MOLAR HEAT CAPACITIES OF THE TELLURITES $CoTeO_3$, $MnTeO_3$ AND $MnTe_6O_{13}$ IN MEDIUM TEMPERATURE RANGE

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The temperature dependence of the molar heat capacities of the tellurites $CoTeO_3$, $MnTeO_3$ and $MnTe_6O_{13}$ 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: *molar heat capacity, tellurites of cobalt, tellurites of manganese*

Introduction

The presented paper is the continuation of the previous studies of the authors [1]. The data concerning the tellurites of cobalt and manganese are rather scarce [2–4]. In [2], cobalt tellurites are obtained by heating $CoCO_3$ and TeO_2 in a nitrogen atmosphere. The compounds are synthesised at 720 K, and at 1080 K they melt. In [3], while drawing the T–X state diagram of the system MnO–TeO_2, it is found that $MnTe_6O_{13}$ is synthesised too. In [4], Trömel and Schmidt studied the solid phases of $\{x\mathrm{MnO}+(1-x)\mathrm{TeO_2}\}$ by X-ray analysis. The compounds $MnTeO_3$, $MnTe_2O_5$, $Mn_2Te_3O_8$ and $MnTe_6O_{13}$ are obtained and their crystal structure are determined. Apart from melting temperatures no other properties had been studied.

The aim of this research is to determine experimentally the specific heats and to calculate the thermodynamic values. These data are not available in literature.

Experimental

$CoCO_3$ and $MnCO_3$ are used for the synthesis of the tellurites of cobalt and manganese. Their purity is higher than 99.99. TeO_3 is qualified as 'exceptionally pure 7–4'. Very well homogenised mechanical mixtures of the carbonates and TeO_2 corresponding to the stoicheometry of the compounds are heated in an inert gas medium at 970 K for $CoTeO_3$ and $MnTeO_3$, and 950 K for $MnTe_6O_{13}$. After heating the samples for 2 h they are cooled, ground and subjected to thermal treatment at the same temperatures and for the same time. The samples are studied by chemical and X-ray phase analysis. Chemical analysis for metal ions are done by volume analysis [5], and TeO_2 is analysed iodometrically and gravimetrically [6, 7]. The results obtained are shown in Table 1. X-ray analysis is carried out on TURM–61 M apparatus at Fe anode and K_α emission. All peaks on the X-ray pattern correspond to those published in the literature regarding their intensity and interplanar distances.

Heat capacities are determined using DSC–111 differential scanning calorimeter ('Setaram', France). For that purpose, the tellurites are ground and shifted through a sieve with opening 0.25 mm^2. The technic used is described in [8, 9], each results for a sample is directly compared with the corresponding results for sappfhire. Four separate determinations of C_p in the whole temperature interval were made for each tellurite and the average values were calculated.

Table 1 Mass fractions of MeO and TeO_2 in the tellurites $CoTeO_3$, $MnTeO_3$ and $MnTe_6O_{13}$

Compound	Calculated		Chemical analyis					
	MeO	TeO_2	MeO			TeO_2		
$CoTeO_3$	0.3195	0.6805	0.3201	0.3194	0.3190	0.6810	0.6801	0.6806
$MnTeO_3$	0.3077	0.6923	0.3181	0.3075	0.3079	0.6920	0.6924	0.6923
$MnTe_6O_{13}$	0.0690	0.9316	0.0689	0.0692	0.0694	0.9312	0.9308	0.9311

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Table 2 Experimental molar heat capacities $C_{p,m}$ of $CoTeO_3$, $MnTeO_3$ and $MnTe_6O_{13}$

T/K	$C_{p,m}$/J K^{-1} mol^{-1}			T/K	$C_{p,m}$/J K^{-1} mol^{-1}		
	$CoTeO_3$	$MnTeO_3$	$MnTe_6O_{13}$		$CoTeO_3$	$MnTeO_3$	$MnTe_6O_{13}$
400	74	126	462	500	90	133	502
410	75	126	464	510	92	133	502
420	76	127	467	520	92	133	518
430	78	128	466	530	44	134	524
440	79	129	468	540	95	133	526
450	81	130	472	550	95	133	526
460	84	130	477	560	97	133	524
470	85	130	481	570	98		531
480	87	132	484	580	99		531
490	88	133	496				

