Journal of Alloys and Compounds 508 (2010) 333–337

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Enthalpy increment and heat capacity of Pb_3Bi

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ARTICLE INFO

Article history:
Received 19 May 2010
Received in revised form 9 August 2010
Accepted 13 August 2010
Available online 28 September 2010

Keywords:
Lead
Bismuth
Intermetallic compound
Calorimetry
Heat capacity
Enthalpy increment

ABSTRACT

Enthalpy increments of $Pb_{0.71}Bi_{0.29}$ compound and enthalpy change associated with peritectic decomposition reaction of the compound were determined using high temperature Calvet calorimeter. The heat capacity of the compound was determined in the temperature range 230–440 K using heat flow DSC. The enthalpy increment data was fitted into the following polynomial equations.

$$\Delta H^{T}_{298.15\,\mathrm{K}}\quad (\mathrm{J/mol}) = -6492.2 + 21.2775T + 0.00919T^2 - \frac{199,341}{T}\quad (298.15\text{–}457\,\mathrm{K})$$

The enthalpy of decomposition reaction of the compound at the peritectic temperature, 457 K, was found to be 984 J/mol. The heat capacity of the compound determined using DSC was fitted into the following polynomial equation.

$$C_P\quad (\mathrm{J/mol\,K}) = 23.486 - 0.01482T + \frac{97,338.4}{T^2}\quad (228\text{–}457\,\mathrm{K})$$

The heat capacity values obtained from DSC were in reasonably good agreement with the values calculated from enthalpy increment equation and both were slightly higher than the heat capacity values calculated using Neumann–Kopp's rule.

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1. Introduction

The lead–bismuth eutectic is considered as a potential candidate for liquid metal spallation neutron source [1] in ADS reactor systems and a coolant for critical and subcritical reactors of new generation [2,3]. There are many useful properties of LBE (lead–bismuth eutectic) for its usage both as spallation target and as coolant in a future accelerator driven system (ADS). A relatively low melting point helps prevent easy freezing of LBE under operation. The low vapour pressure and the non-existence of quick reactions with oxygen or nitrogen make the handling of LBE quite uncomplicated. However, small interactions between steels and LBE can result in liquid metal embrittlement of structural materials over a long reactor operation period [4–6]. Production of polonium isotopes and volatile elements during irradiation can also give problems during reactor operation [7,8]. To be able to predict the behaviour of this system with the cladding material, it is important to understand thermo-physical properties of Pb–Bi system. The Pb–Bi binary system is characterized by an intermetallic, hexagonal, superconducting, lead rich non-stoichiometric ε-compound (Fig. 1) that melts peritectically at 457 K and decomposes below ~228 K [9,10]. Hultgren et al. [11] have compiled and assessed all the available thermodynamic data of this system. Lukas [12] and Taskinen and Teppo [13] carried out optimization calculations of available thermodynamic and phase-diagram data of the system. Though liquid phase of this system is sufficiently studied, very limited data is available on thermodynamic properties of this intermetallic compound [14–17]. In fact there is no experimental data available in the literature for heat capacity or enthalpy increment of the intermetallic compound. In our earlier work [18] we have discussed enthalpy of formation of this compound at different temperatures. In this paper we will present the enthalpy change for decomposition reaction of the compound at peritectic temperature, 457 K, and enthalpy increment and heat capacity data of the compound.

2. Experimental

The compound, $Pb_{0.71}Bi_{0.29}$, was prepared by melting weighed amounts of lead (purity 99.9%) and bismuth (purity 99.9%) in a quartz ampoule sealed under high purity argon atmosphere. The ampoule was first heated to 650 K for 72 h, above the melting points of both the elements, to ensure complete mixing. The ampoule was then slowly cooled to 450 K, below the peritectic decomposition temperature of the compound. The alloy was maintained at this temperature for 240 h, to attain complete equilibrium in the solid phase and to anneal the compound. Then it was very slowly cooled to the ambient temperature to avoid any built-in strains of quenching. There was no visible interaction between the quartz ampoule and the compound. Formation of pure compound was confirmed by XRD analysis, as reported in our earlier work [18].

