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Thermochemical properties of Bi_2CuO_4

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Abstract

The heat capacity and the heat content of Bi_2CuO_4 were measured by Calvet calorimetry (300–570 K) and by drop calorimetry (670–970 K), respectively. The temperature dependence of the heat capacity in the form $C_{pm} = 185.249 + 1.453 \times 10^{-3}T - 4.730 \times 10^{6}T^{-2} + 4.620 \times 10^{8}T^{-3}$ was derived by the least square method. The enthalpy of solution of Bi_2CuO_4 as well as the stoichiometric mixture of Bi_2O_3 and CuO in the lead borate melt were measured at 970 K. The heat of formation of Bi_2CuO_4 from the constituent binary oxides and elements at 298.15 K are -14.63 ± 1.47 and $-740.12\,kJ\,mol^{-1}$, respectively.

Keywords: Bismuth cuprate; Bi_2CuO_4; Heat capacity; Heat content; Heat of formation

1. Introduction

Bismuth cuprate Bi_2CuO_4 has been investigated intensively in the last few years. It is an interesting material from the theoretical (3D antiferromagnetic ordering below 50 K) as well as technological (accompanying phase in the BiSrCaCuO superconductor system) point of view. Although the thermodynamic properties have been studied several times, a complete set of reliable data has not yet been reported.

The heat of formation of Bi_2CuO_4 from the constituent binary oxides Bi_2O_3 and CuO was determined by Idemoto et al. [1] by means of solution calorimetry in 1.53 M $HClO_3$ solvent. They obtained a slightly exothermic value $\Delta H_{ox}(298\,K) = -13.1 \pm 2.8\,kJ\,mol^{-1}$. Using the galvanic cells with solid electrolytes (YSZ or CaF_2), Mallika and Sreedharan [2] measured the Gibbs energy change for the reaction

$$Bi_2O_3(s) + CuO(s) = Bi_2CuO_4(s) \quad (1)$$

In the temperature range 650–950 K, they derived a linear temperature dependence in the form

$$\Delta G_{ox}(J\,mol^{-1}) = -35040 + 11.89\,T\,(\pm 570) \quad (2)$$

Hence the values of the heat of formation $\Delta H_{ox} = -35.04\,kJ\,mol^{-1}$ and the entropy of formation $\Delta S_{ox} = -11.89\,J\,K^{-1}\,mol^{-1}$ of Bi_2CuO_4 from the constituent binary oxides Bi_2O_3 and CuO can be deduced from Eq. (2) for the above mentioned temperature range. The heat capacity of Bi_2CuO_4 was measured by Castro et al. [3] from 5 to 350 K in an adiabatic calorimeter. A value of $C_{pm}(298.15\,K) = 151.73 \pm 0.42\,J\,K^{-1}\,mol^{-1}$ has been obtained. Gaidukov et al. [4], Gaidukov and co-workers [5], and Yamaguchi et al. [6] measured the heat capacity of Bi_2CuO_4 in a low temperature region (below 300 K). Their results have been presented in the graphical form only.

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Thermodynamic evaluation of the Bi–Cu–O system was published by Hallstedt et al. [7]. Based on a critical assessment of thermochemical and equilibrium data the temperature dependence of ΔG_{ox} for Bi_2CuO_4 was expressed in the form

$$\Delta G_{ox}(\mathrm{J\,mol^{-1}}) = -13100 + 4.44\,T \quad (3)$$

from which the values $\Delta H_{ox} = -13.10\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S_{ox} = -4.44\,\mathrm{J\,K^{-1}\,mol^{-1}}$ can be derived. Thermodynamic functions of Bi_2CuO_4 were estimated by Kasenov et al. [8]. Using the ionic contribution method the values of $C_{pm}(298.15\,\mathrm{K}) = 149.8 \pm 6.1\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and $S^{\circ}_{m}(298.15\,\mathrm{K}) = 188.9 \pm 5.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$ were obtained. The standard heat of formation of Bi_2CuO_4 from elements $\Delta H_f(298.15\,\mathrm{K}) = -755\,\mathrm{kJ\,mol^{-1}}$ was calculated by the comparative method.

