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Short Communication

HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS OF THE TELLURATES(IV) OF ZINC AND CADMIUM

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The temperature dependencies of the molar heat capacities of $ZnTeO_3$, $Zn_2Te_3O_8$, $CdTeO_3$ and $CdTe_2O_5$ are determined. The experimental data are statistically processed using the least squares method to determine the parameters in the equations for the corresponding compounds: $C_{p,m}=a+b(T/K)-c(T/K)^{-2}$. These equations and the standard molar entropies are used to determine $\Delta_0^T S_m^0$, $\Delta_{T'}^T H_m^0$ and $(\Phi_m^0 + \Delta_0^{T'} H_m^0 / T)$ for T'=298.15 K.

Keywords: *molar heat capacity, tellurates(IV) of zinc and cadmium*

Introduction

The crystalline and vitreous metal tellurates(IV) are perspective materials for semiconductor and luminescent technology. They belong to the compounds whose physico-chemical properties have not been studied thoroughly.

The aim of the present work is to study the temperature dependence of the isobaric molar heat capacity since the data on it have not been reported so far.

Experimental, results and discussion

The following substances are used for the synthesis of zinc and cadmium tellurates(IV) (basic compound content): $Zn(CH_3COO)_2$: 99.99; $CdTeO_3 \cdot 4H_2O$: 99.999; ZnO: 99.999; CdO: 99.99; TeO_2: 99.995; $Na_2TeO_3 \cdot 5H_2O$ prepared by the authors according to a method described in [1].

The tellurates(IV) are synthesized by two methods [2–10]:

- Wet method. Equimolar solutions of the corresponding metal salts and $Na_2TeO_3 \cdot 5H_2O$ are prepared and mixed. The preparation procedure has been described in [1].
- Dry method. Mechanical mixtures of MeO and TeO_2 are prepared at the exact stoichiometry of the tellurate(IV) to be synthesized. The mixtures are thoroughly homogenized, placed in quartz ampoules which are then vacuumed and sealed under vacuum. They are tempered at temperatures about 50°C lower than the melting temperature of the corresponding tellurates(IV). After 5 h heating, the ampoules are opened and the product obtained is thoroughly ground. It is sealed again in ampoules under vacuum and is heat treated for a second time. This procedure is repeated three times.

In both cases, the phase uniformity of the samples is controlled by X-ray, differential-thermal and chemical analyses. The X-ray analyses of the samples are carried out on an apparatus URD-6 (Germany) at CuK_α emission and Ni filter for the β-radiation. The thermal analyses are carried out on a derivatograph MOM (Hungary), type OD-102. The chemical analyses of zinc and cadmium ions are performed complexonometrically using xylenol orange [11] as indicator while the tellurate(IV) ions are determined iodometrically and gravimetrically [12].

The heat capacities of the metal tellurates(IV) are studied on a calorimeter DSC-III ('Setaram', France). The samples obtained are finely ground, shifted through a sieve with opening size ∅=0.25 mm and subjected to calorimetric experiments by a method described in [13]. The experimental conditions used are: heating rate – 1 K min^{-1} within temperature interval 350–550 K, with sapphire (α-Al_2O_3) used as reference material. The temperature depend-

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encies of the heat capacities of solid crystalline substances at temperatures higher than 298 K are determined using the following equations, depending on some properties of the substances studied:

$$C_{p,m}(T)/(\text{J K}^{-1}\text{ mol}^{-1})=a+b(T/\text{K})+... \quad (1)$$

$$C_{p,m}(T)/(\text{J K}^{-1}\text{ mol}^{-1})=a+b(T/\text{K})-c(T/\text{K})^{-2} \quad (2)$$

Equation of type (1) describes the temperature dependences of the heat capacity of substances with lower Debye temperature, Q_D (Q_D<298.15 K). In this case, the temperature dependence of the heat capacity increases linearly with temperature, i.e. the heat capacity obeys the law of Einstein $c \sim aT$. Equation (2), called also equation of Meyer–Kelly, corresponds to faster change of the heat capacity at comparatively lower temperatures and practically constant dC_p/dT at higher temperatures. It is usually used to describe the temperature dependence of the heat capacity of solid substances with higher Debye temperature ($Q_D \geq 298.15$ K) and corresponds to $C_p(T)$ dependence more complex than the linear one. When these considerations are not taken into account, then the extrapolation would give abrupt change of C_p curve both at low and high temperature and its physical meaning can not be sensibly explained.

