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Heat capacities and thermodynamic functions of $BaCuO_2$ in the temperature range 8–305 K

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Abstract

The heat capacity of two samples of $BaCuO_2$ was measured in a vacuum adiabatic calorimeter in the temperature range 8–305 K. The thermodynamic functions of barium cuprate (entropy, enthalpy, Gibbs free energy) were calculated on the basis of C_p–T dependences. Both samples exhibited an anomalous rise in C_p at low temperatures (below 12 K). Our data are compared with previously measured data.

Keywords: Calorimetry; Heat capacity; Ternary system

1. Introduction

The aim of this research was to measure the low temperature heat capacities of $BaCuO_2$ and to calculate the barium cuprate thermodynamic functions in the temperature range 8–305 K.

Interest in $BaCuO_2$ is associated with high temperature superconductors. Barium cuprate is one of the most important related phases in Ln–Ba–Cu–O systems (Ln is lanthanoid). For example, as reported in our earlier papers [1,2], the mixtures $(0.5Y_2O_3 + 2BaCuO_2 + CuO, 0.5Y_2BaCuO_5 + 1.5BaCuO_2 + CuO)$, including $BaCuO_2$, are more thermodynamically stable than the $YBa_2Cu_3O_x$ superconductor at room and lower temperatures.

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A good knowledge of the thermodynamic properties of superconducting and related phases over a wide temperature range is necessary to understand and to optimize the synthesis of high-T_c oxide superconductors. A great number of studies have been performed on the thermodynamics of the Y–Ba–Cu–O system. However, we are not aware of heat capacity measurements of $BaCuO_2$ in the range 8–305 K. The authors of Refs. [3,4] have measured the low temperature heat capacities of barium cuprate only from 1.3 to 20 K. These papers are of great significance in creating a theory for new high-T_c superconductors and they are focused on understanding the anomalous low temperature behaviour of the heat capacities of $YBa_2Cu_3O_x$, $BaCuO_2$ and other phases. The purpose of our research is different. This investigation is part of our complex investigations of the Y–Ba–Cu–O system thermodynamics [1,2] and is aimed at obtaining heat capacities, absolute entropies, and other thermodynamic functions of $BaCuO_2$ in the temperature range 8–305 K. We need these values to simulate further the phase equilibria of high-T_c superconductors at high temperatures.

2. Sample preparation

Two samples of $BaCuO_2$, prepared by different methods, were employed in the calorimetric experiments.

Sample 1 was synthesized from stoichiometric amounts of $BaCO_3$ (high purity) and CuO (high purity). The components were thoroughly mixed and ground in ethanol (C_2H_5OH), using a "Pulverizette" mill. After the ethanol had been evaporated, the reactants were heated at 1113 K in air for 24 h. Then the sample was cooled, ground repeatedly, pressed, and heated again at 1173 K in air for 120 h.

Sample 2 was prepared from $BaCO_3$ (high purity) and CuO (high purity) powders in the appropriate stoichiometry. The thoroughly mixed and ground reagents were rapidly fused in an arc furnace. Then the sample was held at 1183 K in air for 6 h and cooled in O_2 flow.

Both samples were characterized by X-ray powder diffraction analysis, chemical analysis, and IR spectroscopy. The content of all the metallic components was determined by atomic absorption [5]. The results of the chemical analysis for sample 1 were: Ba, 57.8%; Cu, 26.4%. For sample 2: Ba, 58.1%; Cu, 26.5%. Sample 1 with an oxygen content of 2.09 ($BaCuO_{2.09}$) and sample 2 with an oxygen content of 2.00 ($BaCuO_{2.00}$) were investigated in this study. The oxygen content was determined by iodide titration [5]. The accuracy of the determination was 0.01. According to the results of the analyses, the two prepared samples of $BaCuO_2$ were found to be single phases with an accuracy of about 1.5%. IR spectroscopy showed that $BaCO_3$ and CuO were the main impurities.

3. Experimental technique and results

The heat capacity of $BaCuO_2$ was measured in a vacuum adiabatic calorimeter, operated in periodic heat input mode. This is considered to be one of the most accurate calorimetric methods [6]. The calorimeter used here and the procedure of measurements have been described in detail elsewhere [7–9].