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doi:10.1016/j.jallcom.2010.08.115

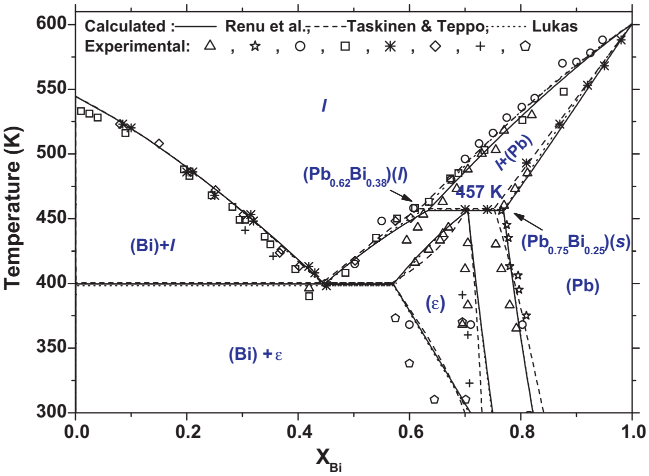

Fig. 1. Phase diagram of Pb–Bi system [9].

The enthalpy increment of the compound was measured using high temperature Calvet calorimeter from Setaram, France. The instrument is described in details in a previous publication [19], but for sake of clarity some of the salient features of the instrument will be described here. The samples were held in a sample holder maintained at ambient temperature, 298.15 K, using a bath circulator. The sample holder was connected to identical twin long one-end closed alumina tubes, which had their closed end in the isothermal temperature zone of the furnace. Thin walled quartz tubes held in the long alumina tubes were used as the reaction crucible. The whole assembly was leak proof and was evacuated and flushed with high purity argon a few times while heating the furnace to the experimental temperature. The experiments were carried out at constant temperature, under argon atmosphere, at ~0.101 MPa. For enthalpy increment measurements, the sample was added from ambient temperature to the reaction crucible at experimental temperature. The thermopile signal thus recorded was calibrated by repeating the same experiment with alumina-sapphire-SRM 720 [20]. Three to four of these additions of the sample and reference material were made at each experimental temperature to find out the precision of measurements. The weights of the samples added for enthalpy increment measurements were in the range of 200–300 mg. The accuracy of the instrument obtained by using enthalpy increment values of high purity molybdenum (99.997% purity) and NBS standard synthetic sapphire (SRM 720) was better than ±2%.

The heat capacity of the compound was determined by heat flow method using Setaram DSC-131. The transducer of DSC-131 has been designed using technology of plate-shaped DSC rods made of chromel-constantan. It is arranged in a small furnace with a metal resistor of low-thermal inertia so as to produce high heating and cooling rates. The transducer also possesses very good sensitivity over the whole temperature range (100–950 K). The temperature calibration of the calorimeter was carried out in the present study by the phase transition temperatures of National Institute of Standards and Technology (NIST) reference materials (mercury: T^{fus} 234.316 K; gallium: T^{fus} 302.914 K; indium: T^{fus} 429.748 K; tin: T^{fus} 505.078 K; lead: T^{fus} 600.600 K) and AR grade samples (n-pentane: T^{fus} 140.490 K; cyclohexane: T^{trs} 190.0 K; T^{fus} 280.1 K; deionised water: T^{fus} 273.160 K, potassium nitrate: T^{trs} 400.850 K; silver sulfate: T^{trs} 703.150 K; potassium sulfate: T^{trs} 856.150 K). Heat calibration of the calorimeter was carried out by using the enthalpies of transition of the above mentioned materials. For heat capacity calibration, NIST standard molybdenum and sapphire-720 (α-Al_2O_3) were used as reference in the temperature range from 300 to 440 K and NIST standard copper and sapphire-720 were used for low temperature values, 230–320 K. The accuracy and reproducibility of measurements were determined by measuring the heat capacities of NIST standards, molybdenum and copper, using synthetic alumina sapphire powder (SRM 720) as reference material and were found to be within ±2% of the literature values. Heat capacity of the compound was determined by the Classical three-step method in the continuous heating mode and step heating mode. In the continuous heating mode the heat flow was measured as a function of temperature at a heating rate of 5 K min^{-1}. In step heating mode, the heat flow was measured as a function of temperature where heating rate was 5 K min^{-1} and isothermal condition was maintained for 10 min in two different temperature ranges: (i) 230–320 K and (ii) 300–440 K. In the first temperature range, heat flow was measured with high purity helium as a carrier gas with a flow rate of 2 dm^3 h^{-1}. For the second temperature range, high purity argon was used as a carrier gas with the same flow rate as that of helium. Two flat bottom aluminium crucibles of identical masses, of capacity ~10^{-4} dm^3, with covering lids were used as containers for sample and reference materials. About 300–350 mg of the samples were used for the heat capacity measurements.