Table 3 Standard molar thermodynamic functions $\Delta_0^{T'}S_m^0$ and temperature dependences of the molar heat capacities $C_{p,m}$ of $CoTeO_3$, $MnTeO_3$ and $MnTe_6O_{13}$, T'=298.15 K

Compound	$\Delta_0^{T'}S_m^0$/J K^{-1} mol^{-1}	a	b	c	$\delta C_p/C_p\cdot10^2$
$CoTeO_3$	123.36	15.94	$145.71\cdot10^{-3}$	$0.046\cdot10^5$	0.96
$MnTeO_3$	150.59	139.34	$5.12\cdot10^{-3}$	$24.63\cdot10^5$	0.47
$MnTe_6O_{13}$	482.29	170.33	$594.96\cdot10^{-3}$	$-78.52\cdot10^5$	0.92

Result and discussion

The obtained values for the temperature interval 400–580 K are shown in Table 2. The temperature dependencies 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 (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 values from the Table 2 are processed by computer and the parameters of Eq. (2) are evaluated. The coefficients a, b and c are given in Table 3.

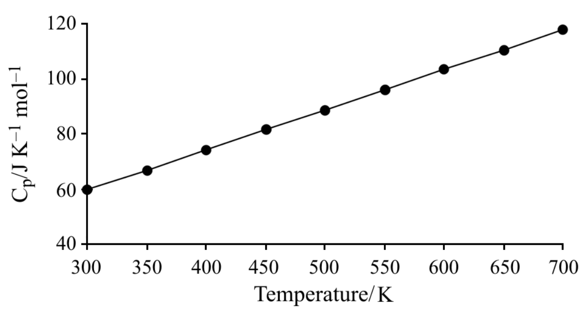

Fig. 1 Dependence of molar heat capacity of $CoTeO_3$ on temperature in the temperature range 300–700 K, calculated by the polynomial $C_{p,m}(T)$/J K^{-1} mol^{-1}=15.94+145.71·10^{-3}T–0.046·10$^5T^{-2}$

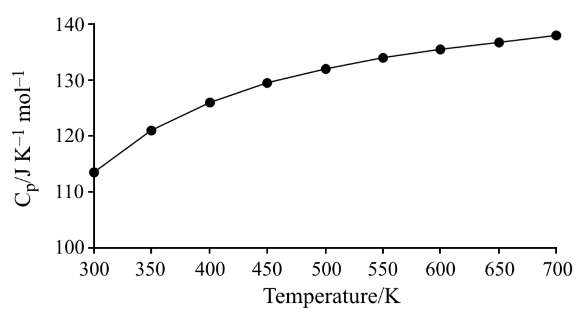

Fig. 2 Dependence of molar heat capacity of $MnTeO_3$ on temperature in the temperature range 300–700 K, calculated by the polynomial $C_{p,m}(T)$/J K^{-1} mol^{-1}=139.34+5.12·10^{-3}T–24.63·10$^5T^{-2}$

The standard thermodynamic characteristics and the temperature dependences of the heat capacities of $CoTeO_3$, $MnTeO_3$ and $MnTe_6O_{13}$ are presented in Table 3 and Figs 1–3.

