Heat Capacity and Thermodynamic Properties of LaBr$_3$ at 300 – 1100 K

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The heat capacity of solid and liquid LaBr$_3$ was measured by Differential Scanning Calorimetry (DSC) in the temperature range 300 – 1100 K. The obtained results were fitted by a polynomial temperature dependence. The enthalpy of fusion of LaBr$_3$ was also measured. By combination of these results with the literature data on the entropy, S_m^0(LaBr$_3$, s, 298.15 K) and the standard molar enthalpy of formation, $\Delta_{form}H_m^0$(LaBr$_3$, s, 298.15 K), the thermodynamic functions of lanthanum tribromide were calculated up to 1300 K.

Key words: Heat Capacity; Lanthanum Bromide; Enthalpy of Fusion; Thermodynamic Functions.

1. Introduction

Numerous experimental investigations were conducted on the lanthanide chlorides (LnCl$_3$) and their mixtures with alkali chlorides (LnCl$_3$-MCl). The enthalpy variation and heat capacity were measured over a wide temperature range of these solid and liquid chlorides [1–4], as well as for several stoichiometric M$_x$LnCl$_{3+x}$ compounds [5–8] that exist in most LnCl$_3$-MCl mixtures. Enthalpies of mixing were also determined [9–13]. Some investigation performed on lanthanide bromides and lanthanide bromide – alkali metal bromide systems were also carried out [14–20]. This work continues our general research program on lanthanide halides, and their mixtures with alkali metal halides, and it presents thermodynamic properties of pure lanthanum(III) bromide.

2. Experimental

2.1. Chemicals

Lanthanum(III) bromide was prepared from lanthanum(III) oxide in a manner similar to that described previously [15]. No insoluble matter was found on dissolving it in water. The chemical analysis of the syn-

Table 1. Chemical analysis of LaBr$_3$.

Compound	Br$_{experimental}$ mass %	Br$_{theoretical}$ mass %	La$_{experimental}$ mass %	La$_{theoretical}$ mass %
LaBr$_3$	63.30	63.31	36.70	36.69

thesised LaBr$_3$ was performed by titration methods for bromide (mercurimetric) and lanthanide (complexometric). These results are presented in Table 1.

Synthesized LaBr$_3$ was handled in an argon glove box with a measured volume fraction of water of about 2×10^{-6} and continuous gas purification by forced recirculation through external molecular sieves.

2.2. Measurements

The heat capacities were measured with a SETARAM DSC 121 differential scanning calorimeter. The apparatus and the measurements procedure were described in [2]. Quartz cells (7 mm diameter and 15 mm length) were filled with lanthanum bromide in a glove box, sealed under vacuum, and then placed into the DSC 121 calorimeter.

Enthalpy of transition measurements were carried out with heating and cooling rates between 1 and 5 K min^{-1}.
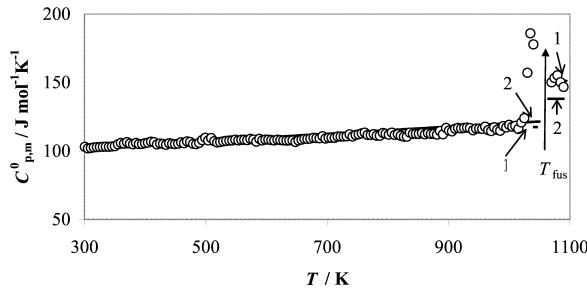
Fig. 1. Molar heat capacity of LaBr₃: open circles – experimental values; dashed line 1 – polynomial fitting of the experimental values; solid line 2 – literature estimation [22, 23].

Heat capacity measurements were performed by the "step method" [2, 6] – each heating step of 5 K was followed by 400 s isothermal delay. The heating rate was 1.5 K min⁻¹. All experiments were started at 300 K and were performed up to 1100 K. The mass difference of the quartz cells in a particular experiments did not exceed 1 mg (mass of the cells: 400 – 500 mg). The mass of the samples was 200 – 500 mg.

3. Results and Discussion

The difference between the fusion enthalpies obtained from heating and cooling DSC curves was less than ±2%. However, fusion temperatures determined from cooling curves were lower by 15 K than those obtained from heating curves. This supercooling phenomenon is common for almost all lanthanide halides [1, 3, 4]. Due to supercooling, the temperature and fusion enthalpy of LaBr₃ were determined from heating DSC curves. LaBr₃ was found to melt at 1058 K with the corresponding enthalpy and entropy of fusion, $\Delta_{\text{fus}}H_m^0 = 54.2$ kJ mol⁻¹ and $\Delta_{\text{fus}}S_m^0 = 51.2$ J mol⁻¹ K⁻¹, respectively. These results agree excellently with the data of Dworkin and Bredig [21], obtained by means of a copper block drop calorimeter (1061 K, 54.4 kJ mol⁻¹ and 51.3 J mol⁻¹ K⁻¹, respectively).

