J Therm Anal Calorim (2012) 107:809–812
DOI 10.1007/s10973-011-1325-z

Heat capacity and thermodynamic properties of tellurites $Yb_2(TeO_3)_3$, $Dy_2(TeO_3)_3$ and $Er_2(TeO_3)_3$

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Received: 16 December 2010 / Accepted: 6 January 2011 / Published online: 12 February 2011

Abstract The experimental results obtained for the specific molar heat capacity of the tellurites $Yb_2(TeO_3)_3$, $Dy_2(TeO_3)_3$ and $Er_2(TeO_3)_3$ are processed by the least squares method. The temperature dependence of the specific molar heat capacity derived is used to determine the thermodynamic properties: entropy $\left(\Delta_{T'}^{T} S_m^0\right)$, enthalpy $\left(\Delta_{T'}^{T} H_m^0\right)$ and Gibbs function $\left(\Delta_{T'}^{T} G_m^0\right)$ of the tellurites $Yb_2(TeO_3)_3$, $Dy_2(TeO_3)_3$ and $Er_2(TeO_3)_3$.

Keywords Heat capacity · Thermodynamic properties · Tellurites of $Yb_2(TeO_3)_3$, $Dy_2(TeO_3)_3$, $Er_2(TeO_3)_3$

Introduction

The tellurites of rare earth elements are little known and studied inorganic substances but the interest towards them has been increasing recently. They are used in modern technology, for the preparation of optical glasses with special properties for electronics, components in medicines, as well as for the production of plant protection chemicals in agriculture.

The thermodynamic properties of the compounds studied can be used to develop industrial technologies for synthesis of rare earth containing compounds and preparation of products based on them with certain properties [1, 2].

The aim of this work is to study the temperature dependence of the specific molar capacity and the thermodynamic properties of the tellurites $Yb_2(TeO_3)_3$, $Dy_2(TeO_3)_3$ and $Er_2(TeO_3)_3$.

Experimental, results and discussion

The tellurites of rare earth elements $Yb_2(TeO_3)_3$, $Dy_2(TeO_3)_3$ and $Er_2(TeO_3)_3$, are synthesized from tellurium dioxide (TeO_2) and oxides of the rare earth elements: Yb_2O_3, Dy_2O_3 and Er_2O_3 of high purity 99.999. The conditions under which the synthesis was carried out are elaborated by the authors. The oxides preliminarily weighed to amounts corresponding to the stoichiometry of the goal product are mixed, homogenized and placed in ampoules which are then vacuumed. The substances are melted in an electric crucible oven. After reaching the melting temperature, it is maintained for 48 h and then the oven is switched off and cooled down. The ampoules are then opened and the samples synthesized are homogenized and separated for chemical, differential thermal and X-ray analyses [3–5].

The composition of the tellurites of rare earth elements studied is determined by chemical analysis. The metal ions in the rare earth oxides Me_2O_3 are determined by the complexonometric method with 0.05 M solution of complexon III and orange-xylene as indicator [3]. The tellurite ions in the oxides of the type TeO_2 are determined iodometrically and gravimetrically [4]. The results obtained showed that the compounds synthesized correspond by their stoichiometric composition to $Yb_2(TeO_3)_3$, $Dy_2(TeO_3)_3$ and $Er_2(TeO_3)_3$.

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Table 1 Experimental molar heat capacities $C_{p,\mathrm{m}}$ of $Yb_2(TeO_3)_3$, $Dy_2(TeO_3)_3$, $Er_2(TeO_3)_3$

T/K	$C_{p,\mathrm{m}}$/J K^{-1} mol^{-1}		
	$Yb_2(TeO_3)_3$	$Dy_2(TeO_3)_3$	$Er_2(TeO_3)_3$
387	307	294	354
398	316	288	349
408	316	293	352
418	320	292	351
428	320	288	352
438	327	286	355
448	323	288	359
458	316	292	364
467	321	284	362
477	324	287	363
487	320	283	362
497	328	280	362
507	334	275	362
517	338	263	362
527	337	270	366
537	338	288	386
547	340	285	389
557	345	291	387
567	333	282	388
577	336	278	388
587	338	284	388

The degree of synthesis is determined by X-ray analysis of the tellurites, performed on URD-6 apparatus (Germany) in regime of diffractometric recording using Cu-K$_\alpha$ emission and Ni-filter for the β radiation. The integral intensities of the diffraction maxima are determined gravimetrically [4].

To find the temperatures of the phase transitions in the tellurites synthesized, thermal analysis is carried out on a derivatograph OD-102 (MOM, Hungary).

