Journal of Thermal Analysis and Calorimetry, Vol. 68 (2002) 973–981

ENTHALPIES OF PHASE TRANSITIONS AND HEAT CAPACITY OF $TbCl_3$ AND COMPOUNDS FORMED IN $TbCl_3$–MCl SYSTEMS (*M*=K, Rb, Cs)*

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Abstract

The molar enthalpies of the solid–solid and solid–liquid phase transitions were determined by differential scanning calorimetry for pure $TbCl_3$ and KTb_2Cl_7, $RbTb_2Cl_7$, $CsTb_2Cl_7$, K_3TbCl_6, Rb_3TbCl_6 and Cs_3TbCl_6 compounds. Both types of compounds, i.e. M_3TbCl_6 and MTb_2Cl_7 (*M*=K, Rb, Cs) melt congruently and show additionally a solid–solid phase transition with a corresponding enthalpy $\Delta_{trs}H^0$ of 6.1, 7.6 and 7.0 kJ mol^{-1} for potassium, rubidium and caesium M_3TbCl_6 compounds and $\Delta_{trs}H^0$ of 17.1 (rubidium) and of 12.1 and 10.9 kJ mol^{-1} (caesium) for MTb_2Cl_7 compounds, respectively. The enthalpies of fusion were measured for all the above compounds with the exception of Rb_3TbCl_6 and Cs_3TbCl_6. The heat capacities of the solid and liquid compounds have been determined by differential scanning calorimetry (DSC) in the temperature range 300–1100 K. The experimental heat capacity strongly increases in the vicinity of a phase transition, but varies smoothly in the temperature ranges excluding these transformations. C_p data were fitted by an equation, which provided a satisfactory representation up to the temperatures of C_p discontinuity. The measured heat capacities were checked for consistency by calculating the enthalpy of formation of the liquid phase, which had been previously measured. The results obtained agreed satisfactorily with these experimental data.

Keywords: alkali metal chlorides, enthalpy of fusion, enthalpy of phase transition, heat capacity, terbium chloride

Introduction

The present work is a continuation of systematic investigations of thermodynamic, structural and electrical properties of lanthanide halide systems by a variety of experimental techniques, such as calorimetry [1–14], electrical conductivity and density measurements [15, 16], X-ray and neutron diffraction [17–20]. Theoretical techniques, such as phase diagram calculations and molecular dynamic simulations have also been performed [6, 21].

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* It was presented at CCTA 8 Zakopane, Poland

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

We report here the thermodynamic investigations of MCl–$TbCl_3$ systems in a liquid as well as in a solid state. Some preliminary results of these investigations were presented previously [22].

Mixtures of terbium chloride $TbCl_3$ with the alkali halides MCl (*M*=K, Rb, Cs) are characterised by the formation of MTb_2Cl_7 and M_3TbCl_6 congruently melting compounds [23]. Very few thermodynamic data were available in literature on M_3TbCl_6 compounds, except the enthalpy values related to the transitions in solid. No data were reported on the MTb_2Cl_7 compounds, either.

Experimental

Synthesis of $TbCl_3$, M_3TbCl_6 and MTb_2Cl_7 compounds (*M*=K, Rb, Cs) as well as experimental procedures were described in details elsewhere [2, 4, 22, 24–25]. Merck Suprapur alkali metal chlorides (min. 99.9%) were dehydrated by heating under a gaseous HCl atmosphere just above the melting point. Excess of HCl was removed by passing argon through the melt.

Table 1 Molar enthalpy of phase transitions of definite compounds from $TbCl_3$–MCl systems (*M*=K, Rb, Cs)

Compound	T_{trs}/K	$\Delta_{trs}H^0$/kJ mol^{-1}	T_{fus}/K	$\Delta_{fus}H^0$/kJ mol^{-1}	Reference
$TbCl_3$	790	13.8	854	20.8	this work
	783	14.2	855	19.4	[26]
	793	23.1	857	36.1	[27]
K_3TbCl_6	641	6.1	1049	53.2	this work
	640(DTA)	–	1049	–	[23]
	642(EMF)	8.1	–	–	[23]
Rb_3TbCl_6	686	7.6	– 1115	–	this work
	681(DTA)	–	–	–	[23]
	663(EMF)	10.6	–	–	[23]
Cs_3TbCl_6	672	7.0	1153	–	this work
	673(DTA)	–	–	–	[23]
	661(EMF)	7.2			[23]
KTb_2Cl_7	–	–	841	47.9	this work
	–	–	842	–	[23]
$RbTb_2Cl_7$	842	17.1	886	67.9	this work
	836	–	883	–	[23]
$CsTb_2Cl_7$	689; 926	12.1; 10.9	937	68.9	this work
	688, 928	–	945	–	[23]

