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THERMODYNAMIC PROPERTIES OF RARE EARTHS TELLURITES

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Abstract

Tellurites of rare earth elements of the type $Ln_2Te_4O_{11}$, where Ln = Er,Yb and Tm are synthesized. Their molar heat capacities are experimentally determined. The temperature dependences of their molar heat capacities are determined using the least squares method. The thermodynamic properties are calculated: entropy, enthalpy and Gibbs function.

Key words: *molar heat capacity, thermodynamic properties, tellurites, rare earth elements, enthalpy*

1. INTRODUCTION

The studies on the tellurites of rare earth elements can be used to fill in data in an important branch of inorganic chemistry as chemistry of tellurium and rare earth elements. It is practically important to know the thermodynamic characteristics of the compounds studied $Er_2Te_4O_{11}$, $Yb_2Te_4O_{11}$, $Tm_2Te_4O_{11}$ since these tellurites are widely used in modern technologies for preparation of optical glasses, in ceramic industry, medicine and agriculture (Kim and al., 1996; Hirano and al., 2001; Masson and al.,1986). Nowadays, a great number of publications are related to studies on various types of tellurites and their application (Lin and Navotsky, 1998; Hamlata and al., 2013; Rimpi and al., 2013; Pankajavalli and al., 2013; Tavlieva and Vlaev, 2007).

The survey of the available literature did not give data related to the preparation and studies on $Er_2Te_4O_{11}$, $Yb_2Te_4O_{11}$, $Tm_2Te_4O_{11}$.

The aim of the present work is to derive the temperature dependence of molar heat capacity and calculate the thermodynamic properties of $Er_2Te_4O_{11}$, $Yb_2Te_4O_{11}$ and $Tm_2Te_4O_{11}$.

2. EXPERIMENTAL

The tellurites of rare earth elements $Er_2Te_4O_{11}$, $Yb_2Te_4O_{11}$ and $Tm_2Te_4O_{11}$ are synthesized from tellurium dioxide (TeO_2) and oxides of the rare earth elements: Yb_2O_3, Er_2O_3 and Tm_2O_3 of high purity 99.999. 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 synthesized samples are homogenized and separated for chemical, differential thermal and X-ray analyses (Umlang and al., 1971; Nazarenko and Ermakov, 1974; Hillebrand and al., 1953).

The composition of the tellurites of rare earth elements 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 (Umlang and al., 1971). The tellurite ions in

the oxides of the type TeO_2 are determined iodometrically and gravimetrically[10]. The results obtained showed that the compounds synthesized correspond to their stoichiometric composition to $Er_2Te_4O_{11}$, $Yb_2Te_4O_{11}$ and $Tm_2Te_4O_{11}$.

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_α emission and Ni-filter for the β - radiation. The integral intensities of the diffraction maxima are determined gravimetrically (Nazarenko and Ermakov, 1974).

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 molar heat capacity of the tellurites is determined using differential scanning calorimeter DSC-III (Setaram, France). The working temperature interval is 448-600 K. The samples are finely ground and sieved through a 0.25 mm^2 sieve. The experimental conditions have been described earlier[12]. For each tellurite, 4 samples are prepared and the average values are calculated (Atanasova and Baikusheva-Dimitrova, 2012).

The relative error did not exceed 0.1 %. The experimental results obtained are presented in Table 1.

3. CALCULATION PROCEDURE, RESULTS AND DISCUSSION

The experimental results are further computer processed by the least squares method (Kafarov, 1976; Vuchkov and Stoyanov, 1986; Bojanov and Vuchkov, 1973) to find the coefficients *a, b* and *c* in the equation for the molar heat capacity (Table 2):

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

The molar heat capacities are calculated according to eq 1, and they are then used to find the temperature dependencies of the entropy ($\Delta_{T'}^{T} S_m^0$), enthalpy ($\Delta_{T'}^{T} H_m^0$) and Gibbs function (- $\Delta_{T'}^{T} G_m^0$ /T) using the following equations (Karapetianc, 1975; Norman, 1988):

$$\Delta_{T'}^{T} S_m^0 = \Delta_0^{T'} S_m^0 + \int_{T'}^{T} Cp,m/T.dT \quad (2)$$

$$\Delta_{T'}^{T} H_m^0 = \int_{T'}^{T} Cp,m.dT \quad (3)$$

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

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Table 1. Experimental molar heat capacities $C_{p,m}$ of $Er_2Te_4O_{11}$, $Yb_2Te_4O_{11}$ and $Tm_2Te_4O_{11}$

