{Bi} + {}^{0}G^{Liq}_{K} -166050+49T$ ${}^{0}G^{Liq}_{Bi,K} = -64039+8T$ ${}^{0}G^{Liq}_{Bi,Bi2K} = -12440+8T$ $G^{Liq}_{Bi,BiK3} = -87513.2+20T$ ${}^{01}G^{Liq}_{Bi,BiK3} = -40000$ ${}^{0}G^{Liq}_{BI2K,K} = +21519-7.00\,T$ ${}^{0}G^{Liq}_{Bi2K,BiK3} = -5000-3\,T$ ${}^{1}G^{Liq}_{Bi2K,BiK3} = -5000+2T$ ${}^{0}G^{Liq}_{Bi2K,BiK3} = -5000-1\,T$ ${}^{0}G^{Liq}_{BiK3,K} = +6500-2T$ ${}^{1}G^{Liq}_{BiK3,K} = -6900$
Bi_2K	$\Delta G_f^{Bi2K} = -30865+0.433T$
Bi_4K_5	$\Delta G_f^{Bi4K5} = - 39873.33+3.54T$
Bi_2K_3 α	$\Delta G_f^{Bi2K3} = -41000+3.7T$
BiK_3	$\Delta G_f^{BiK3} = -42747.5+7.49T$
βBiK_3	$\Delta G_f^{BiK3} = -43025+8\,T$

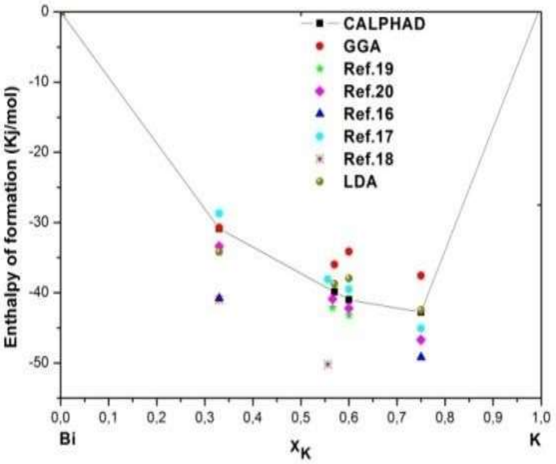

Figure3. Enthalpies of formation of the intermetallic compounds in the Bi-K system.

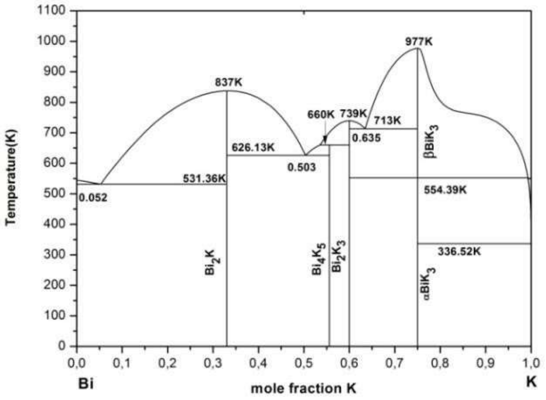

Figure 1. Calculated phase diagram of the Bi-K system

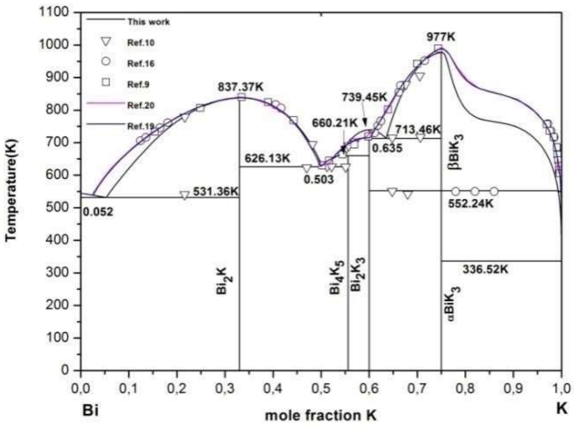

Figure 2. The assessed Bi –K phase diagram using the associate model in comparison with the optimized and experimental data.

