ELSEVIER

Thermochimica Acta 352–353 (2000) 247–253

thermochimica acta

www.elsevier.com/locate/tca

An adiabatic calorimeter for heat capacity measurements of small samples

The heat capacity of nonlinear optical materials $KTiOPO_4$ and $RbTiOAsO_4$ crystals

Zhi-Cheng Tan[a,*], Guang-Yu Sun[a], Yong-Ji Song[a], Lan Wang[a],
Jian-Ru Han[b], Yu-Sheng Liu[b], Min Wang[b], De-Zhen Nie[b]

[a] *Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*
[b] *State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China*

Received 2 June 1999; received in revised form 20 August 1999; accepted 4 September 1999

Abstract

A small sample size automated adiabatic calorimeter for measuring heat capacities in the temperature range of 60–360 K has been constructed. The sample cell of the calorimeter was made of thin-walled gold-plated copper with an internal volume of 6 cm^3, equipped with a miniature platinum thermometer, surrounded by two adiabatic shields and housed in a high vacuum can. Two sets of six-junction chromel–constantan thermocouples were mounted between the cell and shields to indicate the temperature difference between them. The lid of the cell was sealed to the main body with a special sealant cycleweld. The adiabatic conditions of the calorimeter cell were automatically controlled by two units of temperature controller. A mechanical pump was used to pump out the vapor of liquid nitrogen in the cryostat to obtain 60 K or even lower temperature. All the experimental data, including the electrical energy and temperature were collected and processed automatically by a personal computer with a predetermined program. The performance of the calorimeter was examined by measuring the heat capacities of α-Al_2O_3. The deviations of experimental results from the smoothed curve lie within ±0.2%, while the inaccuracy is within ±0.5% compared with the recommended reference data.

The heat capacities of two important nonlinear optical crystals $KTiOPO_4$ and $RbTiOAsO_4$ have been measured by using this calorimeter in the range of 60–360 K. No thermal anomaly was observed from the heat capacity measurements for the two materials in the above-mentioned range.

Keywords: Adiabatic calorimetry; Heat capacity; Nonlinear optical material; $KTiOPO_4$; $RbTiOAsO_4$

1. Introduction

In accordance with the recent rapid progress in the field of materials sciences, needs for studies on the thermodynamic properties of a considerable variety of materials have become more and more urgent. The heat capacity is not only a fundamental thermodynamic property but also the characteristic quantity closely related to energetics and structure of materials. From heat capacity data many other thermodynamic properties such as enthalpy and Gibbs free energy,

---

[*] Corresponding author. Fax: +86-411-4691570.
E-mail address: tzc@ms.dicp.ac.cn (Z.-C. Tan)

PII: S0040-6031(99)00473-6

which are of importance to both theoretical and practical purposes, can be calculated. As it is well known, adiabatic calorimetry at low temperature is a classical method for heat capacity measurement. High accuracy of heat capacity measurement results from precise adiabatic control and rather large quantity of the sample used. In the adiabatic calorimeter of traditional type [1–6], the sample vessel has the large internal volume of 30–100 cm^3 to contain a large amount of specimen so as to reduce the effect of undetectable heat leak on experimental results to a negligible level. The requirement of large amount of sample has made the traditional calorimeter unfit for investigation of new substances which are difficult to provide in a large enough quantity but worth studying. Nowadays, the progress in adiabatic calorimetry [7–10] enables the reduction of the sample amount required and acquirement of a high accuracy. In the present work, we have constructed a computerized adiabatic calorimeter with a sample vessel of 6 cm^3 for the temperature range of 60–360 K. With this calorimeter the heat capacities of two important nonlinear optical materials $KTiOPO_4$ (KTP) and $RbTiOAsO_4$ (RTA) have been measured precisely in the above-mentioned temperature region. The thermal behavior of the two materials was discussed.