T/K	$C_{p,m}/(J.K^{-1}.mol^{-1})$		
	$Er_2Te_4O_{11}$	$Yb_2Te_4O_{11}$	$Tm_2Te_4O_{11}$
388	391	388	381
398	387	394	379
408	391	397	377
418	395	400	383
428	390	396	381
438	395	396	387
448	393	395	391
458	389	386	387
467	391	388	391
477	397	392	388
487	384	378	382
497	391	387	380
507	394	394	390
517	395	394	390
527	399	390	395
537	397	396	401
547	396	397	402
557	397	398	403
567	385	373	398
577	393	374	396
587	391	373	399

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

Compound	$\Delta_0^{T'}S_m^0$ / J. K^{-1}. mol^{-1}	a	b	c	$10^2 x \frac{\delta Cp}{Cp}$
$Er_2Te_4O_{11}$	473.60	392.10	$5.18x10^{-3}$	$4.98x10^5$	0.78
$Yb_2Te_4O_{11}$	451.10	247.15	$205.58x10^{-3}$	$-104.03x10^5$	1.03
$Tm_2Te_4O_{11}$	457.80	71.50	$472.22x10^{-3}$	$-199.75x10^5$	1.26

For the determination of the temperature dependencies of the thermodynamic values, the standard molar entropy ($\Delta_0^{T'}S_m^0$) is calculated by the method of Kelly and Koumok (Kireev, 1975; Koumok, 1987; Kassenov and Pashinkin, 1989; Atanasova and Baikusheva, 2012).

The calculated coefficients *a, b, c* in eq.(1), $\Delta_0^{T'}S_m^0$, as well as the calculation errors are shown in Table 2.

The results from the calculations of these thermodynamic functions are presented in Tables 3-5 and Figures 1-3.

Table 3. Standard molar thermodynamic functions of $Er_2Te_4O_{11}$, $T' = 298.15$ K

T/K	$C_{p,m}$/ J. K^{-1}. mol^{-1}	$\Delta_{T'}^{T}H_m^0$ / J. mol^{-1}	$\Delta_{T'}^{T}S_m^0$ / J. K^{-1} mol^{-1}	$(-\Delta_{T'}^{T}G_m^0/T)$/ J. K^{-1}. mol^{-1}
450	391.97	59329.20	634.42	502.58
500	392.69	78946.55	675.76	517.86
550	393.30	98596.98	713.21	533.95
600	393.82	118275.45	747.46	550.33
650	394.29	137978.48	778.99	566.72
700	394.71	157703.58	808.23	582.94
750	395.10	177448.94	835.48	598.88
800	395.46	197213.16	860.99	614.47
850	395.81	216995.22	884.98	629.69
900	396.15	236794.30	907.61	644.51
950	396.47	256609.75	929.04	658.92
1000	396.78	276441.06	949.38	672.94

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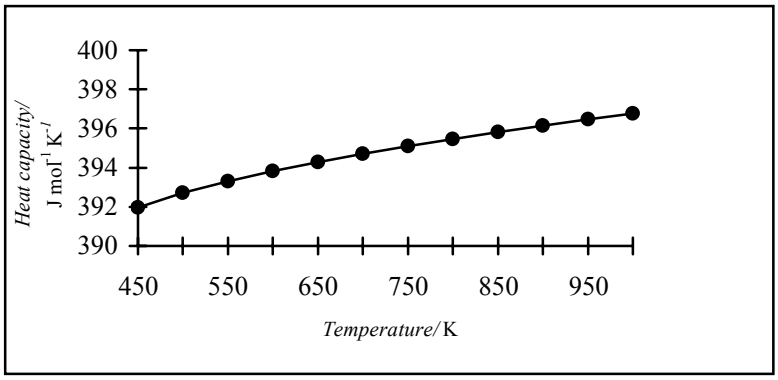


Figure 1. Dependence of molar heat capacity of $Er_2Te_4O_{11}$ on temperature (450-1000 K).

$C_{p,m}(T)/(J\ mol^{-1}\ K^{-1}) = 392.10 + 5.18x10^{-3}xT - 4.98x10^{5}xT$

Table 4. Standard molar thermodynamic functions of $Yb_2Te_4O_{11}$, $T' = 298.15$ K

T/K	$C_{p,m}$/ $J.K^{-1}.mol^{-1}$	$\Delta_{T'}^{T}H_m^0$ / J. mol^{-1}	$\Delta_{T'}^{T}S_m^0$ / $J.K^{-1}\ mol^{-1}$	$(-\Delta_{T'}^{T}G_m^0/T)$/ $J.K^{-1}.mol^{-1}$
450	391.03	60981.40	616.88	481.37
500	391.55	80533.20	658.08	497.02
550	394.61	100178.63	695.53	513.39
600	399.40	120022.77	730.06	530.02
650	405.40	140138.36	762.26	546.66
700	412.29	160577.38	792.55	563.15
750	419.83	181377.91	821.25	579.41
800	427.87	202568.56	848.60	595.39
850	436.29	224171.16	874.79	611.06
900	445.02	246202.72	899.97	626.41
950	453.98	268676.66	924.27	641.45
1000	463.13	291603.72	947.79	656.18