The results obtained are presented in Table 1. The values are processed by computer and the parameters of Eq. (2) are evaluated. The coefficients a, b and c are given in Table 2.

The standard thermodynamic characteristics and the temperature dependences of the heat capacities of $ZnTeO_3$, $Zn_2Te_3O_8$, $CdTeO_3$ and $CdTe_2O_5$, are presented in Table 2.

The standard molar entropy $\Delta_0^T S_m^0$ is calculated by the method of Kelly. Using the results from Table 2, the thermodynamic functions of the zinc and cadmium tellurates(IV) are calculated (Tables 3–6).

Table 1 Experimental molar heat capacities $C_{p,m}$ of $ZnTeO_3$, $Zn_2Te_3O_8$, $CdTeO_3$ and $CdTe_2O_5$

Temperature/K	$C_{p,m}$/J K^{-1} mol^{-1}			Temperature/K	$C_{p,m}$/J K^{-1} mol^{-1}
	$ZnTeO_3$	$Zn_2Te_3O_8$	$CdTe_2O_5$		$CdTeO_3$
403	104	335	199	350	146
413	104	339	201	360	153
423	105	344	202	370	162
433	108	347	201	380	170
443	108	352	205	390	176
453	112	357	207	400	184
463	116	368	208	413	184
473	116	368	210	423	187
483	120	369	211	433	190
493	126	374	214		
503	125	377	213		
513	128	381	213		
523	131	382	216		
533	134	382	219		
543	135	383	220		
553	140	383	221		

Table 2 Standard molar thermodynamic functions $\Delta_0^{T'} S_m^0$ and temperature dependences of the molar heat capacities $C_{p,m}$ of $ZnTeO_3$, $Zn_2Te_3O_8$, $CdTeO_3$ and $CdTe_2O_5$, T'=298.15 K

Compound	$\Delta_0^{T'} S_m^0$/J K^{-1} mol^{-1}	a	b	c	$10^2(\delta C_p/C_p)$
$ZnTeO_3$	103	–128.67	$430.17 \cdot 10^{-3}$	$-94.50 \cdot 10^5$	0.73
$Zn_2Te_3O_8$	265	533.88	$-120.38 \cdot 10^{-3}$	$247.03 \cdot 10^5$	0.54
$CdTeO_3$	114	507.16	$-391.42 \cdot 10^{-3}$	$273.79 \cdot 10^5$	0.91
$CdTe_2O_5$	173	139.86	$147.03 \cdot 10^{-3}$	$0.32 \cdot 10^5$	0.35

Table 3 Standard molar thermodynamic functions of $ZnTeO_3$, T'=298.15 K

Temperature/K	$C_{p,m}$/J K^{-1} mol^{-1}	$\Delta_0^T S_m^0$/J K^{-1} mol^{-1}	$\Delta_{T'}^T H_m^0$/J mol^{-1}	$(\Phi_m^0 + \Delta_0^{T'} H_m^0 / T)$/J K^{-1} mol^{-1}
350	99.03	119.31	5267.90	104.25
400	102.46	132.68	10274.90	106.98
450	111.57	145.23	15607.30	110.54
500	124.21	157.61	21490.10	114.63
550	139.16	170.14	28066.49	119.11
600	155.68	182.94	35431.91	123.89
650	173.31	196.10	43652.44	128.94
700	191.73	209.61	52775.30	134.22