2. Experimental

2.1. Adiabatic calorimeter

The calorimeter consists of the sample cell, adiabatic shields, differential thermocouples, vacuum can and Dewar vessel as shown Fig. 1. The cross sectional view of the sample cell is shown in Fig. 2. The cylindrical main body was made of 0.3 mm thick gold-plated copper, 20 mm long, 20 mm in diameter. On the top of cell, there is a flange for sticking the sealant. At the bottom of the cell, an Ω-shaped sheath was silver-soldered to hold a miniature platinum resistance thermometer. A heater (varnished Karma wire of 0.12 mm in diameter, 105 Ω) was wound bifilarly on the surface of the cell and covered with aluminum foil. Four L-shaped 0.10 mm thick radial gold-plated copper vanes were placed in the cell to promote the thermal equilibrium. The lid of the cell was made of gold-plated silver. A small amount of cycleweld (epoxy binder, type 504, produced by Shanghai Adhesive Company) was used to seal the lid to the main body of the cell. No leakage was found when the cell was kept in 1×10^{-3} Pa vacuum in the temperature range of 60–360 K. At the center of the lid, there is a length of copper capillary for introducing the helium gas. The miniature platinum resistance thermometer (IPRT No. 3, produced by Shanghai Institute of Industrial Automatic Meters, calibrated in terms of ITS-90 by the Station of Low-temperature Metrology and Measurements, Academia Sinica,

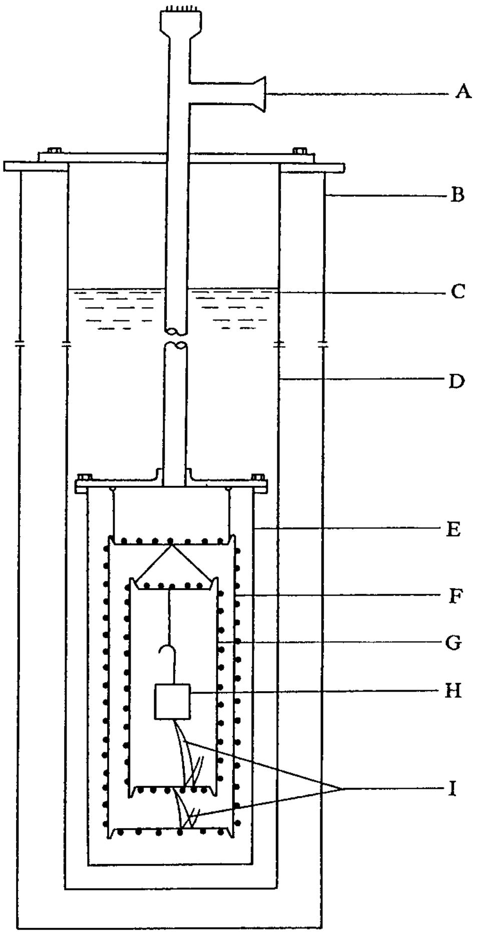

Fig. 1. Cross-sectional view of the adiabatic calorimetric cryostat. A — high vacuum pump; B — steel frame of the Dewar vessel; C — liquid nitrogen; D — Dewar vessel; E — vacuum can; F — outer adiabatic shield; G — inner adiabatic shield; H — sample cell; I — differential thermocouples.

$R_0 = 100\ \Omega$) was placed in the copper sheath at the bottom of the cell to measure the temperature of the sample cell.

The sample cell was surrounded in turn by two adiabatic shields and a vacuum can immersed in liquid nitrogen. The two adiabatic shields were made of chromium-plated copper and equipped with manganin heating wires. Two sets of six-junction chromel–constantan (Ni 55%, Cu 45%) thermocouples were used to measure the temperature differences between the sample cell and the inner adiabatic shield and between the inner and the outer shields. The temperatures of the two shields were controlled separately with two units of auto adiabatic controller (model ACD-79, made by the National Institute of Metrology). The temperature drift rate of the sample cell could be controlled within $5 \times 10^{-6}\ \mathrm{K\ s^{-1}}$ under this shield control condition. The vacuum can was evacuated to about 1×10^{-3} Pa by an oil diffusion pump system during heat capacity measurements. A mechanical pump was used to pump out the nitrogen vapor from the Dewar vessel to solidify the remaining liquid nitrogen, and then 60 K or an even lower temperature was obtained.