The molar heat capacity of the sample, $C_p^0(T)_{Sample}$, is calculated for each temperature reading from the specific heat capacity (weight) of the reference material, $c_p^0(T)_{Ref}$ taken in J g^{-1} using the following expression:

$$C_p^0(T)_{Sample} = \left(\frac{HF_{Sample} - HF_{Blank}}{HF_{Ref} - HF_{Blank}}\right) \times \left(\frac{m_{Ref}}{m_{Sample}}\right) \times c_p^0(T)_{Ref} \times M_{Sample} \quad (1)$$

where HF_{Blank}, HF_{Ref} and HF_{Sample} represent heat flow measured during DSC runs between blank–blank, blank–reference and blank–sample, respectively, M_{Sample} is molecular mass of the compound, and m_{Sample} and m_{Ref} are masses of sample and reference, respectively.

3. Results and discussion

The average enthalpy increment data of the compound at each temperature is given in Table 1, along with corresponding measurement errors. The experimental errors of the enthalpy increment values were less than 2%. The following polynomial equation was obtained by least square fitting the enthalpy increment data of $Pb_{0.71}Bi_{0.29}$ compound with constraints (i) enthalpy increment value is zero at 298.15 K and (ii) heat capacity of the compound is 29 J/mol K, at 298.15 K. The heat capacity value of the compound at 298.15 K was obtained from the present low temperature DSC measurements.

$$\Delta H^T_{298.15\,\mathrm{K}}\ \ (\mathrm{J/mol}) = -6492.2 + 21.2775T + 0.00919T^2 - \frac{199,341}{T} \quad (298.15\text{–}457\,\mathrm{K}) \quad (2)$$

The experimental enthalpy increment values are compared with the values calculated using the above equation in Table 1. The per-

Table 1
Comparison of experimental and fit enthalpy increment values.

T (K)	$\Delta H^T_{298.15\,\mathrm{K}}$ (exp.) (J/mol)	Measurement error %	$\Delta H^T_{298.15\,\mathrm{K}}$ (calc.) (J/mol)	% RD
323.15	711	1.79	726	2.17
333.15	1030	1.03	1018	1.11
341.15	1259	1.01	1252	0.57
348.15	1451	0.05	1457	0.44
356.15	1696	1.00	1692	0.25
363.15	1874	1.09	1898	1.29
373.15	2190	1.61	2193	0.13
378.15	2286	1.22	2341	2.40
383.15	2482	0.94	2489	0.30
393.15	2795	0.25	2786	0.30
403.15	3032	1.79	3085	1.74
413.15	3380	0.66	3385	0.15
423.15	3691	0.11	3686	0.15
433.15	3998	0.46	3988	0.23
443.15	4240	1.31	4292	1.22
448.15	4448	0.31	4444	0.07
453.15	4597	0.14	4597	0.01
457.15	4713	0.13	4715	0.03

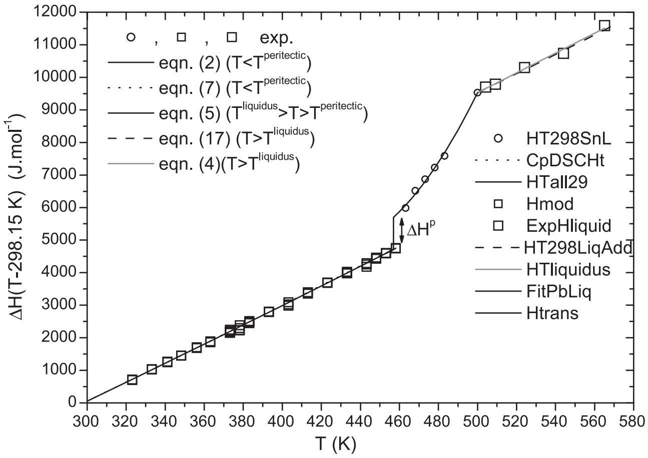

Fig. 2. Comparison of measured enthalpy increment data with calculated values, and enthalpies of transitions at peritectic decomposition temperature (ΔH^{p}) and liquidus (ΔH^{m}) temperature.

