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ENTHALPY OF PHASE TRANSITIONS AND HEAT CAPACITY OF STOICHIOMETRIC COMPOUNDS IN $LaBr_3$–MBr SYSTEMS (*M*=K, Rb, Cs)

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Abstract

Molar enthalpies of solid–solid and solid–liquid phase transitions of the $LaBr_3$, K_2LaBr_5, Rb_2LaBr_5, Rb_3LaBr_6 and Cs_3LaBr_6 compounds were determined by differential scanning calorimetry. K_2LaBr_5 and Rb_2LaBr_5 exist at ambient temperature and melt congruently at 875 and 864 K, respectively, with corresponding enthalpies of 81.5 and 77.2 kJ mol^{-1}. Rb_3LaBr_6 and Cs_3LaBr_6 are the only 3:1 compounds existing in the investigated systems. The first one forms from RbBr and Rb_2LaBr_5 at 700 K with an enthalpy of 44.0 kJ mol^{-1} and melts congruently at 940 K with an enthalpy of 46.7 kJ mol^{-1}. The second one exists at room temperature, undergoes a solid–solid phase transition at 725 K with an enthalpy of 9.0 kJ mol^{-1} and melts congruently at 1013 K with an enthalpy of 57.6 kJ mol^{-1}. Two other compounds existing in the CsBr-based systems (Cs_2LaBr_5 and $CsLa_2Br_7$) decompose peritectically at 765 and 828 K, respectively.

The heat capacities of the above compounds in the solid as well as in the liquid phase were determined by differential scanning calorimetry. A special method – 'step method' developed by SETARAM was applied in these measurements. The heat capacity experimental data were fitted by a polynomial temperature dependence.

Keywords: alkali metal bromides, enthalpy of formation, heat capacity, lanthanum bromide

Introduction

The present work is a part of our systematic investigation of lanthanide halide melts. Their thermodynamic, structural and transport properties were determined by multiinstrumental techniques [1–8]. We report here the thermodynamic investigations of the stoichiometric compounds in the $LaBr_3$–MBr systems, both in the solid and in the liquid state.

Experimental

Chemicals

Lanthanum(III) bromide was prepared from lanthanum oxide supplied by 'Hydromet' Kowary Inc. (Poland). La_2O_3 was dissolved in concentrated HBr solution

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and NH_4Br was then added to the solution (molar ratio $LaBr_3$:NH_4Br=1:4). The solution was gradually evaporated to remove excess of water. This wet mixture of hydrated $LaBr_3$ and ammonium bromide was first heated up to 570 K in a quartz ampoule under vacuum (to remove the rest of water) and then heated up to 650 K for sublimation of NH_4Br. Finally the salt was melted at 1100 K and the quartz ampoule containing $LaBr_3$ was opened in a dry-box. Crude lanthanum bromide was purified by distillation under reduced pressure (~0.1 Pa) in another quartz ampoule at 1150 K. $LaBr_3$ prepared in this way was of a high grade – min. 99.9%.

MBr alkali metal bromides were Merck reagents (min. 99.9%). Before their use, they were treated by progressive heating up to fusion under gaseous HBr atmosphere. Excess HBr was removed from the melt by argon.

The M_2LaBr_5 or M_3LaBr_6 stoichiometric compounds were prepared from the MBr and $LaBr_3$ bromides, which were weighed in appropriate molar ratio. All mixtures were prepared in a glove-box filled with purified and water-free argon. Although only a small amount of samples were used for the differential scanning calorimetry (DSC) experiments (300–500 mg), bigger amounts of each compound were synthesised in order to avoid deviation from stoichiometry. The stoichiometric mixtures of bromides were melted in vacuum-sealed quartz ampoules in an electric furnace. The melts were homogenised by shaking and solidified. These samples were ground in agate mortar in a glove-box.

Procedure

Enthalpy of phase transitions

The molar enthalpies of the solid–solid and solid–liquid phase transitions were determined by DSC. The apparatus used was SETARAM DSC 121 differential scanning calorimeter. The experimental quartz cells, 7 mm in diameter and 15 mm long, were filled with the required amount of sample and sealed under vacuum. DSC experiments were carried out at heating or cooling rates ranging from 1–5 K min^{-1}. The experimental uncertainty in enthalpy measurements was 2–4% depending on the nature of the sample and the magnitude of thermal effects.