Results and discussion

The difference in enthalpies determined during heating and cooling runs did not exceed 2%. Because some supercooling effects were observed, only temperatures taken during heating cycles are presented in this work (Table 1).

As the compounds investigated here undergo phase transitions on the experimental range, the heat capacity increases and decreases strongly in the vicinity of a phase transition but other varies smoothly. The classical heat capacity polynomial equation

$$C_p=a+bT+cT^2 \tag{1}$$

was used to fit the experimental results, which are presented in Figs 1 and 2. The parameters of Eq. (1) are presented in Table 2.

Table 2 Coefficients of the polynomial fitting of the experimental data for $TbCl_3$ and compounds from the $TbCl_3$–MCl systems according to Eq. (1); C_p (J mol^{-1} K^{-1}; SE standard error of estimation, (s) solid; (l)liquid

Compound	T_{range}/K	a/J mol^{-1} K^{-1}	$b \cdot 10^2$/ J mol^{-1} K^{-2}	$c \cdot 10^5$/ J mol^{-1} K^{-3}	SE/ J mol^{-1} K^{-1}
$TbCl_3$(s)	300–702	96.79	2.0566	–	1.15
$TbCl_3$(s)	730–780	40.67	10.0068	–	0.34
$TbCl_3$(s)	795–830	111.38	–	–	2.03
$TbCl_3$(l)	866–965	139.27	–	–	1.22
K_3TbCl_6(s)	300–598	279.42	–7.475	11.0	1.77
K_3TbCl_6(s)	648–960	634.29	–90.998	57.8	3.4
K_3TbCl_6(l)	1059–1094	348.32	–	–	2.2
Rb_3TbCl_6(s)	300–643	287.59	–12.352	18.0	2.11
Rb_3TbCl_6(s)	697–1030	645.26	–87.278	53.4	2.96
Rb_3TbCl_6(l)	–	–	–	–	–
Cs_3TbCl_6(s)	300–648	286.58	–13.705	20.9	2.21
Cs_3TbCl_6(s)	682–1049	578.79	–72.422	43.3	2.52
Cs_3TbCl_6(l)	–	–	–	–	–
$RbTb_2Cl_7$(s)	300–831	281.17	–12.619	18.5	2.82
$RbTb_2Cl_7$(s)	851–862	293.80	–	–	2.11
$RbTb_2Cl_7$(l)	355.27	–	–	–	2.12
$CsTb_2Cl_7$(s)	300–688	215.09	15.695	–9.4	2.49
$CsTb_2Cl_7$(s)	702–886	1051.01	–215.8	151.0	2.81
$CsTb_2Cl_7$(l)	355.88	–	–	–	2.05

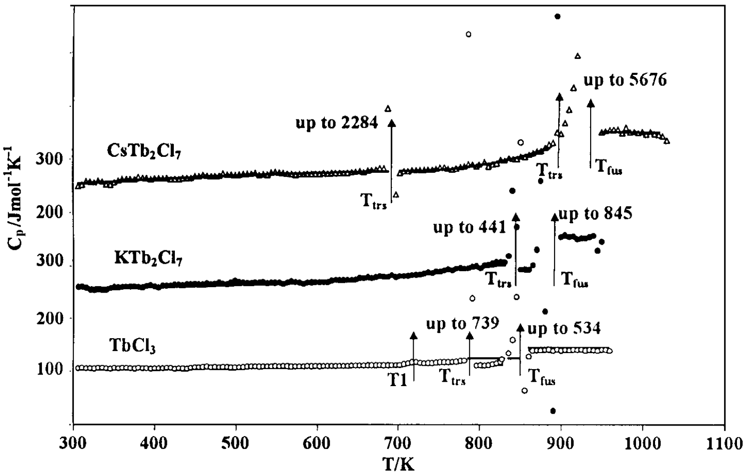

Fig. 1 Molar heat capacity of TbCl$_3$, RbTb$_2$Cl$_7$ and CsTb$_2$Cl$_7$: open circles, black circles and triangles – experimental values, solid line – polynomial fitting of experimental values, dashed line – literature data for TbCl$_3$