centage of relative difference (% *RD*) of the two values given in the table was calculated using the following relation:

$$\% \quad RD = \left| \frac{(\Delta H^{T}_{298.15\,\mathrm{K}})_{Experimental} - (\Delta H^{T}_{298.15\,\mathrm{K}})_{Calculated}}{(\Delta H^{T}_{298.15\,\mathrm{K}})_{Experimental}} \right| \times 100 \quad (3)$$

The enthalpy increment values determined experimentally are plotted in Fig. 2 along with the ones calculated from Eq. (2). The compound undergoes peritectic decomposition at 457 K and melts completely above 500 K. The enthalpy increment of the compound was determined above its peritectic decomposition temperature as well as above its liquidus temperature. The enthalpy increment values determined above the liquidus temperature were least square fitted in the following linear equation.

$$\Delta H^{T}_{298.15\,\mathrm{K}}(\mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29})(l) \quad (\mathrm{J/mol}) = -5675.3 + 30.41T \quad (> 500\,\mathrm{K}) \quad (4)$$

At the liquidus phase boundary, the enthalpy increment values of the two equilibrium phase fields, i.e., (Pb) + *l* and liquid phase, are same. Therefore, enthalpy increment of liquid solution calculated using Eq. (4) at the liquidus temperature, 500 K, was used as a constraint while calculating the following polynomial least square fit equation for enthalpy increment of (Pb) + *l* phase field from experimental data obtained in the temperature range 457–500 K.

$$\Delta H^{T}_{298.15\,\mathrm{K}}((\mathrm{Pb}) + l) \quad (\mathrm{J/mol}) = 142130 - 652.7T + 0.775T^2 \quad (457\text{–}500 \quad \mathrm{K}) \quad (5)$$

The experimental enthalpy increment values are plotted in Fig. 2 along with the values calculated from Eqs. (4) and (5).

The heat capacity of the compound calculated by differentiating enthalpy increment equation (2) with respect to temperature is as follows:

$$C_P \quad (\mathrm{J/mol} \quad \mathrm{K}) = 21.2775 + 0.01838T + \frac{199,341}{T^2} \quad (298.15\text{–}457 \quad \mathrm{K}) \quad (6)$$

The heat capacity values of the compound obtained in the temperature range 228–457 K by DSC were fitted in the following equation:

$$C_P \quad (\mathrm{J/mol\,K}) = 23.486 - 0.01482T + \frac{97,338.4}{T^2} \quad (228\text{–}457\,\mathrm{K}) \quad (7)$$

The following equation can be used to calculate Neumann–Kopp's heat capacity values for the compound, obtained from the heat capacity coefficients of pure elements given in Dinsdale data bank [21]:

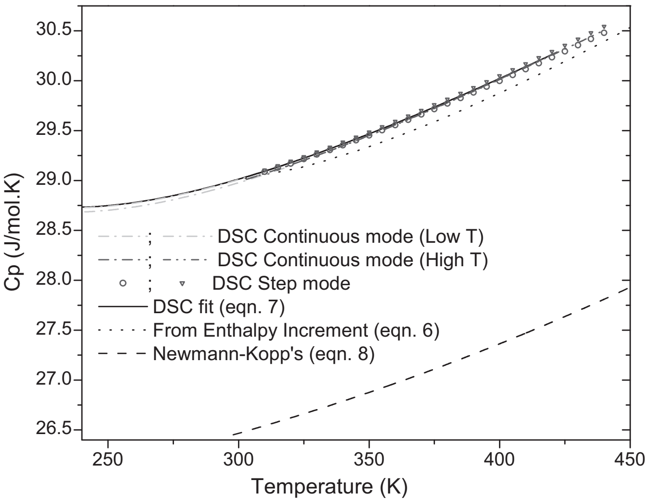

Fig. 3. Comparison of heat capacity data obtained from DSC with the ones calculated from enthalpy increment data and from Neumann–Kopp's additivity rule.