Heat capacity

Heat capacity measurements were carried out with a SETARAM DSC 121 differential scanning calorimeter. The special method – 'step method' developed by the SETARAM [9] have been applied. In this method small heating steps are followed by isothermal delays. During these delays, thermal equilibrium of sample is achieved. Two correlated experiments should be carried out with this method to determine the heat capacity of a sample. The first one with two empty cells (containers) of the same masses, the second with the same cells but one of them (laboratory cell) filled with the sample under investigation. The heat flow as a function of time and temperature is recorded for the both runs. The heat flow difference in these experiments is proportional to the amount of heat necessary to increase the temperature of

the sample. The same conditions for both experiments (i.e. starting temperature, temperature increment and isothermal delay) are required. Data aquisition and data processing (heat capacity calculation) are computerized.

The apparatus was calibrated by the Joule effect. The same quartz cells as for enthalpy of phase transitions measurements were used. The measurements were performed by the 'step method' – each heating step of 5 K was followed by an isothermal delay of 400 s. The heating rate was 1.5 K min^{-1}. All experiments were started at 300 K and were performed up to 1100 K. Differences between masses of quartz cells in a particular experiment did not exceed 1 mg. (Masses of the cells ranged from 400 to 500 mg).

Results and discussion

Enthalpy of phase transition

The phase diagrams of the $LaBr_3$–MBr systems (M=K, Rb, Cs) have been investigated by DTA and EMF methods [10]. They are characterised by the K_2LaBr_5, Rb_2LaBr_5, Rb_3LaBr_6 and Cs_3LaBr_6 congruently melting compounds as well as Cs_2LaBr_5 and $CsLa_2Br_7$, which decompose peritectically.

All the above compounds were also confirmed by powder diffraction experiments [10]. No thermal data were reported so far on these compounds, except the enthalpy of solid–solid phase transitions for Rb_3LaBr_6 and Cs_3LaBr_6 only. We therefore decided to reinvestigate the enthalpy features of pure $LaBr_3$ and of all the existing compounds in $LaBr_3$–MBr systems.

The values of enthalpies of phase transitions obtained from heating and cooling were almost the same and the difference less than ±2% was within the experimental uncertainty. Because of supercooling, which was observed in several measurements, only values of temperatures and enthalpies of phase transitions determined from heating curves are presented in this work (Table 1).

$LaBr_3$ has been reported to melt at 1061 K with an enthalpy of 54.4 kJ mol^{-1} [11]. Our results are in excellent agreement with these literature data. We observed melting at 1058 K with an enthalpy of 54.2 kJ mol^{-1}. K_2LaBr_5 and Rb_2LaBr_5 melt congruently at 875 and 864 K, respectively, with corresponding enthalpies of 81.5 and 77.2 kJ mol^{-1}. These melting temperatures are in a good agreement with literature [10]. The enthalpy data obtained in the present work were determined for the first time. Cs_2LaBr_5 differs from its potassium and rubidium analogues and decomposes peritectically at 766 K.

Rb_3LaBr_6 and Cs_3LaBr_6 are the only 3:1 compounds existing in the investigated systems. Cs_3LaBr_6 exists at ambient temperature. It undergoes a solid–solid phase transition at 725 K with enthalpy of 9.0 kJ mol^{-1} and melts at 1013 K with an enthalpy of 57.6 kJ mol^{-1}. These temperatures are very close to those reported by Seifert [10]. Rb_3LaBr_6 does not exist at ambient temperature. According to literature data [10] it forms from RbBr and Rb_2LaBr_5 at 701 K. We determined the temperature and enthalpy of formation as 700 K and 44.0 kJ mol^{-1}, respectively. The melting temperature and enthalpy are 1013 K and 46.7 kJ mol^{-1}, respectively.

Table 1 Molar enthalpy of phase transitions of $LaBr_3$ and congruently melting compounds from $LaBr_3$–MBr systems (M=K, Rb, Cs)

Compound	T_f/ K	$\Delta_f H_m$/ kJ mol^{-1}	T_{trs}/ K	$\Delta_{trs} H_m$/ kJ mol^{-1}	T_{fus}/ K	$\Delta_{fus} H_m$/ kJ mol^{-1}
$LaBr_3$	–	–	–	–	1058	51.2
Ref. [11]	–	–	–	–	1061	51.3
K_2LaBr_5	–	–	–	–	875	81.51
Ref. [10]	–	–	–	–	878	–
Rb_2LaBr_5	–	–	–	–	864	77.21
Ref. [10]	–	–	–	–	868	–
Rb_3LaBr_6	700	44.0	–	–	940	46.74
Ref. [10]	701	–	–	–	942	–
Cs_3LaBr_6	–	–	725	9.0	1013	57.59
Ref. [10]	–	–	721	9.4	1013	–