The standard molar entropy (at 298.15 K) is calculated by ion increments' method introduced by Kumok [10] and for different temperature by formula (3) [11]:

$$\Delta_0^T S_m^0 = S_T^0 - S_{298.15}^0 = \int_{298.15}^{T} \frac{C_p(T)}{T} dT \qquad (3)$$

The changes in enthalpies are calculated analogically by formula (4):

$$\Delta_0^T H_m^0 = H_T^0 - H_{298.15}^0 = \int_{298.15}^{T} C_p(T) dT \qquad (4)$$

The functions Φ^* and Φ^{**} allows the calculation of the free Gibbs energy. These functions correspond more to system of the modern thermodynamic manuals. The base temperature for Φ^{**} shows 298.15 K, and for Φ^* we accept 0 K for base temperature. These

Table 4 Molar thermodynamic functions of $CoTeO_3$, T'=298.15 K

T/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	59.31	123.36	0.00	123.36
300	59.60	123.76	118.90	123.36
350	66.90	133.49	3281.34	124.12
400	74.20	142.90	6808.57	125.88
450	81.49	152.06	10700.42	128.28
500	88.78	161.02	14956.77	131.11
550	96.06	169.83	19577.56	134.23
600	103.35	178.50	24562.74	137.56
650	110.64	187.06	29912.27	141.04
700	117.93	195.53	35626.14	144.63

Table 5 Molar thermodynamic functions of $MnTeO_3$, T'=298.15 K

T/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	113.13	130.59	0.00	130.59
300	113.51	131.35	226.64	130.59
350	121.02	149.45	6103.98	132.01
400	125.99	165.96	12287.34	135.24
450	129.48	181.01	18678.97	139.50
500	132.05	194.79	25220.24	144.35
550	134.01	207.47	31873.82	149.52
600	135.57	219.20	38614.84	154.84
650	136.84	230.10	45426.07	160.22
700	137.90	240.28	52295.21	165.58

Table 6 Molar thermodynamic functions of $MnTe_6O_{13}$, T'=298.15 K

T/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	436.05	482.29	0.00	482.29
300	436.06	485.21	872.11	482.30
350	442.66	552.78	22795.75	487.65
400	457.39	612.79	45272.04	499.61
450	476.84	667.75	68612.55	515.28
500	499.22	719.13	93004.24	533.12
550	523.51	767.83	118566.08	552.26
600	549.12	814.48	145377.38	572.18
650	575.64	859.47	173493.05	592.56
700	602.83	903.12	202952.30	613.19

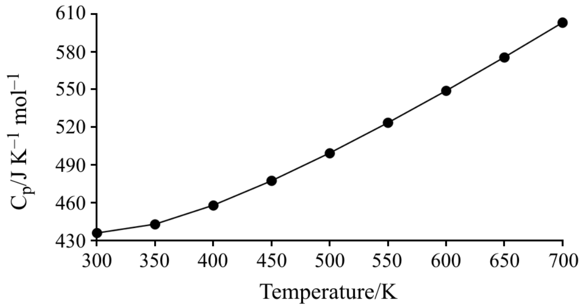

Fig. 3 Dependence of molar heat capacity of $MnTe_6O_{13}$ on temperature in the temperature range 300–700 K, calculated by the polynomial $C_{p,m}(T)$/J K^{-1} mol^{-1}=170.33+594.96·10^{-3}T+78.52·10$^5T^{-2}$

functions are affected by the changes in heat capacities of solid compounds on temperature by the following dependence:

$$\Phi_T^{**} = S_T^0 - \frac{H_T^0 - H_{298.15}^0}{T} \tag{5}$$

$$\Phi_T^{*} = \Phi_T^{**} - \frac{H_{298.15}^0 - H_0^0}{T} \tag{6}$$

The calculation of the two functions is needed to the extent of getting acquainted with Gibbs thermodynamic potential for formation of compounds. The functions Φ^* and Φ^{**} permits the calculation of free Gibbs energy, which is an important factor for thermodynamical interpretation of complex multi-co mponent systems. In Tables 4–6 below the cited thermodynamic potential $\Phi_m^0 + \Delta_0^{T'} H_m^0 / T$ is shown the Gibbs potential Φ^{**}. Using the results from Table 3 and Eqs (3)–(4), the thermodynamic functions of $CoTeO_3$, $MnTeO_3$ and $MnTe_6O_{13}$ are calculated (Tables 4–6).

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