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SPECIFIC THERMAL AND THERMODYNAMIC PROPERTIES OF THE TELLURITES $Fe_2(TeO_3)_3$, Fe_2TeO_5 AND $Fe_2Te_4O_{11}$

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The temperature dependence of the molar heat capacities of the tellurites $Fe_2(TeO_3)_3$, Fe_2TeO_5 and $Fe_2Te_4O_{11}$ were determined. By statistical manipulation of the values obtained, the parameters in the equations for the corresponding compounds showing this dependence were determined using the least-squares method. These equations together with the standard molar entropies were used to determine the thermodynamic functions $\Delta_0^T S_m^0$, $\Delta_{T'}^T H_m^0$ and $(\Phi_m^0 + \Delta_0^{T'} H_m^0 / T)$ for T'=298.15 K.

Keywords: *iron tellurites, molar heat capacity*

Introduction

It is well known that metal halogenides are easily oxidated under heating in presence of oxygen. The oxidation products composition is determined mainly by the thermal properties of the phases formed and is different for the different metals. The studies on the processes of metal tellurites oxidation are interesting for the extraction of tellurium by processing cuprous electrolyte slime, as well as in semi-conductor technology – mainly for determination of the composition of tellurite oxidation products used as thermoelectric power generators with working temperature 700–1000°C.

For detailed description of this matter and proper control of the technological processes, thermodynamic analysis should be performed requiring knowledge on the thermodynamic properties of the tellurites.

The aim of the present paper is to study the molar heat capacities and the other thermodynamic properties of $Fe_2(TeO_3)_3$, Fe_2TeO_5 and $Fe_2Te_4O_{11}$.

Experimental

The Fe_2O_3 and TeO_2 used for the synthesis were with purity at least 99.995%.

The solid phase vacuum synthesis was carried out according to a method described in [1, 2]. The samples were heated three times (24 h each) and each heat treatment was followed by grinding and homogenization. According to the chemical analysis (performed by a method described in [3, 4]) the products obtained had the same stoichiometry as the compounds. The phase uniformity was confirmed by X-ray analysis. The reflections of Fe_2TeO_5, $Fe_2(TeO_3)_3$ and $Fe_2Te_4O_{11}$ corresponded to these reported in [1, 2] with regard both to relative intensity and interplanar distances. Fe_2TeO_5 crystallizes in monoclinic syngony with space group P2/C, with unit cell parameters a=7.6650, b=4.9340, c=10.8150 and β=103.10, z=4. The calculated density was $D_{calc.}$=5.324. $Fe_2(TeO_3)_3$ crystallizes in orthorhombic syngony, space group Pbma, with unit cell parameters a=9.5050, b=7.5030, c=11.0030, number of formula units z=4 and calculated density of $D_{calc.}$=5.405. $Fe_2Te_4O_{11}$ crystallizes in monoclinic syngony with space group P2/C and parameters of unit cell a=11.8800, b=6.9500, c=14.1300 and β=123.44. The number of structure units per unit cell is z=4 and the calculated density, $D_{calc.}$=5.445.

After the synthesis, the tellurites were ground, shifted through 0.25 mm^2 sieve and then subjected to thermodynamic experiments by the method described in [5].

Results and discussion

The experimental values of the specific heat capacities measured are presented in Table 1. The relative error of the experiments was ≤0.1%. The data were computer processed by the least squares method to determine the coefficients in the equation for the specific heat capacity $C_{p,m}(T)$:

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

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Table 1 Experimental molar heat capacities $C_{p,m}$ of $Fe_2(TeO_3)_3$, Fe_2TeO_5 and $Fe_2Te_4O_{11}$

T/K	$C_{p,m}$/J K^{-1} mol^{-1}			T/K	$C_{p,m}$/J K^{-1} mol^{-1}		
	$Fe_2(TeO_3)_3$	Fe_2TeO_5	$Fe_2Te_4O_{11}$		$Fe_2(TeO_3)_3$	Fe_2TeO_5	$Fe_2Te_4O_{11}$
403	311	198	500	483	346	217	542
413	316	200	504	493	345	219	546
423	320	202	508	503	345	225	558
433	325	203	508	513	348	226	561
443	340	208	525	523	350	228	565
453	340	207	524	533	350	226	573
463	341	211	544	543	356	231	570
473	345	218	537	553	359	229	586