A very interesting phenomenon was observed on DSC curves in the case of Rb_3LaBr_6. There was only one effect observed on heating curves before melting at 700 K. It is the effect of compound formation. However, during cooling this effect was divided into two independent peaks. The first one at 673 K with an enthalpy of 9.4 kJ mol^{-1} and second one at 646 K with corresponding enthalpy of 31.5 kJ mol^{-1}. According to Seifert [10], a metastable phase of Rb_3LaBr_6 can be obtained at slow cooling rates. Taking into account this information one can ascribe the first effect to the solid–metastable solid phase transition and the second one to the decomposition of this metastable phase. This metastable phase could be observed on a very wide temperature range. Cooling runs were conducted at very low rates (0.2 K min^{-1}) and showed that metastable Rb_3LaBr_6 can be obtained even at room temperature: under these experimental conditions, a single peak was observed in the cooling curves at temperature and enthalpy identical to those obtained at higher cooling rates (673 K and 9.4 kJ mol^{-1}, respectively). The second peak, observed at 646 K at higher cooling rates, related to compound decomposition, had disappeared. On subsequent heating curve a well shaped exothermic effect was observed at 497 K with enthalpy of 27.3 kJ mol^{-1}. This exothermic effect is undoubtedly due to the decomposition of metastable Rb_3LaBr_6. Very similar thermal properties were reported by Seifert for Rb_3PrCl_6 [12].

Heat capacity

Heat capacity measurements were carried out on all compounds. The classical heat capacity polynomial equation

$$C_{p,m} \text{ (in J mol}^{-1}\text{K}^{-1}) = a + bT + cT^{-2} \quad (1)$$

was used to fit the experimental results.

Table 2 Coefficients of the polynomial fitting of the experimental data for $LaBr_3$ and compounds from the $LaBr_3$–MBr systems according to equation C_p,m (J mol^{-1} K^{-1})=$a+bT+cT^2$

Compound	Temp. range/ K	a/ J mol^{-1} K^{-1}	$b\ 10^2$/ J mol^{-1} K^{-1}	$c\ 10^4$/ J mol^{-1} K^{-1}	SE/ J mol^{-1} K^{-1}
$LaBr_{3(s)}$	300–1025	96.48	2.0113		1.39
$LaBr_{3(l)}$	1070–1090	151.12			3.13
$K_2LaBr_{5(s)}$	300–832	231.04	–7.3204	0.72	4.66
$K_2LaBr_{5(l)}$	886–1090	277.41			4.72
$Rb_2LaBr_{5(s)}$	300–826	199.41	0.3251	0.48	4.17
$Rb_2LaBr_{5(l)}$	905–1090	272.05			2.48
$Cs_2LaBr_{5(s)}$	300–752	225.84	–6.1162	0.81	2.78
$Cs_3LaBr_{6\,(s)}$	300–707	314.22	–30.574	4.5	2.78
$Cs_3LaBr_{6\,(s)}$	727–985	851.24	–128.6105	7.55	4.68
$Cs_3LaBr_{6\,(l)}$	1015–1090	364.35			5.59

SE – standard error of estimation, (s) – solid, (l) – liquid

The results obtained for pure $LaBr_3$ as well as for K_2LaBr_5, Rb_2LaBr_5, Cs_2LaBr_5 and Cs_3LaBr_6 compounds are presented in Table 2 and in Figs 1–5. The scale of these figures has been set to show the detailed features of heat capacity dependence on temperature. However, large C_p values (2000–10000 J mol^{-1}K^{-1}) were obtained at temperatures close to phase transitions (solid–solid phase transition or melting) and being beyond the scale range, are not displayed. The results for Rb_3LaBr_6 are not

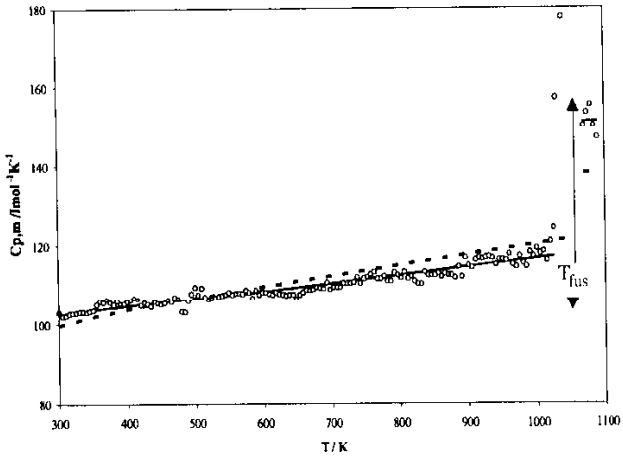

Fig. 1 Molar heat capacity of the $LaBr_3$: o – experimental values, —– linear fitting of the experimental values, - - - – estimation of Knacke, Kubaschewski and Hesselman [13]