The calorimetric vessel (about 10 ml) containing the sample was made of nickel, a material with a high resistance to corrosion. The sample under study was loaded into the calorimetric vessel; then the vessel was hermetically sealed and hung on thin kapron wires into the space between two adiabatic shields. The calorimeter was operated under vacuum (10^{-4} atm).

The temperature of the calorimetric vessel was measured by a platinum resistance thermometer ($R_0 = 100.2608\,\Omega$). From 13.81 to 305 K, the temperatures were calculated using a standard function [10]. The equation $R(T) = A + BT^2 + CT^5$ [11] was used to calculate temperatures below 13.81 K. The sensitivity of the thermometer circuit was $2\text{–}5 \times 10^{-5}$ K. Two heat shields were used in the adiabatic calorimeter. As shown in Ref. [12], two heat shields are enough to achieve high precision adiabatic conditions. The accuracy of the temperature control of the heat shields was 10^{-3} K. It was attained by using a high precision isodromic temperature regulator [12]. The calorimeter heater made of (Cu + Zn) alloy had a resistance of 300 Ω. The power of the heater was measured with a multimeter (DATRON 7061).

The heat capacity of the empty nickel vessel (C_e) was measured from 8 to 305 K over 99 experimental points. The data $C_e = f(T)$ calculated on the basis of these experimental values were used to obtain the heat capacity of the investigated samples. The average deviation of the experimental heat capacities values from the smoothed C_p curve for an empty vessel was 0.35% in the range 8–20 K and 0.03% in the range 20–305 K.

The accuracy of this calorimeter was tested by measuring the heat capacity of 6.0381 g of benzoic acid (C_6H_5OOH), recommended by the Calorimetry Conference (NBS-49) as a standard substance [13]. These measurements performed over 32 experimental points from 8 to 305 K agree with literature data [14] to within 1% in the temperature range 8–30 K and within less than 0.2% in the temperature range 30–305 K.

To measure the heat capacity of $BaCuO_2$, sample 1 (weight, 9.45 g) or sample 2 (weight, 11.81 g) was loaded into the nickel calorimetric vessel. It was necessary to crush the samples to a coarse powder to load into the calorimeter.

80 experimental values of C_p were obtained for sample 1, and 65 experimental values of C_p were measured for sample 2. The experimental values of $BaCuO_2$ heat capacities obtained were treated using a computer program described elsewhere [7–9]. Smoothed values of heat capacities, entropies, enthalpies and Gibbs free energies at different temperatures, calculated on the basis of experimental data, are given in Table 1 for sample 1 and in Table 2 for sample 2.

The average deviation of the experimental heat capacity values from the smoothed C_p curve for sample 1 was 0.5% in the temperature range 8–20 K, 0.11% in the temperature range 20–70 K, and 0.05% in the temperature range 70–305 K. The same data for sample 2 were 1.52% in the range 7–20 K, 0.22% in the range 20–50 K, and 0.06% in the range 50–301 K. They are relative uncertainties.

The thermodynamic functions (heat capacities, absolute entropies, enthalpies, free Gibbs energies) calculated under standard conditions are:

Table 1
Smoothed values of the thermodynamic functions of $BaCuO_{2.09}$

T/K	$C_p(T)/\mathrm{J\,K^{-1}\,mol^{-1}}$	$S(T)/\mathrm{J\,K^{-1}\,mol^{-1}}$	$H(T)-H(\mathrm{O})/\mathrm{J\,mol^{-1}}$	$\Phi(T)/\mathrm{J\,K^{-1}\,mol^{-1}}$
8.0	1.019	1.950	6.283	1.164
9.0	0.972	2.066	7.274	1.258
10.0	1.030	2.170	8.260	1.334
15.0	2.023	2.731	15.34	1.708
20.0	3.975	3.556	29.97	2.06
25.0	6.701	4.727	56.40	2.471
30.0	9.887	6.226	97.74	2.968
35.0	13.31	8.005	155.7	3.557
40.0	16.81	10.01	230.9	4.236
45.0	20.27	12.19	323.7	4.998
50.0	23.66	14.5	433.5	5.832
60.0	30.14	19.40	703.0	7.681
70.0	35.97	24.49	1034.0	9.717
80.0	41.24	29.64	1421.0	11.89
90.0	46.05	34.78	1857.0	14.14
100.0	50.55	39.87	2341.0	16.46
110.0	54.65	44.88	2867.0	18.82
120.0	58.33	49.80	3432.0	21.20
130.0	61.83	54.61	4033.0	23.58
140.0	65.07	59.31	4668.0	25.97
150.0	68.10	63.90	5334.0	28.34
160.0	71.04	68.39	6030.0	30.71
170.0	73.91	72.79	6755.0	33.05
180.0	76.49	77.09	7507.0	35.38
190.0	78.84	81.29	8284.0	37.69
200.0	80.99	85.38	9083.0	39.97
210.0	83.19	89.39	9904.0	42.23
220.0	85.19	93.31	10746.0	44.46
230.0	87.03	97.13	11607.0	46.67
240.0	88.74	100.9	12486.0	48.85
250.0	90.31	104.5	13381.0	51.00
260.0	91.79	108.1	14292.0	53.13
270.0	93.15	111.6	15217.0	55.23
273.15	93.57	112.7	15511.0	55.89
280.0	94.44	115.0	16155.0	57.31
290.0	95.70	118.3	17105.0	59.35
298.15	96.89	121.0	17890.0	61.17
300.0	97.18	121.6	18069.0	61.37