Table 2 Standard molar thermodynamic functions $\Delta_0^{T}S_m^0$ and temperature dependences of the molar heat capacities $C_{p,m}$ of $Fe_2(TeO_3)_3$, Fe_2TeO_5 and $Fe_2Te_4O_{11}$, T'=298.15 K

Compound	$\Delta_0^{T'}S_m^0$ /J K^{-1} mol^{-1}	a	b	c	$10^2\cdot\delta C_p/C_p$
$Fe_2(TeO_3)_3$	301.16	657.12	$-351.03\cdot10^{-3}$	$332.08\cdot10^{5}$	0.82
Fe_2TeO_5	160.34	196.20	$104.92\cdot10^{-3}$	$68.52\cdot10^{5}$	0.78
$Fe_2Te_4O_{11}$	371.56	370.02	$424.29\cdot10^{-3}$	$71.39\cdot10^{5}$	0.64

Table 3 Molar thermodynamic functions of $Fe_2(TeO_3)_3$, T'=298.15 K

T/K	$\Delta_0^{T}S_m^0$ / 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	301.16	0.00	301.16
300	302.37	361.41	301.16
350	337.17	11699.68	303.74
400	375.59	26113.68	310.31
450	413.66	42285.63	319.69
500	449.76	59424.88	330.91
550	483.32	77028.26	343.26
600	514.17	94760.34	356.24

Table 4 Molar thermodynamic functions of Fe_2TeO_5, T'=298.15 K

T/K	$\Delta_0^{T}S_m^0$ / 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	160.34	0.00	160.34
300	161.35	301.85	160.34
350	186.74	8553.95	162.30
400	211.63	17884.05	166.92
450	235.49	28020.27	173.22
500	258.19	38799.45	180.60
550	279.76	50117.79	188.64
600	300.27	61906.05	197.09
650	319.81	74116.34	205.79
700	338.48	86714.42	214.60

Table 5 Molar thermodynamic functions of $Fe_2Te_4O_{11}$, T'=298.15 K

T/K	$\Delta_0^{T}S_m^0$ / 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	371.56	0.00	371.56
300	374.35	834.05	371.57
350	442.08	22830.08	376.85
400	505.87	46736.68	389.03
450	565.99	72270.58	405.39
500	622.84	99261.78	424.31
550	676.84	127602.13	444.84
600	728.36	157219.52	466.33
650	777.73	188064.02	488.40
700	825.20	220099.95	510.77

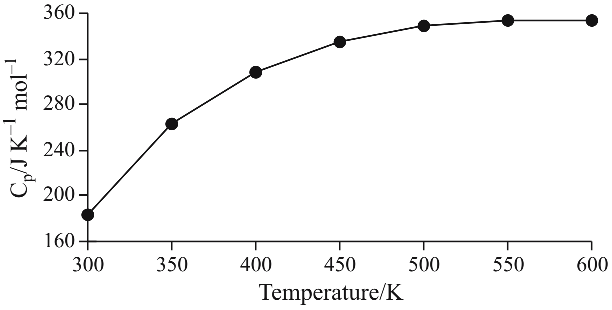

Fig. 1 Dependence of molar heat capacity of $Fe_2(TeO_3)_3$ on temperature in the temperature range 300–600 K, calculated by the polynomial $C_{p,m}(T)$/J K^{-1} mol^{-1} = $657.12–351.03\cdot10^{-3}T–332.08\cdot10^{5}T^{-2}$

