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THERMODYNAMIC PROPERTIES OF GERMANIUM AND LEAD TELLURITES

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The temperature dependence of the molar heat capacities of the tellurites $PbTeO_3$, $Pb_2Te_3O_8$ and $Ge(TeO_3)_2$ are determined. By statistical manipulation of the values obtained, the parameters in the equations for the corresponding compounds showing this dependence are determined using the least-squares method. 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.

Keywords: *DSC, molar heat capacity, tellurites of germanium and lead*

Introduction

The knowledge on the thermodynamic properties of tellurium plays an important role in general, physical and analytical chemistry, in studies on the chemical and metallurgical processes used for production of tellurium and its compounds. The present paper is devoted to a study on the temperature dependence of the molar isobar heat capacity and calculation of the temperature dependence of the thermodynamic properties of the tellurite compounds. It is the continuation of the previous studies of the authors [1, 2].

Experimental

Germanium and lead tellurites were synthesized from compounds with purity not lower than 99.999 ($GeCl_4$, $Pb(NO_3)_2$, $Pb(CH_3COO)_2$, PbO and TeO_2), under conditions developed by the authors. The interaction of the solid phase was performed thrice in vacuumed ampoules at temperatures 50°C lower than the melting temperatures of the corresponding tellurites. The tellurites obtained were then finely ground. Additionally, crystallization conditions were provided under the conditions for preparation of tellurites through precipitation reactions in the solution. Then, the phase composition and phase homogenization were determined by chemical, X-ray and differential thermal analyses [3–5].

The chemical analysis of lead tellurite was carried out complexonometrically, using complexon III with indicator eriochrome black *T* [3], while tellurium was analyzed in both cases iodometrically and gravimetrically [4]. Germanium was determined using the reactant manit [5]. Phase diagrams were drawn for the binary systems metal oxide–tellurium oxide to determine the areas of existence and the stabilities of the substances synthesized.

X-ray analysis is carried out on TURM–61 M apparatus at Cu anode, K_α emission and Ni filter for the β radiation. All peaks on the X-ray pattern correspond to those published in the literature regarding their intensity and interplanar distances.

The heat capacity of the tellurites studied was determined using differential scanning calorimeter DSC-III (Setaram, France). The samples were finely ground and sieved through 0.25 mm^2 sieve. The experimental conditions were as described in [6].

Results and discussion

The parameters of the germanium iodide lattice unit cell were calculated. It was found to crystallize in tetragonal syngony with space group P4/m and unit cell parameters: a=15.4968 and c=15.0572. $PbTeO_3$ crystallized in monoclinic syngony, space group C2/m with parameters: a=27.5902; b=4.6104; c=12.9705 and β=112.90. $Pb_2Te_3O_8$ crystallized in orthorhombic syngony with lattice unit cell parameters: a=7.140; b=18.771 and c = 19.490.

Three samples were studied for each tellurite and the average values obtained were considered to be representative. The relative error was not higher than 0.1%. The obtained values of heat capacity are shown in Table 1. These results were computer processed by

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Table 1 Experimental molar heat capacities $C_{\mathrm{p,\,m}}$ of $PbTeO_3$, $Pb_2Te_3O_8$ and $Ge(TeO_3)_2$

T/K	$C_{\mathrm{P,m}}$/J K^{-1} mol^{-1}			T/K	$C_{\mathrm{P,m}}$/J K^{-1} mol^{-1}		
	$PbTeO_3$	$Pb_2Te_3O_8$	$Ge(TeO_3)_2$		$PbTeO_3$	$Pb_2Te_3O_8$	$Ge(TeO_3)_2$
403	115	1043	198	483	121	1315	216
413	115	1125	201	493	123	1328	217
423	117	1193	204	503	126	1348	217
433	115	1217	206	513	129	1349	218
443	117	1248	209	523	129	1374	220
453	118	1251	210	533	131	1375	220
463	118	1260	212	543	132	1379	221
473	120	1281	214	553	133	1386	224

Table 2 Standard molar thermodynamic functions $\Delta_0^T S_m^0$ and temperature dependences of the molar heat capacities $C_{\mathrm{p,m}}$ of $PbTeO_3$, $Pb_2Te_3O_8$, $Ge(TeO_3)_2$, T'=298.15 K

Compound	$\Delta_0^T S_m^0$/J K^{-1} mol^{-1}	a	b	c	$10^2 \cdot \frac{\delta C_P}{C_P}$
$PbTeO_3$	137.75	–51.42	$287.24 \cdot 10^{-3}$	$-81.20 \cdot 10^5$	0.68
$Pb_2Te_3O_8$	345.90	3172.80	$-1994.38 \cdot 10^{-3}$	$2087.38 \cdot 10^5$	1.10
$Ge(TeO_3)_2$	192.89	300.59	$-70.44 \cdot 10^{-3}$	$119.89 \cdot 10^5$	0.26

