J. Chem. Thermodynamics 110 (2017) 171–174

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Low-temperature heat capacity of *tetrakis*(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium

M.A. Bespyatov *, I.S. Cherniaikin, K.V. Zherikova, V.N. Naumov, I.K. Igumenov, N.V. Gelfond, N.B. Morozova

Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk 630090, Russia

ARTICLE INFO

Article history:
Received 17 October 2016
Received in revised form 13 February 2017
Accepted 28 February 2017
Available online 2 March 2017

Keywords:
Heat capacity
Thermodynamic functions
Zirconium(IV) beta-diketonates

ABSTRACT

The heat capacity of *tetrakis*(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium ($Zr(C_{11}H_{19}O_2)_4$) was measured over the temperature range (9–306) K by adiabatic-shield calorimetry and found to be without transitions or thermal anomalies. The data obtained were used to calculate its thermodynamic functions (entropy, enthalpy, reduced Gibbs energy) in the range (0–306) K. They have the following values at 298.15 K: $C^\circ_p = (1195.7 \pm 1.8)\ J\cdot K^{-1}\cdot mol^{-1}$, $\Delta_0^{298.15}S^\circ_m = (1298 \pm 3)\ J\cdot K^{-1}\cdot mol^{-1}$, $\Delta_0^{298.15}H^\circ_m = (194.7 \pm 0.3)$ $kJ\cdot mol^{-1}$, $\Phi^\circ_m = (645.2 \pm 1.9)\ J\cdot K^{-1}\cdot mol^{-1}$. The value of the absolute entropy were used to calculate the entropy of formation of $Zr(C_{11}H_{19}O_2)_4$ at $T = 298.15$ K.

1. Introduction

Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato) zirconium ($Zr(C_{11}H_{19}O_2)_4$ or $Zr(thd)_4$) belongs to the class of metal beta-diketonates that crystallize in the lattice of molecular type. Beta-diketonates of zirconium are used as precursors in the technologies of chemical vapour deposition (CVD) to produce high quality oxide materials which are considered as thermal barrier coatings for the blades of gas turbines [1], ceramic electrolyte for solid oxide fuel cell [2], high-*k* dielectric [3] and ferroelectric [4] films for microelectronics. The application of the materials is getting broader permanently which stimulates the further investigation of features of the CVD precursors. In this regard, the heat capacity is one of the physico-chemical properties the knowledge of which is necessary for the directed synthesis of beta-diketonates with the desired characteristics. The data on heat capacity in a wide temperature range are necessary to calculate reliably integral thermodynamic functions (enthalpy, entropy, reduced Gibbs energy) [5], which, in turn, are necessary for the study of equilibrium characteristics of the crystal–gas system and the stability [6,7] of these volatile compounds.

The high-temperature thermodynamic properties (heat capacity, temperature and heat of phase transition in the range (308 – 565) K [8], thermodynamic characteristics of sublimation [9] and melting processes [9,10]) of the compound $Zr(thd)_4$ are now well investigated. However, low temperature data on heat capacity for $Zr(thd)_4$ is unavailable.

This paper presents the results of an experimental study of the heat capacity of *tetrakis*(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium in the temperature range from 9 to 306 K by adiabatic calorimetry. The data obtained were used to calculate $Zr(thd)_4$ thermodynamic functions (entropy, enthalpy, reduced Gibbs energy) in the range (0–306) K.

2. Experimental

Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium has been synthesized, purified and identified as described in [9,11]. $ZrCl_4$ (mass fraction purity no less than 0.995) and 2,2,6,6-tetramethyl-3,5-heptanedione (mass fraction purity no less than 0.99) were used as initial reagents [all chemicals used in the synthesis were commercially available reagents grade and applied without further purification (see Table 1)]. After synthesis, the product was purified by means of double sublimation in a vacuum gradient furnace at $p = 7$ Pa and $T = (353–373)$ K. Mass fraction purity of the final compound is not lower than 0.99.