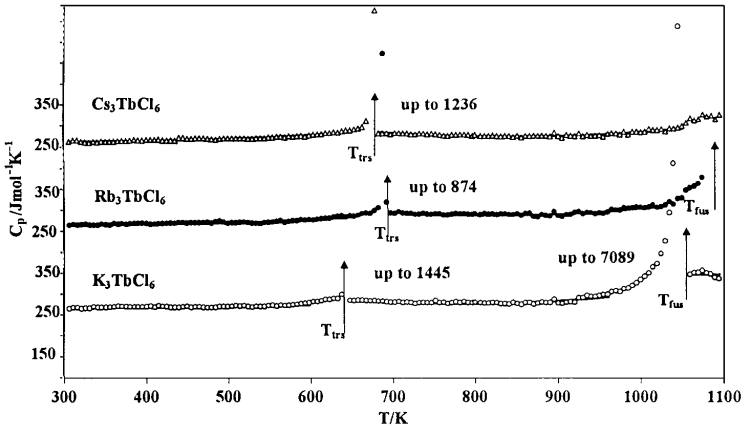

Fig. 2 Molar heat capacity of K$_3$TbCl$_6$, Rb$_3$TbCl$_6$ and Cs$_3$TbCl$_6$: open circles, black circles and triangles – experimental values, solid line – polynomial fitting of experimental values

TbCl$_3$

Our DSC results indicated that TbCl$_3$ melts at 854 K with a related enthalpy of 20.8 kJ mol^{-1}. A solid–solid phase transition occurs at 790 K with an enthalpy of 13.8 kJ mol^{-1}. These results are in a good agreement with the data reported by Dworkin and Bredig [26] using adiabatic calorimetry, with a minor difference in the temperature of solid–solid phase transition, 7 K lower than ours. Other literature data obtained from a semi-quantitative procedure significantly deviate from our results [27].

The only heat capacity data available so far in literature [28–30] were derived from enthalpy measurement [26] on solid and liquid $TbCl_3$ in the temperature range 440–950 K. A single equation was used to describe the temperature dependence of these literature data in the solid range up to the temperature of phase transition (783 K).

However, we did observe a small heat capacity jump in this range at 715 K, which was then followed by a change in the slope of C_p *vs.* T. While very small in magnitude, this effect was observed reproducibly on several runs conducted on different samples. Also because of this small magnitude, no enthalpy change was detected during the DSC runs. This heat capacity anomaly may be related to a metastable phase ($PuBr_3$-type) obtained from a low temperature phase (UCl_3-type) as described by Mitra [23].

Taking the above information into account we decided to describe the heat capacity dependence on temperature on three temperature ranges: (300 K–T_1, T_1–T_{trs} and T_{trs}–T_{fus}). Figure 1 shows C_p *vs.* T plot and compares it with data from literature. In the solid range before the phase transition, both sets of data agree quite well with the exception of singularity at T_1=715 K reported in this work. Also a moderate deviation, less than 9%, can be noticed at lower temperatures up to 400 K. In a very narrow range between solid–solid transition and melting (790–854 K) the influence of premelting effect on heat capacity occurs and it is difficult to determine the dependence of C_p on temperature. In the range 795–830 K we have found a constant value C_p=111.4 J mol^{-1} K^{-1}. We have also measured the heat capacity of the liquid $TbCl_3$ in the temperature range 854–965 K and its mean value C_p=139.3 J mol^{-1} K^{-1} was found. It is slightly lower than the value 144.5 J mol^{-1} K^{-1} given in literature [26].

KTb_2Cl_7

KTb_2Cl_7 is the only one from all existing M_3TbCl_6 and MTb_2Cl_7 compounds, in which the solid–solid transition does not occur. It melts congruently at 842 K [23]. According to our measurements it melts at 841 K with a related enthalpy of 47.9 kJ mol^{-1}. The heat capacity measurements are in progress and will be reported later.