The results of calorimetric investigation on Bi_2CuO_4 are presented in this paper. Further, thermodynamic functions calculated on the basis of our experimental results and reported value of molar entropy of Bi_2CuO_4 are given.

2. Experimental

Bi_2CuO_4 was prepared from Bi_2O_3 and CuO (Aldrich 99.99%) weighted with accuracy of 0.1 mg in the required stoichiometric ratio. The powdered mixture was annealed two times in air at temperature of 1023 K for 60 h with intermediate homogenisation. Partially reacted specimens were pressed into pellets (10 mm in diameter, thickness of 2–3 mm) and finally annealed under the same conditions. The composition of prepared samples was checked by the powder XRD analysis. The AAS was used in order to find the actual Bi/Cu ratio.

The heat conduction Setaram C-80 calorimeter was used for the heat capacity determination. The measurements were carried out in the incremental temperature scanning mode with a number of 5–10 K steps (heating rate $0.2\,\mathrm{K\,min^{-1}}$) followed by isothermal delays of 9000 s. Three runs should be performed – with empty crucible (blank), with the reference material (synthetic sapphire, NIST Standard reference material no. 720) and with the sample. For the heat capacity of the sample the following relation holds:

$$C_{pm,s}(T_i \rightarrow T_{i+1}) = \frac{Q_s - Q_{blank}}{Q_{ref} - Q_{blank}} c_{p,ref} \frac{m_{ref}}{m_s} M_s \quad (4)$$

where Q is the relevant peak area for the sample (s), reference material (ref) and blank, $c_{p,ref}$ the mean specific heat capacity of the reference material in the temperature range T_i–T_{i+1}, m the mass and M the molar mass. The typical mass of samples was approx. 6 g. The accuracy of heat capacity measurements is estimated to be better than ±2%.

Heat content determinations were carried out by the drop method using the high temperature calorimeter Setaram (Multi HTC 96). Isothermal measurements were made in air by alternating dropping of the reference material (small pieces of synthetic sapphire, NIST Standard reference material no. 720) and the sample (Bi_2CuO_4 pellets, 5 mm in diameter, thickness of 2–3 mm) being initially held at room temperature (T_0) through a lock into the working cell of the preheated calorimeter. Endothermic effects are detected and the relevant peak area $Q(T)$ is proportional to the heat content of the dropped specimen $\Delta H(T)$:

$$Q(T) = S(T)\frac{m}{M}\Delta H(T), \quad \Delta H(T) = \int_{T_0}^{T} C_{pm}\,\mathrm{d}T \quad (5)$$

where m and M are the mass and the molar mass of the specimen, respectively. The sensitivity of calorimeter $S(T)$ at temperature T is determined from the known heat content of the standard. The measurements were performed at temperatures 670–970 K on samples with the masses 100–150 mg. The delays between two subsequent drops were 40–50 min. In order to check the accuracy of the present measurement, the heat contents of CuO as well as platinum were measured first. The results for CuO are given in Table 1. It

Table 1
Heat content of CuO

T (K)	ΔH (kJ mol^{-1}) experimental	ΔH (kJ mol^{-1}) calculated [9]	S.D. (%)
770	23.42	23.30	1.0
	23.53	23.30	0.5
970	33.41	34.09	−2.0
		33.51[a]	−0.3
	33.69	34.09	−1.2
		33.51[a]	0.5
1168	44.19	45.15	−2.1
	44.13	45.15	−2.3

[a] Ref. [15], recalculated from temperature 977 K using $C_{pm}(T)$ [9].

should be concluded, that the literature values [9] are reproduced with the accuracy of about 1.5%. The values $\Delta H(970) = 18.76$ and $18.78\,\mathrm{kJ\,mol^{-1}}$ were observed for Pt differing in approx. 0.8% from the recommended SGTE data [10].