The sample of $Zr(thd)_4$ is a white crystalline powder at room temperature. The elemental analysis was carried out in Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS using Carlo-Erba-1106 (Italy) rapid elemental analyser. The uncertainties in elemental determinations did not exceed 0.3% [12]. Elemental analyses for $C_{44}H_{76}O_8Zr$ (%): Calcd: C 64.11, H 9.29; Found: C 63.94, H 9.17. ^1H NMR spectrum was recorded on a TESLA BS-567 spectrometer (100 MHz, 25 °C), and $CDCl_3$ was used as a solvent. ^1H NMR (ppm): 5.62 (m, CH), 1.01 (s, $-C(CH_3)_3$).

$Zr(thd)_4$ could form different polymorphic modifications depending on synthetic procedure and purification method

* Corresponding author.
E-mail addresses: bespyatov@niic.nsc.ru, m.a.bespyatov@gmail.com (M.A. Bespyatov).

http://dx.doi.org/10.1016/j.jct.2017.02.026
0021-9614/

Table 1
Characterization of the chemicals used.

Chemicals	Source/supplier	State	Mass fraction purity
$ZrCl_4$	Dalchem	Solid	≥0.995
$C_{11}H_{20}O_2$	Dalchem	Liquid	≥0.99
NaOH	"Component-reaktiv" Co., Ltd	Solid	≥0.98
$CHCl_3$	"Component-reaktiv" Co., Ltd	Liquid	≥0.9995
C_2H_6O	"Component-reaktiv" Co., Ltd	Liquid	≥0.95
Zr $(C_{11}H_{19}O_2)_4$			Synthesis (purification – double fractional sublimation)
Solid	≥0.99 (elemental CH analysis)		

[10,11,13]. The X-ray powder diffraction study of the polycrystalline sample using a Shimadzu XRD-7000 diffractometer (CuK_α radiation, range $2\theta = (5–60)°$, room temperature) showed that the synthesized product is a single phase. Diffraction pattern (see Fig. 1) was indexed by the results of single crystal study of Zr(thd)$_4$ [13]; it corresponds to monoclinic phase of Zr(thd)$_4$ with lattice parameters: $a = (22.545 \pm 0.006)10^{-1}$ nm, $b = (11.275 \pm 0.003)$ 10^{-1} nm, $c = (19.763 \pm 0.005)$ 10^{-1} nm, $\beta = (106.550 \pm 0.007)°$, $Z = 4$, $V = 4.816$ nm^3 (standard uncertainties, type A), space group $P2/c$ [13]. Peaks corresponding to other phases were not found. The calculated X-ray density, according to the data of the paper [13], was 1.14 g·cm^{-3}.

The melting temperature of the sample was determined using a Setaram DSC 111 calorimeter, heating rate 1.0 K·min^{-1}; sample mass (13–15 mg). During the measurements the investigated substance was contained in an evacuated glass ampoule. Temperature calibration was performed using melting of benzoic acid and indium. A peak associated with the melting of Zr(thd)$_4$ is shown in Fig. 2. The melting temperature was taken as the extrapolated onset temperature for the endothermic peak in the DSC response. The result obtained is 614.0 K (standard uncertainty for temperature $u(T)$ is 0.5 K). Shown in the literature for melting temperature, there are (614 ± 1) K [9] and (592 ± 1) K [10]. We have reproduced the result of the work [9]. However, our values differ from the data presented in [10]. The sample investigated in [10] has the other parameters of a crystal lattice. This fact explains the observed deviation of our results from those presented in this work.

The heat capacity of Zr(thd)$_4$ measurements were made by the adiabatic calorimetry method with a periodic heat pulse on the installation described in [14,15]. The calorimeter ampoule with

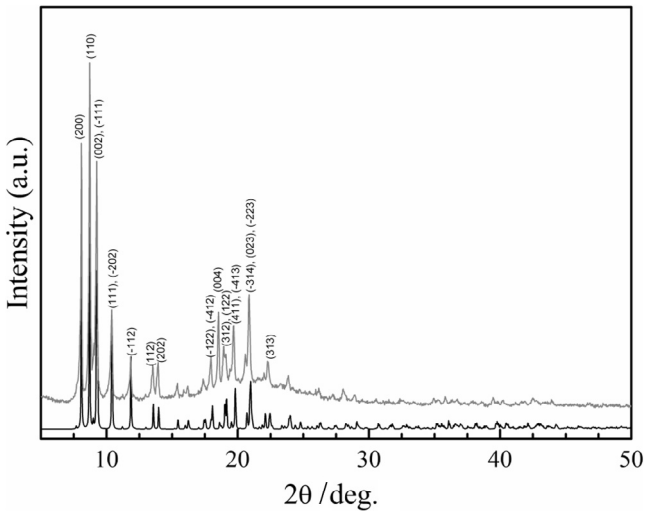

Fig. 1. XRD (CuKa) pattern of Zr(thd)$_4$ powder under study (grey line) and diffraction diagram of Zr(thd)$_4$ calculated from X-ray structural data of [13] (black line).