Table 4 Standard molar thermodynamic functions of $Zn_2Te_3O_8$, T'=298.15 K

Temperature/K	$C_{p,m}$/J K^{-1} mol^{-1}	$\Delta_0^T S_m^0$/J K^{-1} mol^{-1}	$\Delta_{T'}^T H_m^0$/J mol^{-1}	$(\Phi_m^0 + \Delta_0^{T'} H_m^0 / T)$/J K^{-1} mol^{-1}
298.15	219.83	265.00	0.00	265.00
300	223.29	266.48	443.13	265.00
350	290.09	306.35	13417.62	268.01
400	331.33	347.99	29032.00	275.41
450	357.72	388.65	46305.98	285.74
500	374.88	427.29	64651.40	298.00
550	386.01	463.58	83693.97	311.41
600	393.03	497.49	103184.16	325.52

Table 5 Standard molar thermodynamic functions of $CdTeO_3$, T'=298.15 K

Temperature/K	$C_{p,m}$/J K^{-1} mol^{-1}	$\Delta_0^T S_m^0$/J K^{-1} mol^{-1}	$\Delta_{T'}^T H_m^0$/J mol^{-1}	$(\Phi_m^0 + \Delta_0^{T'} H_m^0 / T)$/J K^{-1} mol^{-1}
298.15	82.21	114.00	0.00	114.00
300	85.52	114.56	167.74	114.00
350	146.66	132.81	6127.55	115.31
400	179.47	154.78	14368.21	118.86
450	195.81	176.98	23803.26	124.09
500	201.93	198.00	33780.81	130.44

Table 6 Standard molar thermodynamic functions of $CdTe_2O_5$, T'=298.15 K

Temperature/K	$C_{p,m}$/J K^{-1} mol^{-1}	$\Delta_0^T S_m^0$/J K^{-1} mol^{-1}	$\Delta_{T'}^T H_m^0$/J mol^{-1}	$(\Phi_m^0 + \Delta_0^{T'} H_m^0 / T)$/J K^{-1} mol^{-1}
298.15	183.31	173.00	0.00	173.00
300	183.61	174.23	366.93	173.00
350	191.06	203.09	9734.09	175.28
400	198.47	229.09	19472.67	180.40
450	205.86	252.89	29581.38	187.15
500	213.25	274.96	40059.47	194.84
550	220.62	295.63	50906.45	203.08
600	227.99	315.15	62122.00	211.61
650	235.35	333.69	73705.90	220.29
700	242.71	351.40	85657.98	229.03

References

1 Z. L. Lechtinskaia and N. M. Selivanova, Zh. Neorg. Chim. Russ., 8 (1963) 1024.
2 G. G. Gospodinov and M. G. Stancheva, J. Therm. Anal. Cal., 55 (1999) 221.
3 G. G. Gospodinov and M. G. Stancheva, J. Therm. Anal. Cal., 65 (2001) 275.
4 G. G. Gospodinov and M. G. Stancheva, J. Therm. Anal. Cal., 67 (2002) 463.
5 G. G. Gospodinov and M. G. Stancheva, J. Therm. Anal. Cal., 73 (2003) 315.
6 G. G. Gospodinov and M. G. Stancheva, J. Therm. Anal. Cal., 73 (2003) 835.
7 G. G. Gospodinov and M. G. Stancheva, J. Therm. Anal. Cal., 73 (2003) 859.
8 G. G. Gospodinov and M. G. Stancheva, J. Therm. Anal. Cal., 75 (2004) 95.
9 G. G. Gospodinov and M. G. Stancheva, J. Therm. Anal. Cal., 76 (2004) 537.
10 G. G. Gospodinov and M. G. Stancheva, J. Therm. Anal. Cal., 78 (2004) 323.
11 V. Umlang, A. Jansen, P. Tierg and C. Winsh, Theorie und Praktische Anwendung von Complexbildern, Dechema, Frankfurt am Main 1971.
12 J. I. Nazarenko and E. I. Ermakov, Analiticheskaya Khimia Selena i Telura, Nauka, Moscow 1974.
13 J. L. McNaughton and C. T. Mortimer, Differential Scanning Calorimetry, Perkin-Elmer Corporation: Norvalk Connection, (1975) 11.

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