The same calorimeter was used for the determination of enthalpy of solution of Bi_2CuO_4 in the $2PbO.B_2O_3$ melt. The lead borate glass was prepared by melting the powder oxides PbO (Alfa Aesar, 99.9%) and B_2O_3 (Aldrich, 99%) in the required ratio at 1023 K for 1 h. The typical amount of 18 g of melt was heated at the temperature of 973 K and held for 3–4 h to reach the steady-state heat flow. For determination of sensitivity, the inert reference material (platinum bullet) was dropped into the melt first. A pellet of the sample (Bi_2CuO_4 or the stoichiometric mixture of $Bi_2O_3 + CuO$) was dropped subsequently. In case of a soluble sample, the overall detected drop-solution heat effect, $\Delta H_{\mathrm{dsol}}(T)$, is due to the heating from room temperature to the temperature of calorimeter T, $\Delta H(T)$, and the solution of the sample in the melt at this temperature, $\Delta H_{\mathrm{sol}}(T)$. For the heat of formation of Bi_2CuO_4 from the constituent binary oxides the following relation holds

$$\Delta H_{\mathrm{ox}}(198\,\mathrm{K}) = \Delta H_{\mathrm{dsol},(Bi_2O_3+CuO)}(T) - \Delta H_{\mathrm{dsol},Bi_2CuO_4}(T) \quad (6)$$

The measurements were performed in air closed atmosphere. The mass of samples was approx. 100 mg. The heat content of platinum used for the sensitivity evaluation was derived from the SGTE data [6]. The accuracy of the present measurement was verified by the determination of the heat of solution of CuO. The acquired value $\Delta H_{\mathrm{sol}} = 34.47$ kJ/mol at 970.3 K is in good agreement with data found in the literature 33.3 ± 0.4 at $T = 977$ K [11], 33.5 ± 0.4 at $T = 977$ K [12] and 31.8 ± 1.3 at $T = 973$ K [13].

3. Results and discussion

The XRD analysis revealed that the prepared sample consists of single phase (Bi_2CuO_4) without any observable diffraction lines from unreacted precursors or other phases. The lattice parameters of tetragonal unit cell assessed using the Rietveld method are $a = 0.8499$ nm and $c = 0.5816$ nm. They are in good agreement with the value given in the relevant

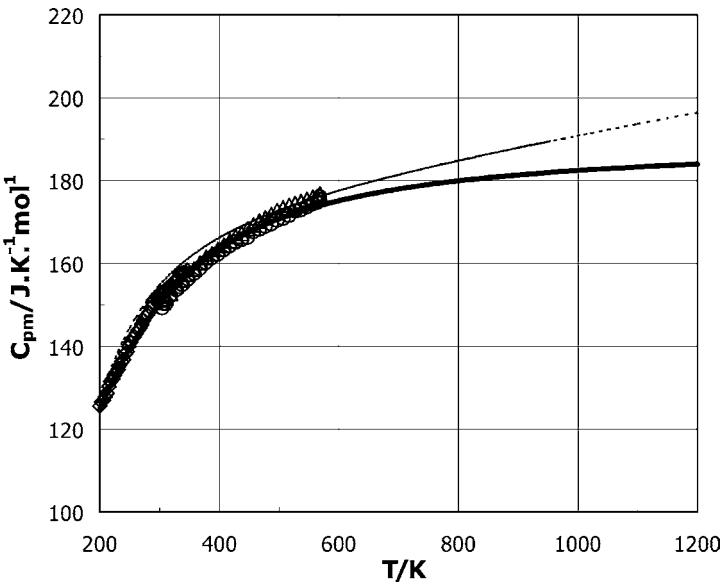

Fig. 1. Temperature dependence of molar heat capacity of Bi_2CuO_4 (○,▲): experimental points (Calvet); (◇): ref. [3]; —: fitted curve (Eq. (7)); - - -: calculated according to the Neumann–Kopp rule as the sum of heat capacity of CuO and Bi_2O_3 reported in [9,14], respectively.