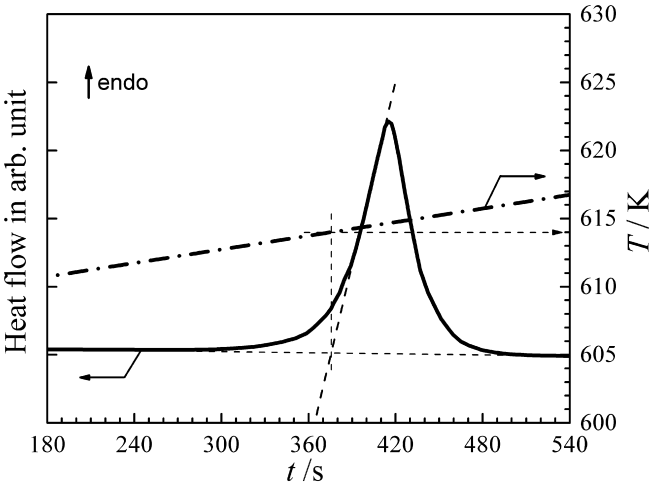

Fig. 2. Temperature profile (dot-dash) and measured heat flow rate (solid line) for Zr(thd)$_4$. The determination of the melting peak onset is indicated by the tangent and peak base line.

the sample was filled helium gas ($p = 1.5$ kPa) to enhance heat transfer. The temperature of the calorimeter was measured by a standard platinum resistance thermometer ($R_0 = 100.4695$ Ohm; temperature coefficient of resistance $\alpha = 0.0039255$) calibrated at FSUE "All-Russian Scientific Research Institute of Physical-Technical and Radiotechnical Measurements" (Moscow region, Russia) using the ITS-90 scale. The standard uncertainty for the temperature was $u(T) = 0.01$ K. Resolution of the thermometric apparatus was 0.00005 K above 50 K falling to 0.0015 K at 10 K. The adiabatic control system gave the temperature stability of the calorimeter vessel within 0.00001 K·min^{-1}. The reliability of the measuring procedure was tested by measuring the heat capacity of the standard benzoic acid. The apparatus and the measurement procedure gives heat capacity values of solids with an uncertainty of no more than 1% in the range of (5–20) K, 0.3% in the range of (20–80) K, and 0.15% in the range of (80–300) K. The sample of Zr(thd)$_4$ of 4.932 g (in a vacuum) was loaded into the calorimetric ampoule. The molar mass used in the calculation of the molar heat capacity was determined from the formula Zr(thd)$_4$ as 824.31 g·mol^{-1}.

3. Results

The heat capacity was measured at 71 points over the range of 9 K to 306 K. The values obtained are presented in Table 2. The analysis of the functional dependence $C_{p,m}(T)$ (Fig. 3) has not revealed any thermal anomaly in its behaviour. In [8], the heat capacity of Zr(thd)$_4$ was obtained over the range of 307.8 K to 565.4 K. Measurements of heat capacities were carried out using a Calvet type calorimeter Setaram C 80. The uncertainty of these data is about ±1% [8]. As can be seen from Fig. 3, our results for the heat capacity at low temperatures are in good agreement (within the experimental uncertainty) with the results presented in this [8].

The experimental results for the heat capacity have been smoothed by the Rumshiskii method [16]. This method approximates the experimental curve by spline functions. Deviation of the experimental values from the smoothed curve is shown in Fig. 4. The standard deviation of the experimental points from the smoothed curve is equal to: 1.0% (9–18) K, 0.07% (18–80) K, 0.04% (80–306) K.

By numerical integration of the smoothed dependence $C_s(T)$ were obtained values of the entropy $\Delta_0^T S°_m$, the enthalpy $\Delta_0^T H°_m$ and the reduced Gibbs' energy $\Phi°_m$ within the range of 0–306 K.