Sample 1

C_p (298.15 K) = 96.89 ± 0.05 J K^{-1} mol^{-1}
S^0 (298.15 K) = 121.0 ± 0.5 J K^{-1} mol^{-1}
Φ^0 (298.15 K) = 61.17 ± 0.60 J K^{-1} mol^{-1}
H^0 (298.15 K) − H^0 (0 K) = 17 890 ± 30 J mol^{-1}

Table 2
Smoothed values of the thermodynamic functions of BaCuO$_{2.00}$

T/ K	$C_p(T)$/J K^{-1} mol^{-1}	$S(T)$/J K^{-1} mol^{-1}	$H(T)-H(\mathrm{O})$/ J mol^{-1}	$\Phi(T)$/ J K^{-1} mol^{-1}
8	1.040	2.218	6.503	1.406
10	1.057	2.448	8.564	1.592
15	1.958	3.008	15.62	1.967
20	3.863	3.812	29.82	2.321
25	6.490	4.945	55.46	2.727
30	9.553	6.395	95.45	3.213
35	12.85	8.112	151.4	3.788
40	16.24	10.05	224.1	4.447
45	19.61	12.16	313.7	5.186
50	22.89	14.39	420.0	5.994
60	29.04	19.12	680.1	7.784
70	34.61	24.02	998.8	9.752
80	39.69	29.98	1371	11.85
90	44.34	33.93	1791	14.02
100	48.65	38.82	2256	16.26
110	52.65	43.65	2763	18.53
120	56.37	48.39	3309	20.82
130	59.85	53.04	3890	23.12
140	63.09	57.60	4505	25.42
150	66.14	62.06	5151	27.72
160	69.02	66.42	5827	30.00
170	71.75	70.69	6531	32.27
180	74.33	74.86	7261	34.52
190	76.76	78.95	8017	36.75
200	79.02	82.94	8796	38.96
210	81.09	86.85	9597	41.15
220	82.99	90.66	10417	43.31
230	84.72	94.39	11256	45.45
240	86.33	98.03	12111	47.57
250	87.86	101.6	12982	49.66
260	89.34	105.1	13868	51.72
270	90.77	108.5	14769	53.76
273.15	91.20	109.5	15055	54.40
280	92.12	111.8	15683	55.77
290	93.34	115.0	16611	57.76
298.15	94.27	117.6	17375	59.36
300	94.48	118.2	17550	59.72

Sample 2

C_p (298.15 K) = 94.27 ± 0.14 J K^{-1} mol^{-1}
S^0 (298.15 K) = 117.6 ± 0.64 J K^{-1} mol^{-1}
Φ^0 (298.15 K) = 59.36 ± 0.74 J K^{-1} mol^{-1}
H^0 (298.15 K) − H^0 (0 K) = 17 375 ± 30 J mol^{-1}

To calculate the thermodynamic functions (C_p, S, H, Φ) listed above, it was necessary to extrapolate the C_p–T dependence to 0 K. This procedure was done according to

Refs. [7–9]. Reported uncertainties for C_p, S, H, Φ were estimated by taking into account the average scatter of the experimental values of the heat capacities only. They are relative uncertainties.