$$C_P \quad (\mathrm{J/mol\,K}) = 25.65 - 0.001961T + 1.561322 \times 10^{-5}T^2 \quad (8)$$

A comparison of all the experimental heat capacity data obtained by DSC with the polynomial fits given in Eqs. (6) and (7), and Neumann–Kopp's values calculated from Eq. (8) is given in Fig. 3. It can be seen that the heat capacity values calculated from enthalpy increment data is in good agreement with the heat capacity data obtained directly from DSC. However, both of them are slightly higher than the values calculated using Neumann–Kopp's rule of additivity.

The enthalpy increment data above and below the transition temperature were used for calculating the enthalpy of peritectic decomposition of the compound at invariant temperature. The difference in the enthalpy increment values calculated from Eqs. (2) and (5) at 457 K gives the enthalpy change of the following reaction:

$$\mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29} \rightarrow (\mathrm{Pb}) + l \quad (9)$$

The two phases formed on decomposition of the compound, (Pb) and liquid, have 75 at.% and 62 at.% Pb, respectively, where (Pb) represents solid lead phase with dissolved bismuth in it. The enthalpy of the above reaction calculated from Eqs. (2) and (5) was 984 J/mol at 457 K. Roy et al. [14] have reported enthalpies of formation of lead solutions of different compositions, at ~400 K. Enthalpies of formation for different compositions of (Pb) were recalculated using enthalpy increment values of Bi(*s*) and Pb(*s*) from the literature [21] and heat changes reported by Roy et al., observed due to addition of alloys from ~400 K in Pb(*l*) at ~654 K. Roy et al. have reported this data for (Pb) phase containing up to 15 at.% Bi. The enthalpy of formation of (Pb) phase with 25 at.% Bi was calculated by extrapolating the recalculated enthalpy of formation values for (Pb) as a function of composition using a least square polynomial fit. This value was found to be 2.9 kJ/mol at 400 K and it was assumed to be valid at 457 K by using Neumann–Kopp's additivity rule. This data was used for calculating enthalpy of mixing of $\mathrm{Pb}_{0.62}\mathrm{Bi}_{0.38}(l)$, at 457 K, using the following reaction scheme:

$$\mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29}(s) \rightarrow 0.698\ \mathrm{Pb}_{0.75}\mathrm{Bi}_{0.25}(s) + 0.302\mathrm{Pb}_{0.62}\mathrm{Bi}_{0.38}(l), \quad \Delta H_{obs} \quad \text{at} \quad 457\,\mathrm{K} \quad (10)$$

$$0.75\mathrm{Pb}(s) + 0.25\mathrm{Bi}(s) \rightarrow \mathrm{Pb}_{0.75}\mathrm{Bi}_{0.25}(s), \quad \Delta H^{0}_{f} \quad (\beta\text{-Pb}) \quad \text{at} \quad 457\,\mathrm{K} \quad (11)$$

$$0.71\mathrm{Pb}(s)+0.29\mathrm{Bi}(s)\rightarrow \mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29}(s),$$
$$\Delta H_f^0\ \ (\varepsilon\text{-}\mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29})\ \ \text{at}\ \ 457\,\mathrm{K} \tag{12}$$

$$\mathrm{Pb}(s)\rightarrow \mathrm{Pb}(l),\quad \Delta H^{\mathrm{Pb}(l)\ \ 457\,\mathrm{K}}_{\mathrm{Pb}(s)\ \ 298.15\,\mathrm{K}} \tag{13}$$

$$\mathrm{Bi}(s)\rightarrow \mathrm{Bi}(l),\quad \Delta H^{\mathrm{Bi}(l)\ \ 457\,\mathrm{K}}_{\mathrm{Bi}(s)\ \ 298.15\,\mathrm{K}} \tag{14}$$

$$0.62\mathrm{Pb}(l)+0.38\mathrm{Bi}(l)\rightarrow \mathrm{Pb}_{0.62}\mathrm{Bi}_{0.38}(l),\quad \Delta H^{mix}\ \ \text{at}\ \ 457\,\mathrm{K} \tag{15}$$