The energy introduced into the sample cell was supplied by a d.c. voltage supplier with a stability of 5 ppm. The heating period was controlled by a digital electronic timer with a resolution of 10^{-3} s. The potential drops across the heater and thermometer

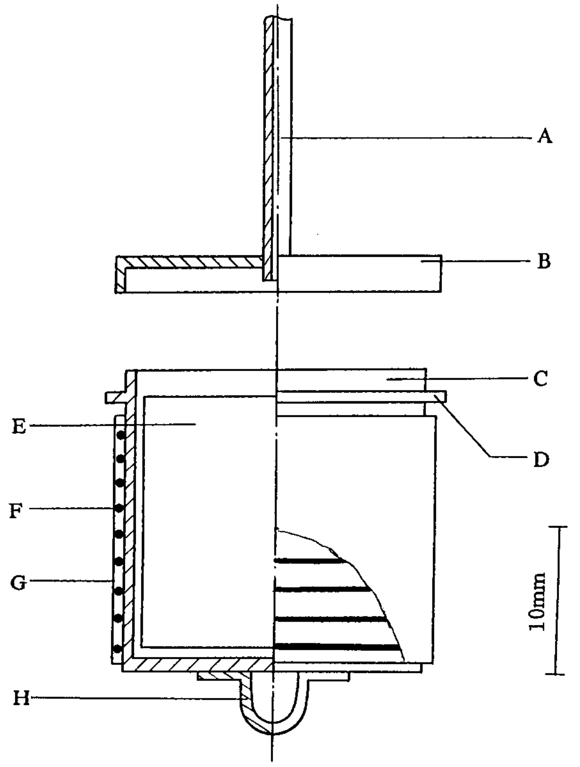

Fig. 2. Cross-sectional view of the calorimeter sample cell. A — copper capillary; B — gold-plated silver lid; C — main body of the sample cell; D — sealing flange; E — gold-plated copper vane; F — Karma heating wire; G — aluminum foil; H — sheath for platinum resistance thermometer.

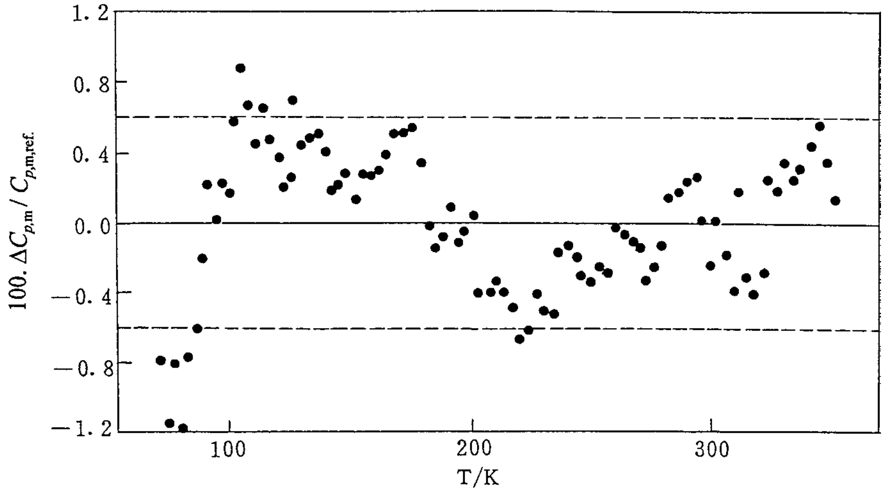

Fig. 3. Plot of deviation 100 × ($\Delta C_{p,\mathrm{m}}/C_{p,\mathrm{m.ref}}$) of the experimental values for the molar heat capacity of α-Al_2O_3, where $C_{p,\mathrm{m.ref}}$ is the molar heat capacity regarded as the reference value given by Ditmars et al. [11] and $\Delta C_{p,\mathrm{m}}$ is the difference between our value and $C_{p,\mathrm{m.ref}}$.

of the sample cell were measured by use of an integration digital multimeter (model 6030, Sabtronics, Switzerland) with a resolution of 0.1 μV. A d.c. constant current source with a stability of 5×10^{-6} (Model JH-821, made by the Beijing Institute of Physics, Academia Sinica) was used for the resistance measurement of the platinum thermometer.