The experimental data of the heat capacities of $BaCuO_2$ from 8 to 20 K are given in Table 3 for sample 1 and in Table 4 for sample 2. These data show that both samples have an anomalous rise in C_p–T dependence at low temperatures (below 12 K). This result agrees with data from Refs. [3,4], where a similar anomalous behaviour of $BaCuO_2$ heat capacities was reported. Our data are in good agreement with the data of Ref. [3] at 10 K, but they are systematically higher than data from Ref. [3] with decreasing temperature. The difference reaches 19% at 8 K. Such a difference can be the result of different accuracies of calorimetric methods and sample compositions. It is impossible to analyse the reasons for the difference in detail because there is not enough information about method accuracy and sample composition (chemical analysis and oxygen content) in Ref. [3].

The heat capacity of four $BaCuO_2$ samples was measured in Ref. [4]. Above $T^2 = 200\ K^2$, the heat capacity does not show much sample dependence. Below this temperature range, the heat capacity is much more sample-dependent [4]. Our data fall between the data obtained for samples d and e in Ref. [4]. The authors state that these samples are the purest. It should be mentioned that the difference between the heat capacities of the four samples of $BaCuO_2$ reaches 30% at temperatures below 10 K. The authors suggest that this results from the different heat treatment of the samples. To analyse differences in $BaCuO_2$ heat capacities obtained in the present research and in Refs. [3,4], it is necessary to have information about the chemical analyses and oxygen contents of all the samples and the accuracy of method. Unfortunately, there is not enough information on the chemical characteristics of the samples described in Refs. [3,4]. So we can only assume that the above-mentioned difference derives from sample compositions and the accuracy of the methods.

As mentioned, the authors of Ref. [4] made heat capacity measurements from 1.3 to 20 K for four samples of $BaCuO_2$ to arrive at a better understanding of the anomalous low temperature behaviour of C_p. All four samples displayed the rise in C/T–T^2 dependence at low temperature. The nature of this anomaly is analysed in Ref. [4].

Table 3
Experimental values of the heat capacities of $BaCuO_{2.09}$

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
7.88	1.046	11.89	1.249
8.11	1.018	12.55	1.366
8.33	1.001	13.28	1.530
8.61	0.971	14.06	1.757
9.00	0.964	14.86	1.988
9.46	0.982	15.93	2.318
9.99	1.016	17.26	2.790
10.57	1.062	18.69	3.379
11.20	1.139	20.51	4.227

Table 4
Experimental values of the heat capacities of $BaCuO_{2.00}$

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
7.19	1.095	12.01	1.278
8.90	0.9757	12.21	1.288
8.91	1.057	12.93	1.410
9.31	1.042	14.62	1.854
9.88	1.082	16.20	2.353
10.40	1.075	16.78	2.544
11.21	1.170	20.16	3.956

The authors report that, although the rise in the C/T–T^2 curve is Shottky-like, it is impossible to obtain a good fit with a single Shottky contribution.

We have measured the heat capacity of $BaCuO_2$ from 8 to 305 K only. To discuss the nature of this anomaly, it is necessary to know the heat capacities at lower temperatures. So we are unable to address this problem in detail.

4. Conclusion

In this study, the thermodynamic functions of two samples of barium cuprate identified as $BaCuO_{2.09}$ and $BaCuO_{2.0}$ were calculated on the basis of the measured C_p–T dependences in the temperature range 7–305 K. To our knowledge, this is the first determination of the heat capacity of $BaCuO_2$ in this temperature range. The obtained values of absolute entropies, $S^0(298.15\ K) = 121.0 \pm 0.5$ J K^{-1} mol^{-1} for $BaCuO_{2.09}$ and $S^0(298.15\ K) = 117.6 \pm 0.64$ J K^{-1} mol^{-1} for $BaCuO_{2.0}$, are in good agreement with the S value estimated as a sum of the entropies of BaO and CuO: $S^0(298.15\ K) = 114$ J K^{-1} mol^{-1}. This confirms the well-known empirical rule that the entropy of complex oxides is the sum of the entropies of the simple oxides. For the formation enthalpy of $BaCuO_2$ from the oxides, the above rule is not obeyed. The enthalpy of the reaction $BaO + CuO = BaCuO_2$ was found to be -66 kJ mol^{-1} [5]. As can be seen, this value is quite different from zero.

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