ISSN 1063-7834, Physics of the Solid State, 2012, Vol. 54, No. 10, pp. 2142–2144. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.M. Denisov, L.T. Denisova, L.A. Irtyugo, N.V. Volkov, G.S. Patrin, L.G. Chumilina, 2012, published in Fizika Tverdogo Tela, 2012, Vol. 54, No. 10, pp. 2012–2014.

THERMAL PROPERTIES

High-Temperature Heat Capacity of Copper Metaborate CuB_2O_4

V. M. Denisov[a], L. T. Denisova[a, *], L. A. Irtyugo[a], N. V. Volkov[b, c], G. S. Patrin[b, c], and L. G. Chumilina[a]

[a] *Institute of Non-Ferrous Metals and Materials Science, Siberian Federal University, pr. im. Gazety "Krasnoyarskii Rabochii" 95, Krasnoyarsk, 660025 Russia*

* *e-mail: antluba@mail.ru*

[b] *Kirensky Institute of Physics, Siberian Branch of the Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*

[c] *Institute of Engineering Physics and Radioelectronics, Siberian Federal University, pr. Svobodnyi 79, Krasnoyarsk, 660041 Russia*

Received March 14, 2012

Abstract—The heat capacity of copper metaborate CuB_2O_4 has been measured over a wide temperature range. A correlation between the composition of the $CuO–B_2O_3$ system and the heat capacity of the oxide compounds has been found.

DOI: 10.1134/S1063783412100113

1. INTRODUCTION

Interest in studying the properties of copper metaborate CuB_2O_4 and materials on its basis is not lost after their low-temperature magnetism had been discovered [1–6]. The equilibrium $B_2O_3–CuO$ phase diagram is given in [7]. It is characterized by the existence of two compounds CuB_2O_4 and $Cu_3B_2O_6$ that are melted congruently. The properties of copper metaborate CuB_2O_4 have been studied in more detail, namely, the magnetic properties [1–3], electromechanical properties and anisotropy of propagation of acoustic waves [4], and crystal structure [8].

At the same time, almost there are no data on the heat capacity and thermodynamic potentials of a CuB_2O_4 crystal. There are only the data on the heat capacity of CuB_2O_4 at temperatures of 2–40 K [3]. The aim of this work is to measure the high-temperature heat capacity and to calculate the thermodynamic properties of CuB_2O_4 using the data measured.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Copper metaborate single crystals were grown from a solution–melt containing CuO, B_2O_3, and Li_2CO_3 (25, 60, and 15 mol %, respectively). All the reagents used were pure for analysis. The technique of growing the single crystals is similar to that described in [2, 3]. The CuB_2O_4 crystals were separated from the solvent by boiling in 20% HNO_3 aqueous solution. They had a bright blue-violet color and maximal sizes of 1 × 1 × 0.5 cm.

The heat capacity C_p was measured in platinum crucibles using a NETZSCH STA 449 Jupiter device similarly to [9, 10].

3. RESULTS AND DISCUSSION

The temperature dependence of the heat capacity of the CuB_2O_4 crystals is shown in Fig. 1. It is seen from the figure that C_p increases regularly in the temperature range under study, and the $C_p(T)$ dependence has no any peculiarities. The measured values of C_p

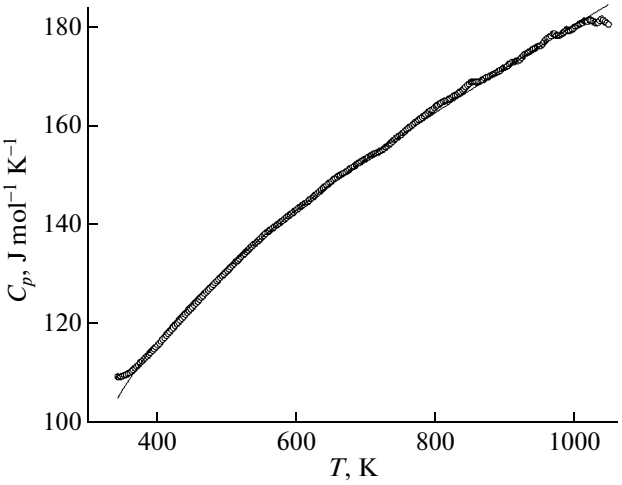

Fig. 1. Temperature dependence of the heat capacity of CuB_2O_4.