2.2. Procedure

The sample was sealed in the cell and cooled down to the lowest temperature (about 55 K). The heat capacity measurements as a function of temperature were then initiated using the standard discrete heating method. In this intermittent mode, the sequence of heat capacity measurements were composed of two successively alternating periods. One was "the drift period" during which the temperature of the calorimeter cell was observed as a function of time. The other was "the energy input period" during which a definite amount of electrical energy was supplied to the calorimeter cell. The supplied energy was determined on the basis of measurements of voltage and current across and through the heater of the sample cell as well as the interval of energy input. The cycles of measurements for temperature and energy input were repeated in the above sequence until the upper limit of the temperature for the measurements was reached. In our experiments the duration of energy input was 10 min, and the thermal equilibrium inside the sample cell was attained within 3–5 min after the energy input. The temperature increment for each experimental point was about 3 K. All above-mentioned measuring operations including temperature and energy measurements were automatically performed by a personal computer based on a predetermined program.

3. Results and discussion

3.1. Heat capacities of α-Al_2O_3

In order to assess the reliability of the present calorimeter, the heat capacity measurements on the "standard reference material" α-Al_2O_3 were made before the measurements on the nonlinear optical material samples. The mass of the α-Al_2O_3 sample used for the measurements amounted to 8.7353 g which is equivalent to 8.567×10^{-2} mol based on its molar mass of 101.9613 g mol^{-1}. The measured $C_{p,\mathrm{m}}$ values were fitted to a sixth-degree polynomial. The overall precision of the calorimeter was ±0.2%, as evaluated from the deviations of the experimental $C_{p,\mathrm{m}}$ values from the sixth-degree polynomial. Fig. 3 shows the deviations of the measured molar heat capacities of α-Al_2O_3 from the recommended values measured by Ditmars et al. [11]. Except for some points near 100 K, our results agreed with the literature values within ±0.5%, as shown in the plot.

Table 1
Experimental molar heat capacities of KTP crystal ($M = 197.9728$ g mol^{-1})

T (K)	$C_{p,\mathrm{m}}$ (JK^{-1} mol^{-1})
62.247	31.57
65.590	34.17
68.985	36.79
72.411	39.29
75.903	41.47
79.526	44.28
83.199	46.89
86.766	49.43
90.182	51.82
93.469	54.00
96.740	56.37
100.071	58.71
103.446	60.79
106.807	62.72
110.106	64.55
113.371	66.54
116.621	68.44
119.866	70.36
123.110	72.27
126.360	73.83
129.619	75.69
132.855	77.28
136.072	79.11
139.308	80.77
142.565	82.38
145.887	83.75
149.231	85.69
152.606	87.31
156.016	88.94
159.465	90.50
162.951	91.99

Table 1 (*Continued*)

T (K)	$C_{p,\mathrm{m}}$ (JK^{-1} mol^{-1})
166.464	93.59
169.941	95.25
173.460	96.73
176.936	98.21
180.418	99.57
183.909	100.87
187.359	102.13
190.819	103.62
194.294	104.78
197.787	105.81
201.292	107.27
204.810	108.34
208.340	109.72
211.887	110.98
215.453	112.29
218.990	113.45
222.491	114.95
226.180	116.40
229.720	117.34
233.286	118.43
236.875	119.57
240.436	120.92
243.970	122.12
247.480	123.22
250.963	124.12
254.525	125.28
258.164	126.53
261.829	127.88
265.521	128.90
269.190	129.64
272.837	130.54
276.573	131.41
280.279	133.09
284.134	134.03
287.682	134.83
291.193	135.60
294.661	136.38
298.182	137.23
301.761	138.91
305.318	139.33
308.865	139.65
312.399	140.01
315.920	140.84
319.422	141.72
322.958	142.66
326.539	143.11
330.106	144.54
333.656	144.90
337.193	145.72
340.705	147.51
344.200	148.45
347.683	149.20
351.200	151.34

