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Investigation of thermodynamic properties of Co_2O_3 powder

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Abstract

The isobaric molar heat capacities of powder of Co_2O_3 were determined by an adiabatic calorimeter in the temperature range from 78 to 350 K. No phase transition takes place in this temperature range. The relationship of $C_{p,m}$ with thermodynamic temperature T was established as $C_{p,m} = -5 \times 10^{-6}T^3 + 0.0026T^2 + 0.0325T + 4.2592$ ($J\,K^{-1}\,mol^{-1}$), fitting coefficient $R^2 = 0.9996$. According to this relationship and the relationships between thermodynamic functions, the thermodynamic functions of powder of Co_2O_3 were derived with 298.15 K as reference temperature. Thermal decomposition of Co_2O_3 powder was studied through thermogravimetry (TG). The possible mechanism of the thermal decomposition reaction was suggested according to the TG result.

Keywords: Heat capacity; Powder of Co_2O_3; Thermodynamic function; Adiabatic calorimeter; TG analysis

1. Introduction

Co_2O_3 as additive has been applied in many fields of material science. Co_2O_3 may affect ceramic and electric characteristics of ZnO varistor [1], improve temperature-stable $BaTiO_3$-based dielectrics [2], and produce ethylene selectively in oxidative coupling of methane as one component of catalyst [3]. Co_2O_3 powder has been used as one of compositions of working fluid in heat pipe [4,5]. Co_2O_3 ultrafine particle solution has been prepared and characterized in literature [6]. The thermodynamic data of CoO and Co_3O_4 have been reported in some handbooks [7,8]. But the thermodynamic properties of Co_2O_3 have not been studied till now because of the difficult preparation of the sample [9].

The aim of the present investigation is to gain the thermodynamic data of powder of Co_2O_3 by measurements of the low temperature heat capacities and study of the thermal decomposition of the sample.

2. Experimental

2.1. Experimental materials

The powder of Co_2O_3 used for calorimetric study was purchased from Shanghai Chemical Agent Factory, and was of spectrum grade. The average grain size of the studied Co_2O_3 sample was determined to be 12 nm.

2.2. Adiabatic calorimeter

Heat-capacity measurements were carried out in a high-precision automatic adiabatic calorimeter de-

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scribed in detail elsewhere [10]. The principle of the calorimeter is based on the Nernst stepwise heating method. The calorimeter mainly consists of a sample cell, an adiabatic (or inner) shield, a guard (outer) shield, a platinum resistance thermometer, an electric heater, two sets of chromel–copel thermocouples, and a high vacuum can. The sample cell was made of gold-plated copper and had an inner volume of 6 cm^3. Four gold-plated copper vanes of 0.2 mm thickness were put into the cell to promote heat distribution between the sample and the cell. The platinum resistance thermometer was inserted into the copper sheath which was soldered at the bottom of the sample cell. The heater wire was wound on the surface of the cell. The lid of the cell with a copper capillary was sealed to the sample cell with cycleweld after the sample was loaded in it. The air in the cell was pumped out and a small amount of helium gas (0.1 MPa) was introduced into it to enhance the heat transfer in the cell. The capillary was pinched off and the resultant fracture was soldered with a little amount of solder to ensure the cell sealing. The evacuated can was kept within ca. 1×10^{-3} Pa during the heat-capacity measurements so as to eliminate the heat loss due to gas convection. Liquid nitrogen was used as the cooling medium. One set of chromel–copel thermocouples was used to detect the temperature difference between the sample cell and the inner shield. Likewise, the other set of thermocouples were installed between the inner and outer shields. The temperature difference between them was kept to be 0.5 mK during the whole experimental process. The sample cell was heated by the standard discrete heating method. The temperature of the cell was alternatively measured. The temperature increment in a heating period was 2–4 K, and temperature drift was maintained at about 10^{-3} K min^{-1} in equilibrium period. All the data were automatically picked up through a Data Acquisition/Switch Unit (Model: 34970A, Aglient, USA) and processed by a computer.

Prior to the heat-capacity measurements of the sample, the reliability of the calorimetric apparatus was verified by heat-capacity measurements of the reference standard material α-alumina. The deviations of our calibration results from the recommended values reported by Ditmars et al. of the National Bureau of Standards [11] are within ±0.1% in the temperature range of 80–400 K.

The mass of powder of Co_2O_3 used for heat-capacity measurements was 2.4287 g.

2.3. TG/DTG analysis

The thermogravimetry (TG) measurements of the sample were carried out by a thermogravimetric analysis system (Model: DT-20B, Shimadzu, Japan) under static air. The amounts of the sample used for TG analysis was 29.3 mg, and the heating rate was 10 °C min^{-1}.