The enthalpy of mixing of liquid alloy containing 38 at.% bismuth, heat change associated with Eq. (15), can be calculated using the following relation:

$$0.302(\Delta H_{15}+0.62\Delta H_{13}+0.38\Delta H_{14})$$
$$=\Delta H_{10}+\Delta H_{12}-0.698\Delta H_{11} \tag{16}$$

where ΔH_i is the heat change for corresponding equations (i) in the above reaction scheme. The enthalpy of mixing of Pb(l) and Bi(l) to form a liquid solution, $\mathrm{Pb}_{0.62}\mathrm{Bi}_{0.38}$ at 457 K from the above relation was calculated as −3.6 kJ/mol, which is comparable with enthalpy of mixing of liquid solution reported at 448 K by Agarwal et al. [18].

The enthalpy increment data obtained at temperatures above peritectic decomposition till liquidus temperature indicate enthalpy increment of ((Pb) + l) system and enthalpy of partial decomposition and melting of (Pb). Above liquidus temperature, the observed enthalpy increment values are due to enthalpy increment of the liquid phase. All these changes can be seen by the inflections in enthalpy increment values. Interestingly the enthalpy increment data above the liquidus temperature ($T > 500$ K) shows a good agreement with the values obtained by adding $(0.71\Delta H^{T}_{500\,\mathrm{K}}(\mathrm{Pb}(l))+0.29\Delta H^{T}_{500\,\mathrm{K}}(\mathrm{Bi}(l))$ in $\Delta H^{500\,\mathrm{K}}_{298.15\,\mathrm{K}}$ (compound), calculated using the following equation (Fig. 2):

$$\Delta H^{T}_{298.15\,\mathrm{K}}(\mathrm{J/mol})=-3659.47+25.651T-9.804\times10^{-4}T^2$$
$$+5.208\times10^{-6}T^3+3.598\times10^{-18}T^7 \tag{17}$$

This shows that the system shows no short range ordering and behaves like an ideal solution above 500 K. It also indicates that Neumann–Kopp's rule can be used to calculate heat capacity of liquid solutions of lead–bismuth above liquidus temperature if the liquidus temperature is reasonably higher than the peritectic temperature. In fact Gokcen [10] has made a similar observation while comparing heat capacity values of eutectic liquid composition reported by Douglas and Dever [22] with Neumann–Kopp's values (Fig. 4). He, however, concluded that the estimated heat capacity values of Bi(l) below its melting point (544.45 K) was not reliable, therefore, the heat capacity values of liquid lead–bismuth system calculated by Neumann–Kopp's additivity rule below this temperature are not reliable but are in reasonable agreement with experimental temperature above 544.45 K. But, present enthalpy increment data for liquid solution of composition ($\mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29}$) follows additivity rule reasonably well in the temperature range 500–544.45 K. The heat capacity values of $(\mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29})_l$, calculated from the present enthalpy increment measurements in the narrow temperature range in liquid phase are also shown in Fig. 4. These values are slightly higher than the Neumann–Kopp's values shown for the liquid phase with eutectic composition because heat capacity of Pb(l) is higher than Bi(l).

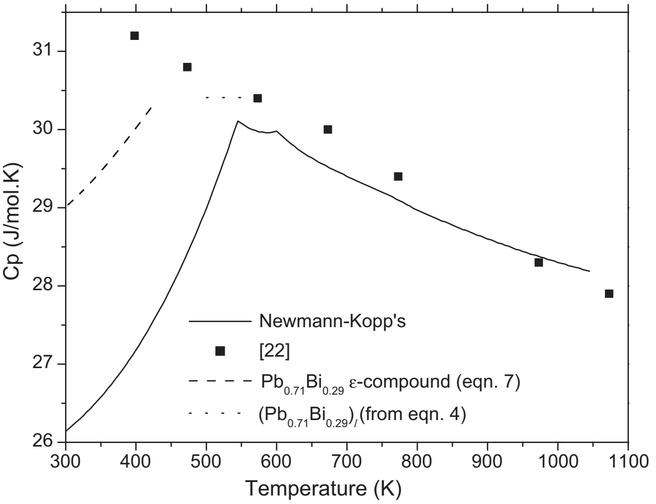

Fig. 4. Comparison of heat capacity of liquid solution of eutectic composition with Neumann–Kopp's values and heat capacity of the composition ($\mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29}$).