The specific heat capacity of the tellurites is determined using differential scanning calorimeter DSC-III (Setaram, France). The working temperature interval is 300–600 K. The samples are finely ground and sieved through a 0.25 mm^2 sieve. The experimental conditions have been described earlier [6]. For each tellurite, four samples are prepared and the average values are calculated. The

Table 3 Molar thermodynamic functions of $Yb_2(TeO_3)_3$, $T' = 298.15$ K

T/K	$C_{p,\mathrm{m}}$/J K^{-1} mol^{-1}	$\Delta_{T'}^{T}H_m^0$/J K^{-1} mol^{-1}	$\Delta_{T'}^{T}S_m^0$/J mol^{-1}	$\Delta_{T'}^{T}G_m^0$/J K^{-1} mol^{-1}
298.15	311.72	0	371.60	371.60
300	311.90	623.63	373.68	371.61
350	316.80	16337.56	422.12	375.44
400	322.37	32314.73	464.78	383.99
450	328.33	48581.03	503.09	395.14
500	334.54	65151.95	538.01	407.70
550	340.90	82037.40	570.19	421.03
600	347.37	99243.94	600.13	434.72
650	353.92	116776.12	628.19	448.54
700	360.53	134637.23	654.66	462.32
750	367.17	152829.64	679.76	475.99
800	373.85	171355.14	703.67	489.48
850	380.55	190215.09	726.54	502.75
900	387.27	209410.56	748.48	515.80
950	394.01	228942.41	769.60	528.60
1000	400.75	248811.30	789.98	541.17

Table 4 Molar thermodynamic functions of $Dy_2(TeO_3)_3$, $T' = 298.15$ K

T/K	$C_{p,\mathrm{m}}$/J K^{-1} mol^{-1}	$\Delta_{T'}^{T}H_m^0$/J K^{-1} mol^{-1}	$\Delta_{T'}^{T}S_m^0$/J mol^{-1}	$\Delta_{T'}^{T}G_m^0$/J K^{-1} mol^{-1}
298.15	257.86	0	388.30	388.30
300	258.12	515.98	390.02	388.30
350	263.67	13567.57	430.25	391.49
400	267.97	26862.28	465.75	398.59
450	271.54	40352.15	497.52	407.85
500	274.66	54008.38	526.30	418.28
550	277.48	67812.66	552.61	429.31
600	280.10	81752.78	576.87	440.61
650	282.59	95820.28	599.38	451.97
700	284.96	110009.12	620.41	463.26
750	287.27	124314.88	640.15	474.40
800	289.51	138734.23	658.77	485.35
850	291.71	153264.64	676.38	496.07
900	293.88	167904.11	693.12	506.56
950	296.01	182651.11	709.06	516.80
1000	298.13	197504.37	724.30	526.80

Table 2 Standard molar entropy $\Delta_0^{T'}S_m^0$, coefficients a, b, c and errors, $T' = 298.15$ K

Compounds	$\Delta_0^{T'}S_m^0$/J K^{-1} mol^{-1}	a	b	c	$10^2\frac{\delta Cp}{Cp}$
$Yb_2(TeO_3)_3$	371.60	263.76	136.34×10^{-3}	6.52×10^5	1.91
$Dy_2(TeO_3)_3$	388.30	259.65	39.69×10^{-3}	-12.09×10^5	4.37
$Er_2(TeO_3)_3$	394.10	250.53	230.02×10^{-3}	-9.24×10^5	2.43

Table 5 Molar thermodynamic functions of $Er_2(TeO_3)_3$, $T' = 298.15$ K

T/K	$C_{p,\mathrm{m}}$/J K^{-1} mol $^{-1}$	$\Delta_{T'}^{T}H_m^0$/J K^{-1} mol $^{-1}$	$\Delta_{T'}^{T}S_m^0$/J mol^{-1}	$\Delta_{T'}^{T}G_m^0$/J K^{-1} mol $^{-1}$
298.15	308.67	0	394.10	394.10
300	309.27	617.94	396.17	394.11
350	323.50	16442.26	444.92	397.95
400	336.77	32951.64	488.99	406.62
450	349.48	50109.40	529.40	418.04
500	361.85	67893.54	566.86	431.08
550	373.99	86290.06	601.92	445.03
600	385.98	105289.64	634.98	459.49
650	397.86	124885.80	666.34	474.21
700	409.66	145073.94	696.26	489.01
750	421.40	165850.67	724.92	503.79
800	433.11	187213.44	752.49	518.48
850	444.77	209160.33	779.10	533.03
900	456.41	231689.81	804.85	547.42
950	468.03	254800.70	829.84	561.63
1000	479.64	278492.03	854.14	575.65