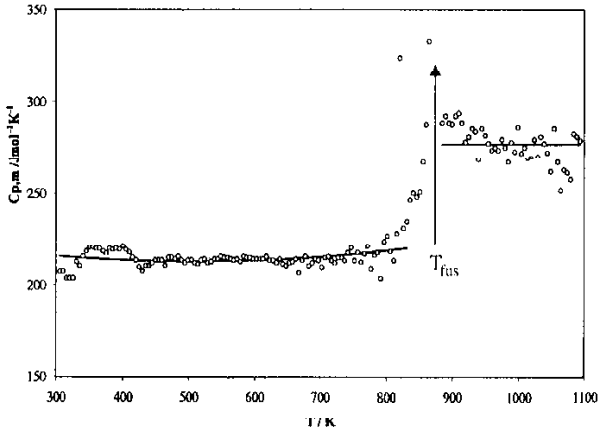

Fig. 2 Molar heat capacity of K_2LaBr_5: o – experimental values, — – polynomial fitting of the experimental values

reproducible (probably because of metastable phase formation and its decomposition) and cannot be presented in this work.

Knacke, Kubaschewski and Hesselman [13] heat capacity estimation of $LaBr_3$ are compared with our experimental results in Fig. 1. The slope of the experimental heat capacity dependence on temperature slightly differs from literature estimation [13]. However the difference does not exceed 2.5% at low temperatures (300–400 K) and 3% at higher temperatures (600–1000 K). For the liquid phase our results are higher of about 9% higher that mentioned above estimations (138.1 J mol^{-1} K^{-1}).

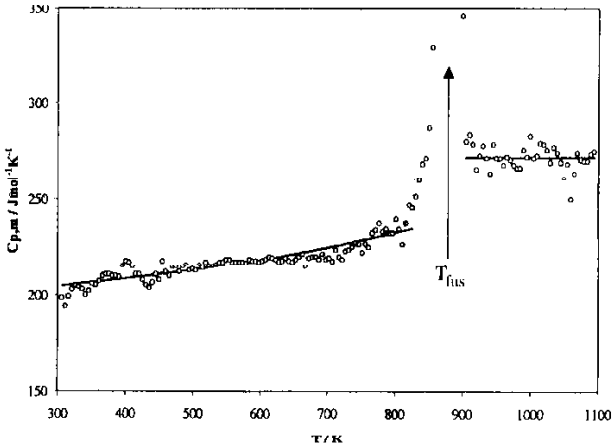

Fig. 3 Fig. 2 Molar heat capacity of Rb_2LaBr_5: o – experimental values, — – polynomial fitting of the experimental values

Our heat capacity results for K_2LaBr_5 and for Rb_2LaBr_5 are presented in Figs 2 and 3. In the solid phase they are quite well described by Eq. (1). The parameters of this equation are given in Table 2. The heat capacity of liquid K_2LaBr_5 and Rb_2LaBr_5 was found to be constant and equal 277.41 and 272.05 J mol^{-1} K^{-1}, respectively.

Cs_2LaBr_5 decomposes peritectically at 766 K. This was the reason that the heat capacity of this compound was determined only in the solid state. The results are shown in Fig. 4. Similarly as in the case of K_2LaBr_5 and for Rb_2LaBr_5 they are well fitted by Eq. (1) (Table 2).

Cs_3LaBr_6 compound is stable at ambient temperature. It undergoes the solid–solid phase transition at 725 K and melts congruently at 1013 K. The results of the heat capacity measurements of this compound are presented in Fig. 5. The heat capacity increase with increase of temperature up to the temperature of solid–solid phase transition. After this transition the heat capacity decreases with increase of temperature in the range of about 120 K (725–850 K). For the liquid phase we have found the constant value of the heat capacity 364.35 J mol^{-1} K^{-1}. The parameters of Eq. (1) for this compound are shown in Table 2.