Table 2
Heat content of Bi_2CuO_4

T (K)	ΔH (kJ mol^{-1}) experimenal	ΔH (kJ mol^{-1}) calculated	T (K)	ΔH (kJ mol^{-1}) experimental	ΔH (kJ mol^{-1}) calculated
670.0	60.42	62.42	670.3	57.58	62.47
670.0	59.30	62.42	670.3	58.39	62.47
670.0	62.15	62.42	720.0	68.36	71.31
671.1	63.75	62.61	720.1	68.46	71.33
770.0	77.99	80.26	820.0	90.52	89.25
770.0	84.44	80.26	820.1	88.92	89.26
770.0	77.58	80.26	870.0	93.63	98.29
770.0	76.79	80.26	870.1	95.63	98.30
869.9	93.70	98.27	920.1	106.25	107.37
869.9	95.12	98.27	920.2	106.20	107.39
869.9	100.27	98.27	970.1	117.47	116.46
870.1	100.56	98.30	970.2	115.78	116.47
970.2	117.11	116.47			
970.2	113.63	116.47			
970.3	114.35	116.49			
970.3	111.57	116.49			

JCPDS file No. 42-0334 ($a = 0.84996$ nm and $c = 0.58172$ nm). The ratio Bi/Cu = 2.04 was determined by the AAS.

The molar heat capacity data are plotted in Fig. 1 The heat content data are listed in Table 2 and shown in Fig. 2. The raw data were simultaneously handled using the least square method with different weights for individual points. To smoothly link our temperature dependence to low-temperature data of Castro et al. [3] three selected points, namely $C_{pm}(200\,K) = 124.71\,J\,K^{-1}\,mol^{-1}$, $C_{pm}(250\,K) = 140.01$ and $C_{pm}(300\,K) = 152.15\,J\,K^{-1}\,mol^{-1}$ were included

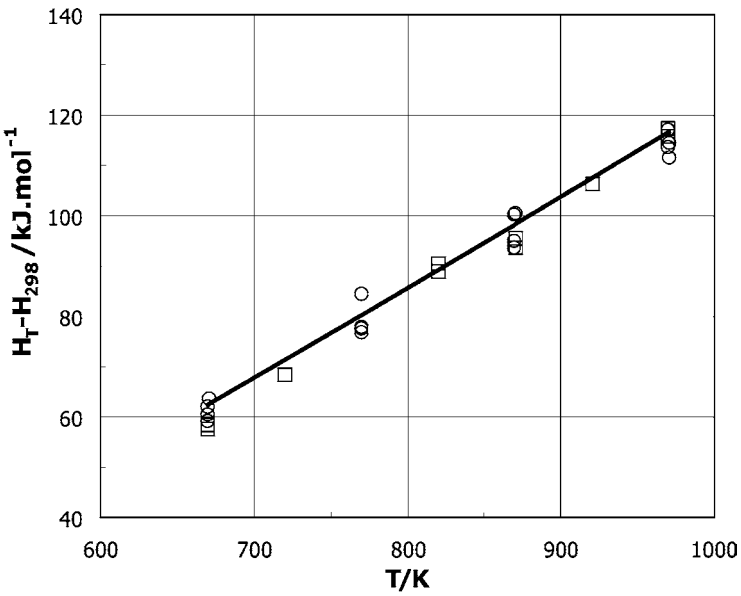

Fig. 2. Temperature dependence of heat content of Bi_2CuO_4 (○,▲): experimental points (drop); —: fitted curve (Eq. (8)).