$RbTb_2Cl_7$

Temperatures of solid–solid transition and of fusion were reported as 836 and 883 K, respectively [23]. We confirmed these temperatures as 842 and 886 K for solid–solid phase transition and fusion, respectively. Additionally, we have determined the enthalpies related to these effects as $\Delta_{trs}H^0$=17 kJ mol^{-1} and $\Delta_{fus}H^0$=67.9 kJ mol^{-1}.

Experimental heat capacities are presented in Fig. 1, whereas the parameters in Eq. (1) used for data representation are given in Table 2. As for the other compounds under investigation, the heat capacity dependence on temperature was described in the two temperature ranges (300–T_{trs}) and (T_{trs}–T_{fus}). Since the solid–solid transition was rather close to fusion, no attempt was made to assess the heat capacity dependence on temperature which was assumed to be constant, C_p=293.8 J mol^{-1} K^{-1}. A constant heat capacity C_p=355.3 J mol^{-1} K^{-1} was also found for the liquid phase.

$CsTb_2Cl_7$

$CsTb_2Cl_7$ is the only compound in the series investigated here undergoing two phase transitions, at 688 and 928 K, respectively, before fusion at 945 K [23]. Our investigations support the above results. We determined the temperature of transitions as 689 and 926 K and the temperature of fusion as 942 K. Additionally, we have determined related enthalpies: $\Delta_{trs}H^0$=12.1 and 10.9 kJ mol^{-1}, respectively and $\Delta_{fus}H^0$= 68.9 kJ mol^{-1}.

Figure 1 shows the experimental heat capacities and values obtained from Eq. (1) as a function of temperature. The parameters in Eq. (1) for the two solid and liquid phases are presented in Table 2. As the second transition anticipates melting only by 16 K, a significant scattering of experimental data was observed in this temperature range.

K_3TbCl_6

Temperatures of solid–solid transition and of fusion were reported as 640 and 1049 K, respectively [23]. We confirmed these temperatures as 641 and 1049 K for solid–solid phase transition and fusion, respectively. The enthalpy of the solid–solid phase transition was measured as 6.1 kJ mol^{-1} while the value $\Delta_{trs}H^0$=8.1 kJ mol^{-1} was derived from e.m.f. measurement [23]. The enthalpy of fusion of K_3TbCl_6 was measured for the first time and its magnitude, 53.2 kJ mol^{-1}, is of the same order as that found for the other similar K_3LnCl_6 compounds investigated previously, with *Ln*=La, Ce, Pr, Nd [2].

Experimental heat capacity data are plotted *vs*. temperature in Fig. 2. The heat capacity dependence on temperature was described in two temperature ranges: (300–T_{trs}) and (T_{trs}–T_{fus}). For each temperature range, Eq. (1) was used for data representation. The calculated values are compared with the experimental heat capacities in Fig. 2; the parameters of Eq. (1) are listed in Table 2. A constant heat capacity C_p=348.3 J mol^{-1} K^{-1} was found for the liquid phase.

Rb_3TbCl_6

Rb_3TbCl_6 undergoes a solid–solid phase transition at 683 K with an enthalpy of 10.6 kJ mol^{-1} and melts congruently at 1115 K [23]. We have determined the enthalpy of solid–solid phase transition $\Delta_{trs}H^0$=7.6 kJ mol^{-1} and found a good agreement with the temperature of this effect (686 K). Unfortunately, we were not able to determine the temperature and enthalpy of fusion because of the temperature limitation of the apparatus used.

Heat capacity measurements were performed only on the solid compound. The heat capacity dependence on temperature was again described with Eq. (1) for two temperature ranges: (300–T_{trs}) and (T_{trs}–T_{fus}). The calculated values are compared with the experimental heat capacities in Fig. 2, the parameters of Eq. (1) are listed in Table 2.

Cs_3TbCl_6

Cs_3TbCl_6 compound undergoes a solid–solid phase transition at 673 K with an enthalpy of 7.2 kJ mol^{-1} and melts congruently at 1153 K [23]. We confirmed the temperature and enthalpy of this transition as 672 K and 7.0 kJ mol^{-1}, respectively. However, because of instrumental limitation, we were unable to determine the temperature and enthalpy of fusion for this compound.