Table 2
Experimental molar heat capacities of RTP crystal ($M = 288.2886$ g mol^{-1})

T (K)	$C_{p,\mathrm{m}}$ (JK^{-1} mol^{-1})
64.231	42.65
67.686	45.32
71.189	47.97
74.676	50.61
78.106	53.19
81.499	55.63
84.904	58.16
88.301	60.62
91.669	63.06
95.024	65.53
98.373	68.03
101.802	70.24
105.333	72.20
108.917	75.27
112.539	77.40
116.228	79.44
119.913	81.71
123.598	83.89
127.291	85.72
130.907	87.82
134.540	90.00
138.193	91.80
141.872	93.69
145.579	95.63
149.223	97.53
152.901	99.23
160.279	102.84
163.894	104.58
167.555	106.09
171.265	107.71
174.931	109.31
178.651	110.89
182.419	113.14
186.188	113.81
189.877	115.55
193.631	116.94
197.455	118.21
201.244	119.70
204.994	121.27
208.709	122.22
212.448	123.60
216.210	125.51
220.112	126.24
223.924	127.60
227.750	128.90
231.609	130.37
235.440	131.44
239.289	132.81
243.155	134.04
246.990	135.54
250.864	135.59
254.764	138.00

Table 2 (*Continued*)

T (K)	$C_{p,m}$ (JK^{-1} mol^{-1})
263.579	140.16
267.430	141.32
271.243	142.62
275.029	143.82
278.795	144.10
282.596	144.83
286.431	146.20
290.236	147.48
293.992	148.05
297.734	148.60
301.482	149.77
305.264	150.75
309.095	150.90
312.912	151.76
316.706	153.51
320.479	154.24
324.228	155.28
328.017	156.13
331.854	157.20
335.726	159.24
339.639	159.55
343.533	160.92
347.476	161.77
351.464	163.60
355.438	164.77

3.2. Heat capacities of $KTiOPO_4$ (KTP) and $RbTiOAsO_4$ (RTA) crystals

The KTP and RTA crystals were prepared in the State Key Laboratory of Crystal Materials, Shandong University. The KTP was synthesized using TiO_2, KH_2PO_4 and K_2HPO_4. The solvent and solute were both made in situ by reacting TiO_2 with the appropriate amounts of mono-basic (KH_2PO_4) and di-basic (K_2HPO_4) orthophosphates. The orthophosphates, in turn, were dehydrated to form KPO_3 (a polyphosphate) and $K_4P_2O_7$ (a di-phosphate), respectively. Single crystals of KTP were grown from flux compositions situated within the KPO_3–$K_4P_2O_7$ binary system. Crystals up to $15 \times 15 \times 15\ mm^3$ in size were obtained from pure and modified fluxes [12].

The RTA was prepared from Rb_2CO_3, H_3AsO_4 and TiO_2. Following chemical reaction and heating, they formed a Rb_2O–As_2O_3–TiO_2 solution system. The solution was contained in a platinum crucible and heated by a resistance heater. The RTA crystals were grown by using the top-seeded flux method. The seed of RTA crystal was hung in the solution and rotated during the crystal growing period. The saturation