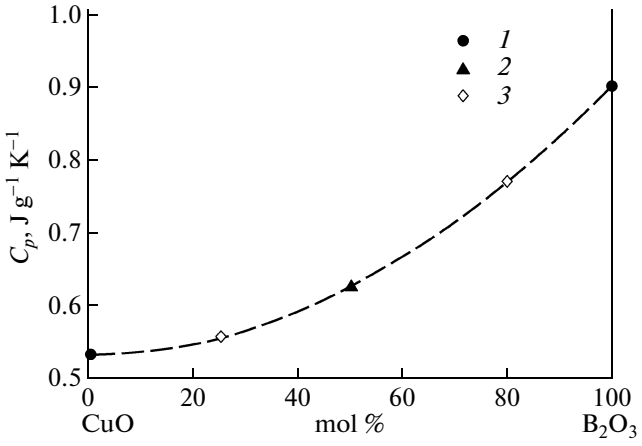

Fig. 2. Dependence of the standard heat capacity on the $CuO–B_2O_4$ system composition: (*1*) data taken from [15], (*2*) this work, and (*3*) estimated data.

can be described as a function of temperature by the following relationship (in units of J mol^{-1} K^{-1}):

$$C_p = a + b \times 10^{-3} T - c \times 10^5 T^{-2} = 103.97 + 79.80 \times 10^{-3} T - 30.64 \times 10^5 T^{-2}. \quad (1)$$

Smoothed-out values of the molar heat capacity and thermodynamic functions of CuB_2O_4

T, K	C_p, J mol^{-1} K^{-1}	$H_T^0 - H_{298}^0$, kJ mol^{-1}	$S_T^0 - S_{298}^0$, J mol^{-1} K^{-1}
298	93.25		
300	93.87	0.424	0.626
340	104.60	6.706	13.06
380	113.07	12.96	25.17
420	120.12	19.17	36.85
460	126.20	25.36	48.05
500	131.61	31.59	58.81
540	136.55	37.86	69.12
580	141.15	44.20	79.04
620	145.48	50.61	88.60
660	149.60	57.11	97.82
700	153.58	63.71	106.7
740	157.43	70.40	115.3
780	161.18	77.20	123.8
820	164.85	84.10	131.9
860	168.46	91.12	139.9
900	172.01	98.24	147.6
940	175.51	105.5	155.1
980	178.98	112.8	162.5
1020	182.42	120.3	169.8
1050	184.98	126.0	175.1

Based on relationship (1), we calculated the thermodynamic functions (changes in the enthalpy $H_T^0 - H_{298}^0$ and entropy $S_T^0 - S_{298}^0$). Here, we used the known equations relating the heat capacity C_p to the enthalpy and entropy functions

$$H_T - H_0 = \int C_p(T) dT, \quad (2)$$

$$S_T - S_0 = \int \frac{C_p(T)}{T} dT. \quad (3)$$

The results are given in the table.

It can be noted that, at temperatures above 930 K, the heat capacity C_p exceeds the classical Dulong–Petit limit $3Rs$, where R is the universal gas constant, and s is the number of atoms in the CuB_2O_4 formula unit ($s = 7$).

Earlier, the correlation was found between the compositions and standard heat capacities of the oxides $GeO_2–PbO$ [11], $Bi_2O_3–B_2O_3$ [12], $Bi_2O_3–GeO_3$ and $Bi_2O_3–SiO_2$ [13], and $Bi_2O_3–Fe_2O_3$ [14] that form in the lead- and bismuth-based oxide systems. We can assume that similar correlation takes place for the $CuO–B_2O_3$ system as well (Fig. 2). It allows, despite small number of the experimental points, the estimation of unknown data on the heat capacity of other oxide compounds of the $CuO–B_2O_3$ system with a smaller error than the error given by the Neumann–Copp additive method [16]. For example, the latter method gives for CuB_2O_4 $C_p = 0.717$ J mol^{-1} K^{-1}, whereas the experiment gives 0.626 J mol^{-1} K^{-1}.

From Fig. 2, it follows that the estimated values of C_p for $Cu_3B_2O_6$ and CuB_8O_{13} are 0.56 and 0.77 J mol^{-1} K^{-1}, respectively.

We could not compare the obtained values of C_p for CuB_2O_4 with other data, since there are no such data in the literature (as noted above, there are only the data obtained at very low temperatures [3]). At the same time, the normalized molar heat capacity of CuB_2O_4 calculated using relationship $C_p^* = C_p^0/s$ is 13.32 J mol^{-1} K^{-1} that is markedly lower than that for other oxide compounds (J mol^{-1} K^{-1}): 17.6 ($Li_2Ge_7O_{15}$), 17.9 ($NaLiGe_4O_9$), 21.0 ($Pb_5(Ge_{1-x}Si_x)_3O_{11}$) [17]; 24.70 ($Pb_3GeO_5$), 21.33 ($Pb_5Ge_3O_{11}$), 21.29 ($PbGeO_3$), and 18.80 ($PbGe_3O_7$) [11]. It is not inconceivable that the result is related to the atomic mass effect [17].

4. CONCLUSIONS

The temperature dependence of the heat capacity (298–1050 K) of oxide CuB_2O_4 compound has been studied. It is shown that there is a correlation between the oxide compositions in the $CuO–B_2O_3$ system and their heat capacities.

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Translated by Yu. Ryzhkov