into the regression procedure. Four parameter fitting equation with the T^{-3} term was used to reach higher flexibility around the room temperature. Thus the temperature dependence of the molar heat capacity of Bi_2CuO_4 can be expressed by the following equation ($T = 298.15$–$1200\,K$)

$$C_{pm}(J\,K^{-1}\,mol^{-1}) = 185.249 + 1.453 \times 10^{-3}\,T - 4.730 \times 10^{6}\,T^{-2} + 4.620 \times 10^{8}\,T^{-3} \quad (7)$$

An estimated temperature dependence of the molar heat capacity calculated according to the Neumann–Kopp's rule (NKR) as the sum of heat capacity of CuO and Bi_2O_3 is also plotted in Fig. 1. It is obvious that the NKR slightly overestimates the heat capacity around the room temperature and the slope of the estimated dependence is greater than the one of the fitted curve. Temperature dependence of the heat content is derived by integration of Eq. (7) according to the temperature as follows:

$$H_T - H_{298}(J\,mol^{-1}) = 185.249\,T + 0.727 \times 10^{-3}\,T^2 + 4.730 \times 10^{6}\,T^{-1} - 2.310 \times 10^{8}\,T^{-2} - 68562.5 \quad (8)$$

The heats of solution in the lead borate melt of Bi_2CuO_4 as well as of the stoichiometric mixture of $Bi_2O_3 + CuO$ at $T = 970\,K$ are summarised in Table 3. The heat of formation of Bi_2CuO_4 from the constituent binary oxides was calculated according to the Eq. (6) giving the value $\Delta H_{ox}(298\,K) = -14.63 \pm 1.47\,kJ\,mol^{-1}$. This value is in very good agreement with $\Delta H_{ox}(298\,K) = -13.1 \pm 2.8\,kJ\,mol^{-1}$ reported by Idemoto et al. [1]. Using the standard heats of formation of constituent binary oxides CuO $\Delta H_f^{\circ}(298.15\,K) = -155.19\,kJ\,mol^{-1}$ and Bi_2O_3 $\Delta H_f^{\circ}(298.15\,K) = -570.30\,kJ\,mol^{-1}$ reported in [9,14], respectively, the standard heat of formation of Bi_2CuO_4 from elements $\Delta H_f^{\circ}(298.15\,K) = -740.12\,kJ\,mol^{-1}$ can be calculated.

A complete set of thermodynamic functions of Bi_2CuO_4 calculated on the basis of the above mentioned value of the heat of formation, the temperature dependence of the molar heat capacity, Eq. (7), and the value of standard molar entropy $S_m^{\circ} = 187.12\,J\,K^{-1}\,mol^{-1}$ [7,9,14] is presented in Table 4.

Table 3
Heat of drop-solution of Bi_2CuO_4 and stoichiometric mixture $Bi_2O_3 + CuO$

Sample	Mass of solute (mg)	ΔH_{drop} (kJ mol^{-1})
Bi_2CuO_4	109.13	242.67
	108.78	240.57
	107.52	240.36
	110.11	241.29
	107.58	240.77
	95.15	241.35
		241.17 ± 0.88[a]
($Bi_2O_3 + CuO$)	106.92	227.17
	112.76	225.12
	104.90	227.78
	104.03	226.08
		226.54 ± 1.18[b]

[a] The value of mean.
[b] The value of mean.

Table 4
Thermodynamic functions of Bi_2CuO_4

T (K)	C_{pm} (J K^{-1} mol^{-1})	H_m (kJ mol^{-1})	S_m (J K^{-1} mol^{-1})	G_m (kJ mol^{-1})
298.15	149.904	−740.120	187.120	−795.910
300	150.240	−739.842	188.048	−796.257
400	163.486	−724.085	233.287	−817.400
500	170.752	−707.340	270.623	−842.652
600	175.121	−690.030	302.171	−871.333
700	177.960	−672.366	329.394	−902.942
800	179.923	−654.467	353.293	−937.101
900	181.351	−636.400	374.571	−973.514
1000	182.434	−618.208	393.737	−1011.945
1100	183.285	−599.920	411.166	−1052.203
1200	183.975	−581.556	427.145	−1094.130

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