A thermodynamic table (Table 2) of this compound was generated using the enthalpy of formation of the compound from the literature [18] and heat capacity values of the compound from the present work. The entropy of formation of the compound at 298.15 K, was estimated from random mixing of the elements and excess entropy of the compound using the following equations:

$$\Delta_f S^{298.15\,\mathrm{K}}_{\mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29}}\ \ (\mathrm{J/mol\,K})=\Delta S^{ideal}+S^{xs}=-R(0.71\,ln(0.71)$$
$$+0.29\,ln(0.29))+(0.71\bar{S}^{xs}_{\mathrm{Pb}}+0.29\bar{S}^{xs}_{\mathrm{Bi}}) \tag{18}$$

$$\Delta_f S^{T}_{\mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29}}\ \ (\mathrm{J/mol\,K})=\Delta_f S^{298.15\,\mathrm{K}}_{\mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29}}+\int_{298.15\,\mathrm{K}}^{T}(C_P(\mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29})$$
$$-0.71C_P(\mathrm{Pb})-0.29C_P(Bi))\,dT \tag{19}$$

Table 2
Thermodynamic table for $\mathrm{Pb}_{0.71}\mathrm{Bi}_{0.29}$ compound ($\Delta_f G^{0,hcp}$ – Gibbs energy of formation from hypothetical hcp-structured Bi and Pb).

T (K)	$\Delta_f H^0$ (J/mol)	$\Delta_f S^0_{ideal}$ (J/mol K)	$\Delta_f S^0$ (J/mol K)	$\Delta_f G^0$ (J/mol)	Δfef (J/mol K)	$\Delta_f G^{0,hcp}$ (J/mol)
298.15	2700	5.01	9.10	−14	9.10	−2289
300	2705	5.02	9.12	−31	9.10	−2301
310	2730	5.11	9.20	−123	9.10	−2366
320	2756	5.19	9.28	−215	9.11	−2431
330	2781	5.27	9.36	−308	9.12	−2497
340	2807	5.35	9.44	−402	9.12	−2564
350	2833	5.42	9.51	−497	9.13	−2632
360	2859	5.49	9.59	−592	9.15	−2700
370	2885	5.56	9.66	−689	9.16	−2769
380	2911	5.63	9.73	−786	9.17	−2839
390	2938	5.70	9.80	−883	9.19	−2910
400	2964	5.77	9.86	−982	9.20	−2981
410	2991	5.84	9.93	−1081	9.22	−3053
420	3018	5.90	9.99	−1180	9.24	−3125
430	3044	5.96	10.06	−1280	9.26	−3198
440	3071	6.03	10.12	−1381	9.28	−3272
450	3098	6.09	10.18	−1483	9.30	−3346

The excess entropy of formation of the compound at 298.15 K was calculated using partial entropies of Pb(*s*) and Bi(*s*) given by Gokcen [10]. The entropy of formation of compound at temperatures higher than 298.15 K was calculated using difference in heat capacities of the compound and its elements in respective ratio (Eq. (19)). If only random entropy of mixing of the elements is considered for entropy of formation of the compound, then Gibbs energy of formation of the hcp-structured ε-compound from Pb(fcc) and Bi(rhombo) was found to be positive at all temperatures, thus making it unstable. However, positive excess entropy value for the compound results in stabilization of this compound. Gibbs energy of formation of the compound was recalculated from Pb(hcp) and Bi(hcp) by adding the Gibbs energies of transitions of Pb(fcc) → Pb(hcp) and Bi(rhombo) → Bi(hcp), taken from Dinsdale databank [21]. Gibbs energy of formation from similar structured pure elements is more negative than that from standard reference states.

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