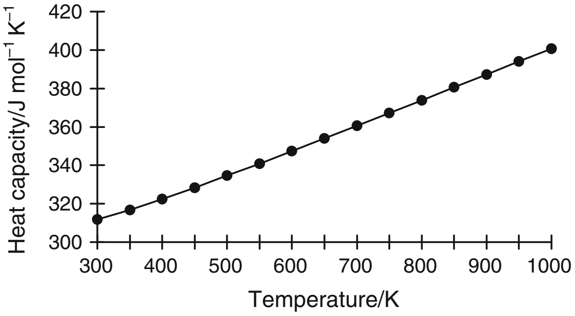

Fig. 1 Dependence of molar heat capacity of $Yb_2(TeO_3)_3$ on temperature in the temperature range 300–1000 K, calculated by the polynomial $C_{p,\mathrm{m}}$ (T)/(J K^{-1} mol^{-1}) $= 263.76 + 136.34 \times 10^{-3}$ T $+ 6.52 \times 10^5$ T^{-2}

relative error did not exceed 0.1%. The results obtained are presented in Table 1. They are further computer processed by the least squares method [7–9] to find the coefficients a, b and c in the equation for $C_{p,\mathrm{m}}(T)$ (Table 2):

$$C_{p,\mathrm{m}}(T) = a + bT - cT^{-2}. \quad (1)$$

For the determination of the temperature dependencies of the thermodynamic values, the standard molar entropy $\left(\Delta_0^{T'}S_m^0\right)$ is calculated by the method of Kelly and Koumok [10–12]. The calculated coefficients a, b and c in Eq. 1, $\Delta_0^{T'}S_m^0$, as well as the calculation errors are shown in Table 2.

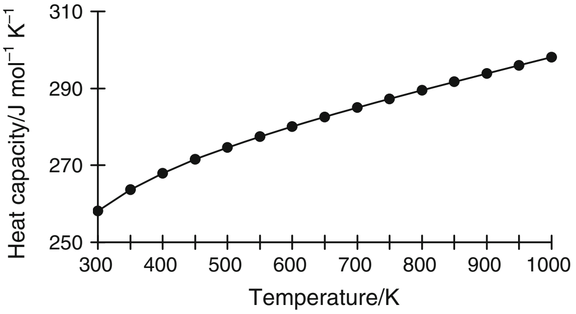

Fig. 2 Dependence of molar heat capacity of $Dy_2(TeO_3)_3$ on temperature in the temperature range 300–1000 K, calculated by the polynomial $C_{p,\mathrm{m}}$ (T)/(J K^{-1} mol^{-1}) $= 259.65 + 39.69 \times 10^{-3}$ T-12.09×10^5 T^{-2}

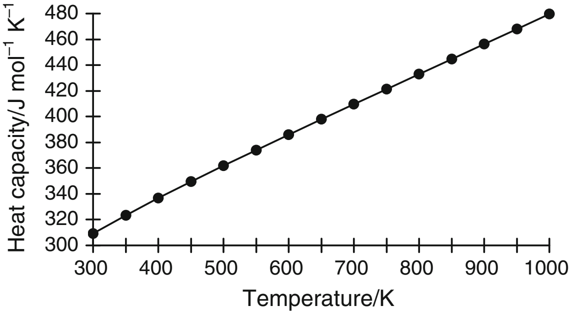

Fig. 3 Dependence of molar heat capacity of $Er_2(TeO_3)_3$ on temperature in the temperature range 300–1000 K, calculated by the polynomial $C_{p,\mathrm{m}}$ (T)/(J K^{-1} mol^{-1}) $= 250.53 + 230.02 \times 10^{-3}$ T-9.24×10^5 T^{-2}

The specific molar heat capacities are calculated according to Eq. 1, and they are then used to find the temperature dependencies of the entropy $\left(\Delta_{T'}^{T}S_m^0\right)$,, enthalpy $\left(\Delta_{T'}^{T}H_m^0\right)$ and Gibbs function $\left(\Delta_{T'}^{T}G_m^0\right)$ using the following equations:

$$\Delta_{T'}^{T}S_m^0 = \Delta_0^{\prime}S_m^0 + \int\limits_{T'}^{T} Cp/T \cdot dT \quad (2)$$

$$\Delta_{T'}^{T}H_m^0 = \int\limits_{T'}^{T} Cp \cdot \mathrm{d}T \quad (3)$$

$$\Delta_{T'}^{T}G_m^0 = \Delta_0^{T}S_m^0 - \Delta_{T'}^{T}H_m^0/T. \quad (4)$$

The results from the calculations of these thermodynamic functions are presented in Tables 3, 4 and 5 and Figs. 1, 2 and 3.

Conclusions

This study is continuation of our research in the field of thermal and thermodynamic properties of some metal tellurites [13]. The experimental data on the molar heat capacity of the tellurites $Yb_2(TeO_3)_3$, $Dy_2(TeO_3)_3$ and $Er_2(TeO_3)_3$ are processed by the least squares method and the temperature dependences of the molar heat capacities of these compounds are derived. The equation is used to calculate the thermodynamic properties: entropy $\left(\Delta_{T\prime}^{T}S_{m}^{0}\right)$, enthalpy $\left(\Delta_{T\prime}^{T}H_{m}^{0}\right)$ and Gibbs function $\left(\Delta_{T\prime}^{T}G_{m}^{0}\right)$ for the tellurites $Yb_2(TeO_3)_3$, $Dy_2(TeO_3)_3$ and $Er_2(TeO_3)_3$.

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