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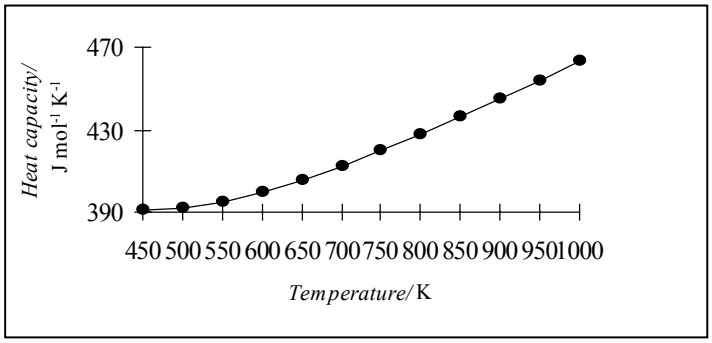


Figure 2. Dependence of molar heat capacity of $Yb_2Te_4O_{11}$ on temperature (450-1000 K).

$C_{p,m}$ (T)/(J mol^{-1} K^{-1}) = 247.15 + 205.58x10^{-3} xT +104.03x10^{5}xT^{-2}

Table 5. Standard molar thermodynamic functions of $Tm_2Te_4O_{11}$, T' = 298.15 K

T/K	$C_{p,m}$/ J. K^{-1}. mol^{-1}	$\Delta_{T'}^{T}H_m^0$ / J. mol^{-1}	$\Delta_{T'}^{T}S_m^0$ / J.K^{-1}. mol^{-1}	(- $\Delta_{T'}^{T}G_m^0$ /T)/ J. K^{-1}. mol^{-1}
450	382.64	60288.51	621.97	488.00
500	387.51	79517.62	662.49	503.45
550	397.25	99120.22	699.85	519.63
600	410.32	119298.06	734.95	536.12
650	425.72	140190.83	768.39	552.71
700	442.82	161898.31	800.56	569.27
750	461.18	184493.67	831.73	585.74
800	480.49	208031.78	862.10	602.06
850	500.53	232554.61	891.83	618.24
900	521.16	258094.78	921.02	634.25
950	542.24	284678.09	949.76	650.10
1000	563.70	312325.12	978.12	665.79

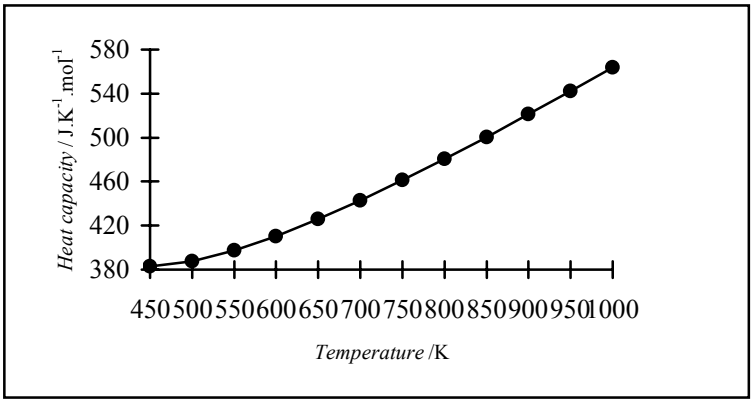


Figure 3. Dependence of molar heat capacity of $Tm_2Te_4O_{11}$ on temperature (450-1000 K).

$$C_{p,m}(T)/(\text{J mol}^{-1}\text{ K}^{-1}) = 71.50 + 472.22\text{x}10^{-3}\text{x}T + 199.75\text{x}10^{5}\text{x}T^{-2}$$

4. CONCLUSION

The present work is continuation of our research on tellurites of rare earth elements of the type $Ln_2(TeO_3)_3$, where Ln = Yb, Dy, Er (Atanasova and Baikusheva, 2012). The molar heat capacities of compounds of the type $Ln_2Te_4O_{11}$, където Ln= Tb, Er, Yb and Tm are determined. The temperature dependence of the molar heat capacity is also determined. The thermodynamic properties: entropy ($\Delta_{T'}^{T}S_m^0$), enthalpy ($\Delta_{T'}^{T}H_m^0$) and Gibbs function ($\Delta_{T'}^{T}G_m^0$) are calculated.

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