3. Result and discussion

3.1. Isobaric molar heat capacity of powder of Co_2O_3

The isobaric molar heat capacities of powder of Co_2O_3 were determined using the adiabatic calorimeter in the temperature range from 78 to 350 K. The results of the isobaric molar heat capacities of powder of Co_2O_3 are shown in Table 1 and Fig. 1. From Fig. 1 it can be seen that no thermal anomaly was observed or no phase transition took place in the temperature range from 78 to 350 K.

The values of isobaric molar heat capacities were fitted in the following polynomial expressions with the least square method.

$$C_{p,m} = -5 \times 10^{-6}T^3 + 0.0026T^2 + 0.0325T + 4.2592\ (\mathrm{J\,K^{-1}\,mol^{-1}}) \qquad (1)$$

where $C_{p,m}$ is the molar heat capacity of the sample, T (K) the thermodynamic temperature, R^2 the fitting coefficient (0.9996).

3.2. Thermodynamic data of powder of Co_2O_3

According to the relationship of thermodynamic functions and the function of the isobaric molar heat capacity with respect to temperature [12], the thermodynamic data of powder of Co_2O_3 were obtained and listed in Table 2.

3.3. The results of TG/DTG analysis of powder of Co_2O_3

The TG/DTG curves of the sample are shown in Fig. 2. It can be seen from TG/DTG curves that the

Table 1
The experimental isobaric molar heat capacities of Co_2O_3 powder in the temperature range of 78–350 K

T (K)	$C_{p,m}$ (J K^{-1} mol^{-1})
78.194	18.373
80.368	20.268
82.345	21.228
84.260	21.899
86.122	23.296
87.949	23.886
89.993	24.903
92.256	25.832
94.474	26.375
96.635	27.841
99.347	28.267
102.570	29.561
105.710	30.840
108.770	32.140
111.763	33.278
114.687	34.895
117.557	36.000
120.380	36.995
123.159	37.992
125.889	39.274
128.579	40.523
131.228	41.855
133.843	42.850
136.421	44.037
138.966	45.183
141.478	46.390
144.049	48.144
147.302	49.617
150.500	51.203
152.659	52.037
155.913	52.879
157.383	53.739
160.399	55.119
163.034	55.992
165.699	57.280
168.337	58.679
170.952	60.300
173.556	61.316
176.185	62.220
178.809	63.483
181.409	64.942
183.989	66.051
186.543	67.586
189.080	68.850
191.592	70.002
194.087	71.105
196.560	72.300
199.016	73.527
201.450	74.901
203.866	76.272
206.266	77.596
208.746	78.842
211.328	80.552
213.876	81.976
216.412	83.191
218.915	84.489
221.161	85.812
223.265	86.970
226.364	88.314
228.813	89.202
231.268	90.499
233.704	91.387
236.113	92.207
238.488	93.573
240.890	93.983
243.387	95.300
245.929	96.210
249.097	97.071
251.967	97.912
253.473	98.625
255.940	99.036
258.359	100.400
260.760	101.600
263.147	102.500
265.513	103.477
267.857	103.886
270.161	104.774
272.443	105.184
274.724	106.000
276.980	106.892
279.221	107.793
281.451	109.037
283.665	109.077
285.845	110.785
287.996	111.700
290.123	112.000
292.232	112.697
294.322	113.380
296.400	113.858
298.445	114.700
300.466	115.753
302.460	116.200
304.401	116.590
306.479	116.727
308.878	117.137
311.289	117.700
313.722	118.017
316.169	118.325
318.599	118.981
321.022	119.254
323.438	119.664
326.048	120.421
328.907	120.880
331.242	121.227
333.981	121.604
337.058	121.986
340.104	122.320
343.096	122.606
346.134	122.852
349.392	123.064

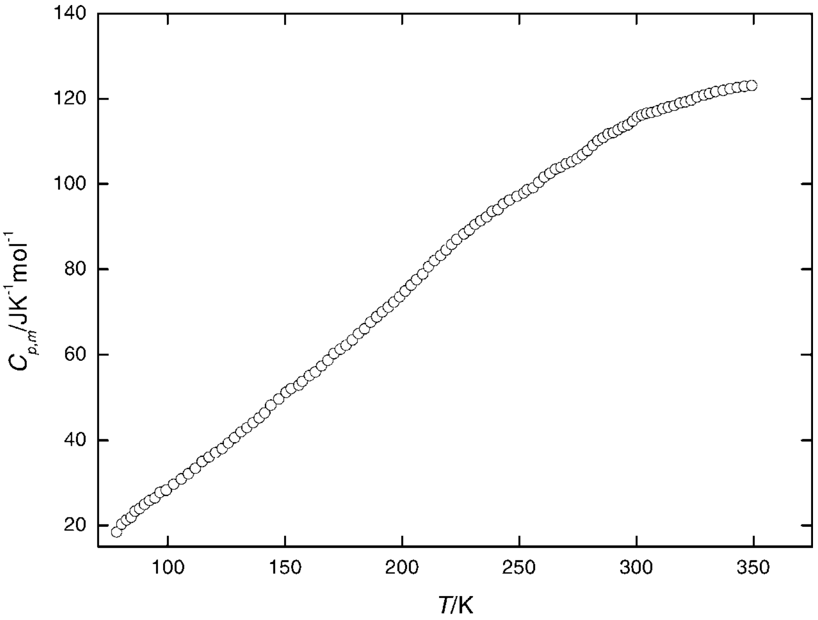

Fig. 1. Experimental isobaric molar heat capacity of Co_2O_3 powder.