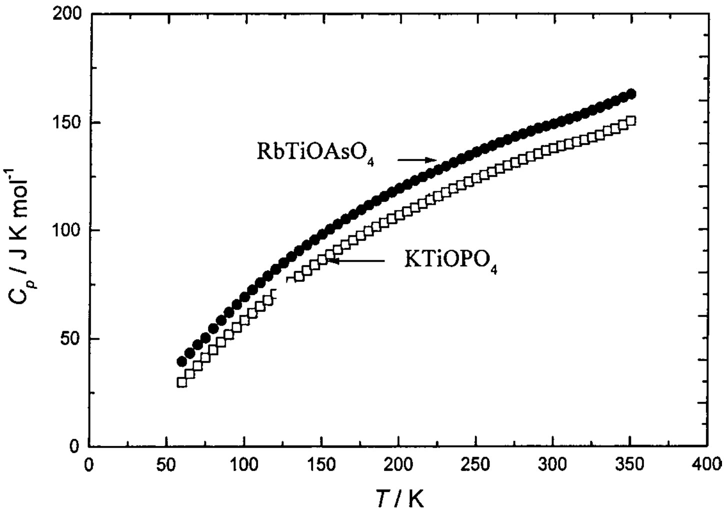

Fig. 4. Molar heat capacities of KTP and RTP crystals.

temperature of RTA crystal in this system was determined by using the trial seed method. The growing temperature was gradually lowered from 1123 to 1003 K for about 5 weeks. The typical size of RTA crystals obtained was $30 \times 15 \times 15\ \mathrm{mm}^3$. The crystals are transparent and very light yellow [13].

The purity of KTP and RTA crystals prepared the by above-mentioned technique was more than 0.9999 mass fraction. The amount of samples used for the calorimetric study was 8.7451 and 10.7849 g for KTP and RTA, respectively, which are equivalent to 4.4173×10^{-2} mol for KTP and 3.7410×10^{-2} mol for RTA based on their molar mass of 197.9728 and 288.2886 g mol^{-1}, respectively.

The heat capacity measurements on the two kinds of nonlinear optical materials were carried out in the range of 60–360 K. The temperature increment for each experimental point was about 3 K in the whole temperature range. The measured molar heat capacities are listed in Table 1 for KTP and Table 2 for RTA in chronological sequence, and shown in Fig. 4 for KTP and RTA.

From Fig. 4 it is obvious that the plot of the experimental molar heat capacity as a function of temperature gives two completely smooth curves with no sign of any phase transition or thermal anomaly in the entire temperature range. From the present calorimetric study, it can be concluded that the nonlinear optical materials KTP and RTA are thermodynamically stable in the temperature range of 60–360 K.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China (NSFC) for providing financial support to this research project under the grant No. 29773048.

References

[1] E.F. Westrum Jr., G.T. Furukawa, J.P. McCullough, in: J.P. McCullough, D.W. Scott (Eds.), Experimental Thermodynamics, Calorimetry of Non-reacting systems, Vol. 1, Butterworths, London, 1968, p. 133.

[2] E. Gmelin, Thermochim. Acta 29 (1979) 1.

[3] M. Tatsumi, T. Matsuo, H. Suga, S. Seki, Bull. Chem. Soc. Jpn. 48 (1975) 3060.

[4] K. Moriya, T. Matsuo, H. Suga, J. Chem. Thermodyn. 14 (1982) 1143.

[5] Z. Zhi-ying, Scientia Sinica, Ser. B 29 (1986) 1239.

[6] T. Zhi-cheng, Y. An-xue, C. Shu-xia, Z. Li-xing, L. Fu-xue, C. Min-zhong, Z. Shu-zhen, P. Ru-wen, L. Shi-ran, X. Yong-jian, Thermochim. Acta 123 (1988) 105.

[7] T. Matsuo, H. Suga, Thermochim. Acta 88 (1985) 149.

[8] M.J.M. Van Oort, M.A. White, Rev. Sci. Instrum. 58 (1987) 1239.

[9] M. Kano, J. Phys. E: Sci. Instrum. 22 (1989) 907.

[10] M. Sorai, K. Kaji, Y. Kaneko, J. Chem. Thermodyn. 24 (1992) 167.

[11] D.A. Ditmars, S. Ishihara, S.S. Chang, G. Bernstein, E.D. Rest, J. Rev. Natl. Bur. Stands. 87 (1982) 159.

[12] J.C. Jacco, G.M. Loiacono, M. Jaso, G. Mizell, B. Greenberg, J. Crystal Growth 70 (1984) 484.

[13] J. Han, Y. Liu, M. Wang, D. Nie, J. Crystal Growth 128 (1993) 864.