Figure 2 shows the experimental heat capacity measurements of solid Cs_3TbCl_6 and compare them with values calculated with Eq. (1). The parameters in Eq. (1) used for $C_p=f(T)$ data representations are given in Table 2.

No heat capacity data were available so far in literature on the 3:1 and 1:2 alkali metal chloride–terbium chloride compound. In order to assess the consistency of our original C_p data with other known thermodynamic data on solid and liquid compounds, they were used in the calculation of the enthalpy of formation of the corresponding liquid compounds and then compared with the experimental enthalpy measured previously by direct calorimetry for $TbCl_3$–MCl melts. The thermochemical cycle given in Fig. 3 describes the synthesis of liquid $RbTb_2Cl_7$ from RbCl and $TbCl_3$. The left branch of this flow chart corresponds to the direct synthesis, while the right one involves an intermediate stage, when $RbTb_2Cl_7$ undergoes a solid–solid phase transition. The thermodynamic data involved in this cycle are: molar heat capacity in the solid and liquid state, molar enthalpy of transition and fusion, molar enthalpy of formation in the solid and liquid state and temperatures of transition and of fusion. The data available so far were the molar heat capacities and enthalpies of phase transitions relative to the pure components MCl [28, 31]. The molar enthalpies of formation of the solid compounds from the system $TbCl_3$–MCl at 298 K were determined by dissolution calorimetry by Mitra [23], while those relative to the formation of liquid compounds were measured by us with using a direct calorimetry [24]. Table 3 reports the values of the enthalpy of formation of the liquid compounds computed from

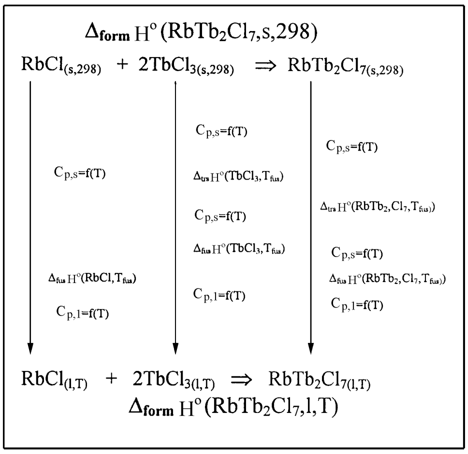

Fig. 3 Thermochemical cycle for the formation of liquid $RbTb_2Cl_7$

the thermochemical cycle. The agreement with the experimental enthalpies measured previously by high temperature calorimetry, is fairly good taking into account that these enthalpies of formation are significantly smaller than the enthalpy increments due to heat capacity and phase transitions.

Table 3 Experimental and calculated enthalpies of formation of K_3TbCl_6 and MTb_2Cl_7 compounds in the liquid state

Compound	T/K	$\Delta_{form}H^0(l,T)$/kJ mol^{-1}	
		experimental	calculated
K_3TbCl_6	1109	–73.1 [24]	–101.8
$RbTb_2Cl_7$	1175	–45.8 [24]	–50.8
$CsTb_2Cl_7$	1175	–53.0 [24]	–60.1

Conclusions

The stoichiometric compounds KTb_2Cl_7, $RbTb_2Cl_7$, $CsTb_2Cl_7$, K_3TbCl_6, Rb_3TbCl_6 and Cs_3TbCl_6 which form in the MCl–$TbCl_3$ systems (*M*=K, Rb, Cs) were investigated by differential scanning calorimetry in the solid and liquid range compatible with the experimental temperature range 300–1100 K.

The temperatures and enthalpies of the solid–solid and solid–liquid phase transitions were determined and compared satisfactorily with literature data, when available. Original data were obtained for the heat capacity of these compounds. Their consistency with other thermodynamic data was assessed from a thermochemical cycle: within the accuracy of the procedure, a satisfactory agreement was obtained between the computed enthalpy of formation of a liquid compound and the experimental value previously obtained by direct calorimetry.

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The authors would like to acknowledge the financial support of the Polish Committee for Scientific Research (Grant 3T09A 091 18).

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