Table 2
Thermodynamic functions of Co_2O_3 powder

T (K)	C_p (J K^{-1} mol^{-1})	$[H_T - H_{298.15\,K}]$ (kJ mol^{-1})	$[S_T - S_{298.15\,K}]$ (J K^{-1} mol^{-1})	$-[G_T - G_{298.15\,K}]$ (kJ mol^{-1})
80	21.026	−16.018	−81.362	9.509
90	24.601	−15.784	−78.612	8.709
100	28.438	−15.511	−75.742	7.937
110	32.507	−15.196	−72.748	7.194
120	36.779	−14.838	−69.632	6.482
130	41.224	−14.433	−66.395	5.802
140	45.813	−13.980	−63.041	5.155
150	50.516	−13.478	−59.575	4.541
160	55.303	−12.924	−56.004	3.963
170	60.146	−12.318	−52.333	3.422
180	65.014	−11.660	−48.571	2.917
190	69.879	−10.948	−44.724	2.451
200	74.710	−10.183	−40.801	2.023
210	79.478	−9.365	−36.810	1.635
220	84.154	−8.494	−32.758	1.287
230	88.708	−7.570	−28.655	0.980
240	93.110	−6.596	−24.508	0.714
250	97.332	−5.572	−20.328	0.490
260	101.343	−4.499	−16.121	0.307
270	105.113	−3.380	−11.899	0.167
280	108.615	−2.217	−7.668	0.070
290	111.817	−1.011	−3.439	0.014
300	114.691	0.233	0.779	0.001
310	117.207	1.514	4.978	0.030
320	119.335	2.827	9.148	0.100
330	121.045	4.170	13.280	0.212
340	122.310	5.538	17.364	0.366
350	123.098	6.928	21.392	0.559
298.15	114.200	0.000	0.000	0.000

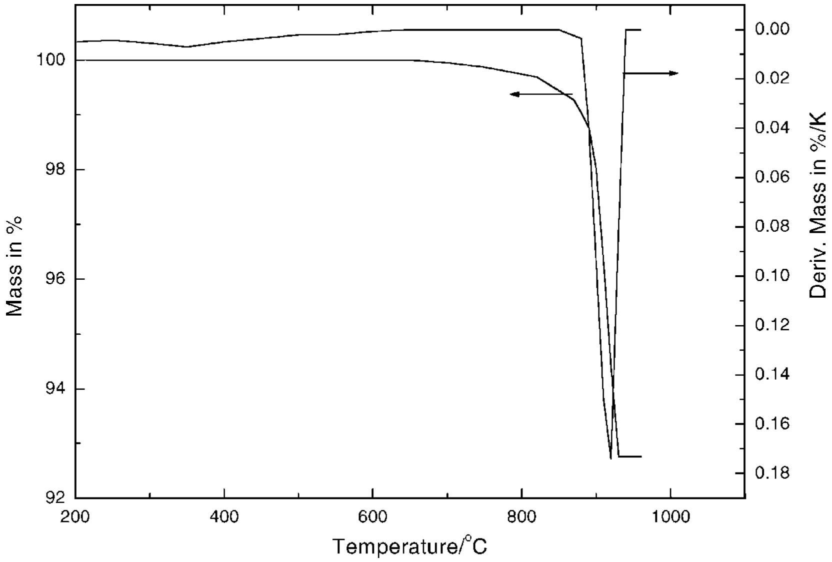

Fig. 2. TG and DTG curves of Co_2O_3 powder.

sample is very stable below 890 °C and started decomposition at this point, and the most mass-loss occurred in the temperature range of 890–930 °C. The actual mass% loss is 7.24%. We consider that the residue should be mixture of 5/4 mol CoO and 1/4 mol Co_3O_4 per mol Co_2O_3, because the corresponding mass% loss is 7.23% which is in excellent agreement with 7.24%. Possible mechanism of the thermal decomposition may be deduced as follows, according to the mass-loss:

$$Co_2O_3 \xrightarrow[7.24\%\,(7.23\%)]{890\text{–}930^{\circ}C} \tfrac{5}{4}CoO + \tfrac{1}{4}Co_3O_4 + \tfrac{3}{8}O_2 \tag{2}$$

The mass% loss in the bracket is the calculated theoretical value.

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