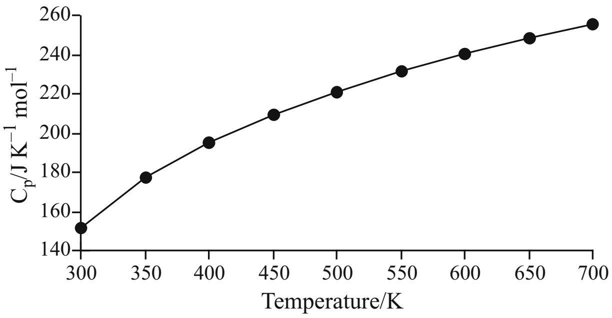

Fig. 2 Dependence of molar heat capacity of Fe_2TeO_5 on temperature in the temperature range 300–700 K, calculated by the polynomial $C_{p,m}(T)/\mathrm{J\ K^{-1}\ mol^{-1}} = 196.20 + 104.92 \cdot 10^{-3} T - 68.52 \cdot 10^{5} T^{-2}$

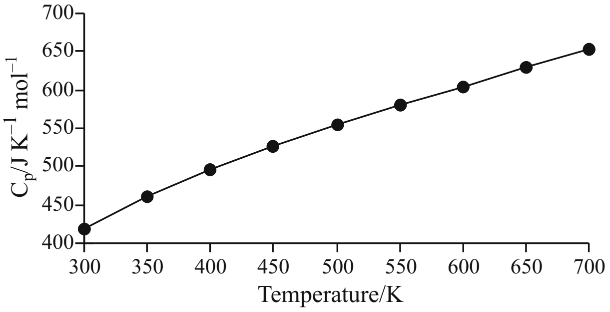

Fig. 3 Dependence of molar heat capacity of $Fe_2Te_4O_{11}$ on temperature in the temperature range 300–700 K, calculated by the polynomial $C_{p,m}(T)/\mathrm{J\ K^{-1}\ mol^{-1}}$, $C_p = 370.02 + 424.29 \cdot 10^{-3} T - 71.39 \cdot 10^{5} T^{-2}$

The values of the coefficients *a*, *b* and *c* calculated using the heat capacity equation ($C_{p,m}(T)$) together with the standard molar thermodynamic functions $\Delta_0^T S_m^0$ are shown in Table 2. Using the values of $\Delta_0^T S_m^0$ and the equation for the specific heat capacity, $C_{p,m}(T)$ (Figs 1–3), $\Delta_0^T S_m^0$, $\Delta_{T'}^T H_m^0$ and $(\Phi_m^0 + \Delta_0^{T'} H_m^0 / T)$ were calculated (Tables 3–5).

Conclusions

The present work is a continuation of our studies in the field of thermal and thermodynamic properties of some metal tellurites [6, 7]. The temperature dependencies of molar heat capacities of the tellurites $Fe_2(TeO_3)_3$, Fe_2TeO_5 and $Fe_2Te_4O_{11}$ are determined. The experimental data are statistically processed using the least squares method to determine the parameters in the equations for the corresponding compounds: $C_{p,m}(T)/(\mathrm{J\ K^{-1}\ mol^{-1}}) = a + b(T/\mathrm{K}) - c(T/\mathrm{K})^{-2}$. These equations and the standard molar entropies are used to determine the thermodynamic functions $\Delta_0^T S_m^0$, $\Delta_{T'}^T H_m^0$ and $(\Phi_m^0 + \Delta_0^T H_m^0 / T$ for T'=298.15 K.

References

1 D. S. Robertson, N. Shaw and I. M. Yong, J. Phys. D: Appl. Phys., 9 (1976) 1257.
2 Fr. Bernard and M. Jaymes, Revue de Chimie Minérale, 9 (1972) 837.
3 V. Umlang, A. Jansen, P. Tierg and C. Winsh, Theorie und Practische Anwendung von Complexbildern, Dechema, Frankfurt am Main 1971.
4 J. I. Nazarenco and E. I. Ermakov, Analiticheskaya Khimia Selena i Telura, Nauka, Moscow 1974.
5 J. L. McNaughton and C. T. Mortimer, Differential Scanning Calorimetry, Perkin-Elmer Corporation: Norvalk Connection, (1975), p. 11.
6 G. Gospodinov and L. Atanasova, J. Therm. Anal. Cal., 82 (2005) 439.
7 G. Gospodinov and L. Atanasova, J. Therm. Anal. Cal., 83 (2006) 273.

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