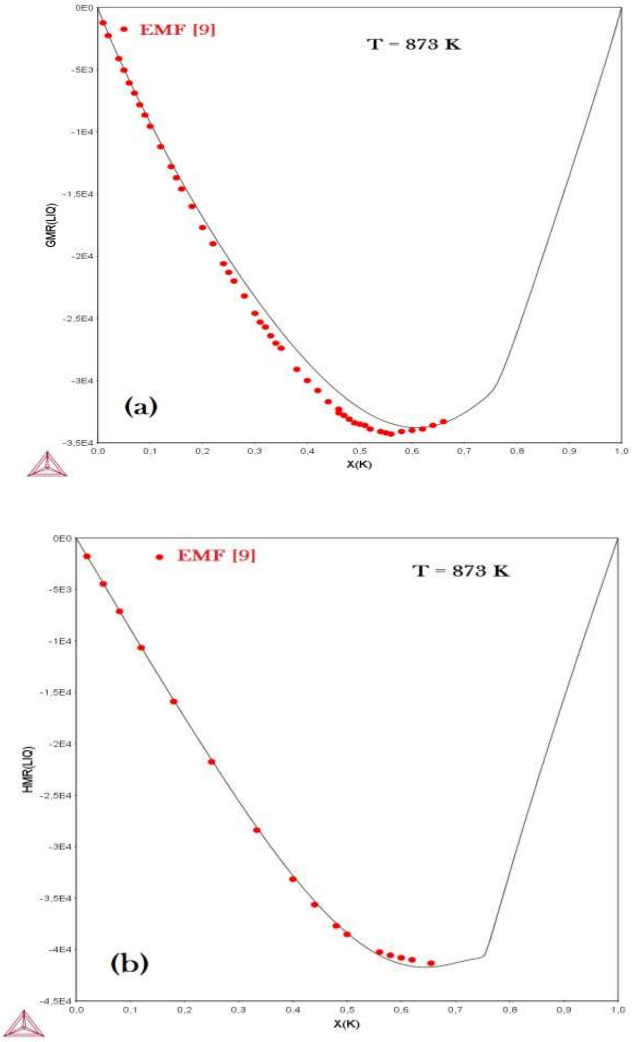

Figure4. (a) Gibbs energy (b) Enthalpy of the liquid phase

Table 4: The invariant reactions in the Bi–K system including calculated and experimental results.

Reaction	Type of reaction	Method	T (K)	Compositions of the respective phases x_K			References
Liq ↔ Bi+Bi_2K	Eutectic	Experiment	538	- - -	- - -	0.333	[10]
		Experiment	~538	0.025	0	0,333	[16]
		Evaluated	538□2	0.025	0	0.333	[9]
		Calculated	538.4	0.026	0	0.333	[19]
		Calculated	540	0.019	0	0.333	[20]
		Calculated	531.36	0.0527	0	0.333	This Work
Liq ↔ Bi_2K	Congruent	Experiment	838		0.333		[10]
		Experiment	838		0.333		[16]
		Evaluated	838□10		0,333		[9]
		Calculated	838		0.333		[19]
		Calculated	841		0.333		[20]
		Calculated	837.37		0.333		This Work

Liq ↔ $Bi_2K+Bi_4K_5$	Eutectic	Experiment	627	- - -	0.333	0.556	[10]
		Experiment	627	- - -	0.333	0.556	[16]
		Evaluated	627□1	0,5	0.333	0.556	[9]
		Calculated	626.9	0.499	0.333	0.556	[19]
		Calculated	631	0.504	0.333	0.556	[20]
		Calculated	626.13	0.503	0.333	0.556	This Work
Liq ↔ $Bi_4K_5+Bi_2K_3$	Peritectic	Experiment	654	- - -	0.556	0.6	[10]
		Experiment	654	- - -	0.556	0.6	[16]
		Evaluated	654□2	0.535	0.556	0.6	[9]
		Calculated	654.1	0,525	0.556	0.6	[19]
		Calculated	660	0.538	0.556	0.6	[20]
		Calculated	660.21	0.535	0.556	0.6	This Work
Liq ↔ Bi_2K_3	Congruent	Experiment	718□5		0.6		[16]
		Evaluated	718□5		0.6		[9]
		Calculated	715.1		0,6		[19]
		Calculated	715		0.6		[20]
		Calculated	739.45		0.6		This Work
Liq ↔ $Bi_2K_3+BiK_3$	Eutectic	Experiment	715	--	0,6	0.75	[10]
		Experiment	715	--	0,6	0,75	[16]
		Evaluated	715□2	0,605	0,6	0.75	[9]
		Calculated	715.1	0.602	0,6	0,75	[19]
		Calculated	715	0.603	0.6	0.75	[20]
		Calculated	713.46	0.635	0.6	0.75	This Work
Liq ↔ BiK_3	Congruent	Experiment	944		0,75		[10]
		Evaluated	988□25		0,75		[9]
		Calculated	988		0,75		[19]
		Calculated	991		0.75		[20]
		Calculated	977		0.75		ThisWork
Liq ↔ BiK_3+(K)	Eutectic	Experiment	336	--	0,75	1	[10]
		Experiment	~333,7	--	0,75	1	[16]
		Evaluated	336.71	~ 1	0,75	1	[9]
		Calculated	336.5	~	0,75	1	[19]
		Calculated	335	~ 1	0.75	1	[20]
		Calculated	336.52	1 0,998	0.75	1	ThisWork
$\alpha BiK_3 \leftrightarrow \beta BiK_3$		Experiment	553				[10]
		Evaluated	553□5				[9]
		Calculated	553				[19]
		Calculated	552				[20]
		Calculated	552,24				This work

6. Conclusion

In the present work we have determined the lattice parameters and the enthalpies of formation for intermetallic compounds in the system Bi-K via first principles calculations. The calculated enthalpies of formation are used in the thermodynamic reassessment of the Bi-K system.

The calculated invariant reactions, congruent melting temperatures of the intermetallic compounds, the calculated liquidus lines of the Bi-K system are in good agreement with experimental data and first principles calculations.

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