No heat capacity data are available so far in literature on the above lanthanum bromide–alkali metal bromides compounds. Due to the lack of data in literature, it was therefore impossible to compare and assess our heat capacity values. Therefore, we decided to use for this purpose the available enthalpies of formation at 298 K as well as in the liquid state and to calculate the corresponding enthalpies of formation in the liquid state, using our experimental heat capacities and enthalpies of phase transitions. The enthalpies of formation of K_2LaBr_5, Rb_2LaBr_5 and Cs_3LaBr_6 298 K were determined by Siefert and Yuan [10]. One can use these data and our present experimental results (heat capacity and enthalpies of phase transitions) and calculate the formation enthalpies of above compounds in the liquid phase. They can be compared subsequently with the experimental enthalpies of formation of these com-

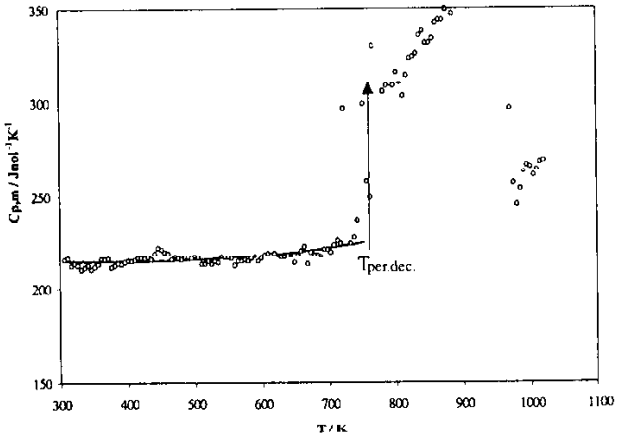

Fig. 4 Molar heat capacity of Cs_2LaBr_5: o – experimental values, — – polynomial fitting of the experimental values

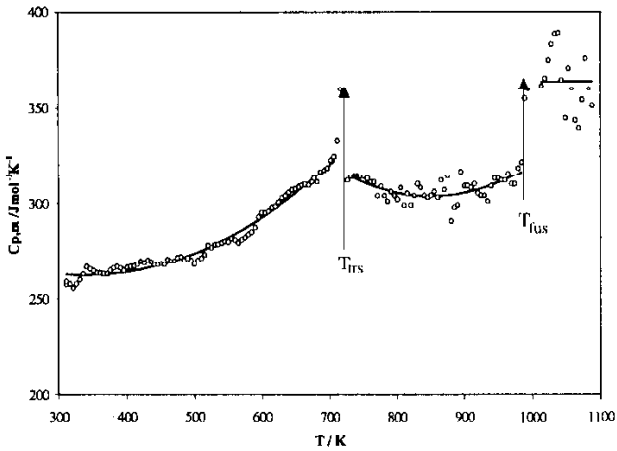

Fig. 5 Molar heat capacity of Cs_3LaBr_6: o – experimental values, — – polynomial fitting of the experimental values

pounds in the liquid phase (1081 K) determined by us in the earlier work [7]. A good agreement between experimental and calculated formation enthalpies in the liquid state should be obtained if our experimental heat capacities and phase transition enthalpies are correct.

The formation enthalpy of K_2LaBr_5 and Rb_2LaBr_5 in the liquid phase can be calculated according to Eq. (2).

$$\begin{aligned}&\Delta_f H_m(M_2LaBr_{5,(l)},T) = \\ &\Delta_f H_m(M_2LaBr_{5,(s)},298\ K) + \Delta H_m(M_2LaBr_{5,(s)},(T_{fus} - 298\ K)) + \\ &+ \Delta_{fus} H_m(M_2LaBr_5,T_{fus}) + \Delta H_m(M_2LaBr_{5,(l)},(T-T_{fus})) - \\ &- \Delta H_m(LaBr_{5,(s)},T_{fus} - 298\ K) - \Delta_{fus} H_m(LaBr_3,T_{fus}) - \\ &-\Delta H_m(LaBr_{3,(l)},(T- T_{fus}) - 2\Delta H_m(MBr_{,(s)},(T_{fus} -298\ K)) - \\ &- 2\Delta_{fus} H_m(MBr,T_{fus}) - 2\Delta H_m(MBr_{,(l)},(T - T_{fus}))\end{aligned} \quad (2)$$

Table 3 K_2LaBr_5, Rb_2LaBr_5 and Cs_3LaBr_6 compounds – formation enthalpies at 298 K and experimental and calculated enthalpies of formation in the liquid state

Compound	$\Delta_f H_m$ (298 K) [10]	$\Delta_f H_m$ (1081 K) exp. [7]	$\Delta_f H_m$ (1081 K) calc.
	kJ mol^{-1}		
K_2LaBr_5	–20.5	–36.8	–43.6
Rb_2LaBr_5	–27.9	–52.3	–51.8
Cs_3LaBr_6	–20.5	–73.0	–61.9

The similar calculations can be done for Cs_3LaBr_6, but the enthalpy of phase transition of this compound must be taken into account.

The data for alkali metal bromides (KBr, RbBr and CsBr) were taken from literature [14, 15]. The results of calculations and their comparison with experimental data are presented in Table 3. A quite good agreement can be observed, which provides a consistency of the reliability of the data measured in this work.

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