Table 3 Standard molar thermodynamic functions of $PbTeO_3$, 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}
400	172.26	11928.65	142.43
450	185.89	17717.06	146.52
500	198.64	23772.45	151.09
550	210.92	30217.86	155.98
600	222.95	37135.32	161.06
650	234.87	44581.59	166.28
700	246.74	52597.25	171.60

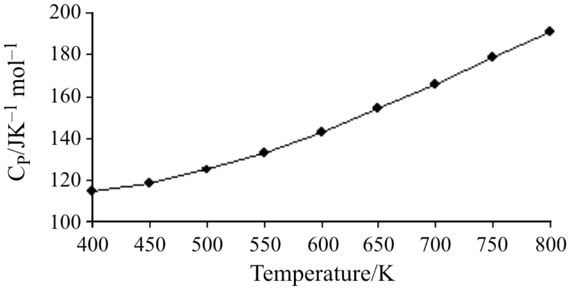

Fig. 1 Dependence of molar heat capacity of $PbTeO_3$ on temperature in the temperature range 300–800 K, calculated by the polynomial $C_{\mathrm{p,m}}(T)$/J K^{-1} mol^{-1}=–51.42+ $287.24 \cdot 10^{-3} T + 81.20 \cdot 10^5 T^{-2}$

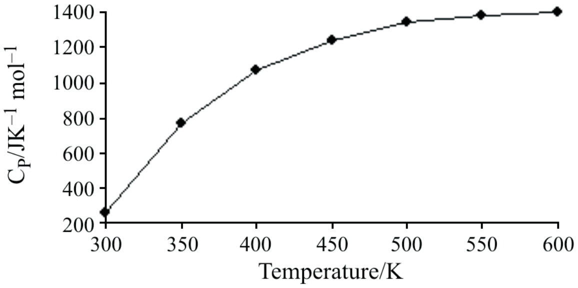

Fig. 2 Dependence of molar heat capacity of $Pb_2Te_3O_8$ on temperature in the temperature range 300–600 K, calculated by the polynomial $C_{\mathrm{p,m}}(T)$/J K^{-1} mol^{-1}= $3172.80 - 1994.38 \cdot 10^{-3}\, T - 2087.72 \cdot 10^5 T^{-2}$

the least squares method to calculate the coefficients in the equation for C_p (Table 2):

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

The values of $\Delta_0^T S_m^0$ are shown in the same Table 2. The value for $PbTeO_3$ was reported by other authors [7] while these for $Ge(TeO_3)_2$ and $Pb_2Te_3O_8$ were calculated by the method of Kelly and Koumok [8].

Using the data in Table 2. $\Delta_0^T S_m^0$, $\Delta_T^T H_m^0$, $\Phi_m^0 + \Delta_0^T H_m^0 / T$ were calculated for the tellurites studied. The results for these thermodynamic functions are summarized in Tables 3–5 and Figs 1–3.

Table 4 Standard molar thermodynamic functions of $Pb_2Te_3O_8$; 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	345.90	0.00	345.90
300	347.51	482.45	345.91
350	429.17	27298.53	351.17
400	553.40	73982.48	368.44
450	690.46	132249.36	396.57
500	827.08	197129.38	432.82
550	957.30	265458.34	474.65
600	1078.53	335127.81	520.00

Table 5 Standard molar thermodynamic functions of $Ge(TeO_3)_2$, 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	192.89	0.00	192.89
300	193.86	290.85	192.89
350	219.01	8466.65	194.82
400	244.16	17893.61	199.42
450	168.18	28095.99	205.74
500	290.70	38788.31	213.12
550	311.67	49788.95	221.14
600	331.13	60976.78	229.50
650	349.21	72267.98	238.03
700	366.01	83602.66	246.58

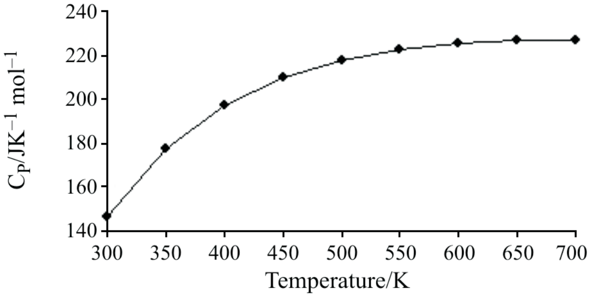

Fig. 3 Dependence of molar heat capacity of $Ge(TeO_3)_2$ on temperature in the temperature range 300–700 K, calculated by the polynomial $C_{p,m}(T)$/J K^{-1} mol^{-1}= $300.59–70.44\cdot10^{-3}\,T–119.89\cdot10^5 T^{-2}$

Conclusions

The temperature dependencies of molar heat capacities of germanium and lead tellurites 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.

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