Our experimental heat capacity values of LaBr₃ are plotted against temperature in Fig. 1, together with available literature information [22, 23]. The overall agreement is remarkably good, in particular in the solid range, since both references report estimated heat capacities. This difference does not exceed 2.5% at low temperatures (300 – 400 K) and 3% at higher temperatures (800 – 1000 K). The only experimental source regarding liquid LaBr₃, and also quoted in [22, 23], originated from Dworkin and Bredig [21]

and was derived from drop calorimetry experiments. Our experimental data, averaged to the constant value $C_{p,m}^0 = 151.12$ J K⁻¹ mol⁻¹, compare satisfactorily with that value derived from heat content measurements, within 9%.

The heat capacity data obtained in the present work on solid LaBr₃ were represented using the classical polynomial temperature expansion

$$C_{p,m}^0 = a + b \cdot 10^{-3}T + c \cdot 10^5 T^{-2}, \tag{1}$$

which was used by Barin et al. [24]. However, due to the strong C_p increase at temperatures anticipating melting, only those data corresponding to a smooth heat capacity dependence on temperature were used.

The thermodynamic functions of LaBr₃ were calculated up to 1300 K using our experimental melting temperature and enthalpy together with heat capacity data. The value $C_{p,m}^0(298.15 \text{ K})$ was determined by extrapolation of our results to 298.15 K.

The standard entropy $S_m^0(\text{LaBr}_3, \text{s}, 298.15 \text{ K}) = 188.28$ J K⁻¹ mol⁻¹ was taken from [25].

The $C_{p,.m}^0 = f(T)$ equation was then used to calculate the heat capacity $C_{p,m}^0(T)$ in J K⁻¹ mol⁻¹, enthalpy increments $H_m^0(T) - H_m^0(298.15 \text{ K})$ in kJ mol⁻¹, entropy $S_m^0(T)$ and Gibbs energy functions $(G_m^0(T) - H_m^0(298.15))/T$ in J K⁻¹ mol⁻¹ both for solid as well as liquid LaBr₃. The corresponding equations are:

LaBr₃ solid, 298.15 K < *T* < 1058 K:

$$C_{p,m}^0 = 96.66 + 19.94 \cdot 10^{-3}T - 0.180 \cdot 10^5 T^{-2},$$
$$H_m^0(T) - H_m^0(298.15) = 96.66 \cdot 10^{-3}T + 9.97 \cdot 10^{-6}T^2$$
$$+ 0.180 \cdot 10^2 T^{-1} - 29.77,$$
$$S_m^0(T) = 96.66 \ln T + 19.94 \cdot 10^{-3}T$$
$$+ 0.090 \cdot 10^5 T^{-2} - 368.51,$$
$$-(G_m^0(T) - H_m^0(298.15))/T = 96.66 \ln T + 9.97 \cdot 10^{-3}T$$
$$- 0.090 \cdot 10^5 T^{-2} + 29767 T^{-1} - 465.18.$$

LaBr₃ liquid, 1058 K < *T* < 1300 K:

$$C_{p,m}^0 = 151.12,$$
$$H_m^0(T) - H_m^0(298.15) = 151.12 \cdot 10^{-3}T - 22.01,$$
$$S_m^0(T) = 151.12 \ln T - 675.47,$$
$$-(G_m^0(T) - H_m^0(298.15))/T = 151.12 \ln T$$
$$+ 22008 T^{-1} - 826.56.$$

T	$C_{\mathrm{p.m}}^0(T)$	$S_{\mathrm{m}}^0(T)$	$-((G_{\mathrm{m}}^0(T)-H_{\mathrm{m}}^0(298.15))/T$	$H_{\mathrm{m}}^0(T)-H_{\mathrm{m}}^0(298.15)$	$\Delta_{\mathrm{form}}H_{\mathrm{m}}^0(T)$	$\Delta_{\mathrm{form}}G_{\mathrm{m}}^0(T)$
K	J K⁻¹mol⁻¹	J K⁻¹mol⁻¹	J K⁻¹mol⁻¹	kJ mol⁻¹	kJ mol⁻¹	kJ mol⁻¹
298.15	102.41	188.28	188.28	0.00	−904.4	−875.5
300	102.45	188.91	188.28	0.19	−904.5	−875.3
331	103.10	199.02	188.82	3.38	−905.6	−872.3
331	103.10	199.02	188.82	3.38	−935.2	−872.3
400	104.53	218.67	192.33	10.54	−928.6	−859.3
500	106.56	242.22	200.03	21.09	−926.4	−840.9
583	108.24	258.71	207.24	30.01	−924.4	−826.1
583	108.24	258.71	207.24	30.01	−924.8	−826.1
600	108.58	261.82	208.74	31.85	−924.3	−823.0
700	110.58	278.71	217.55	42.81	−921.8	−805.5
800	112.59	293.61	226.15	53.97	−919.2	−788.3
900	114.59	306.98	234.40	65.33	−916.6	−771.5
1000	116.59	319.16	242.28	76.88	−913.9	−754.9
1058	117.74	325.77	246.67	83.68	−912.4	−745.5
1058	151.12	376.97	246.67	137.88	−858.2	−745.5
1100	151.12	382.85	251.76	144.23	−855.6	−740.8
1138	151.12	387.98	256.23	149.97	−853.4	−736.7
1138	151.12	387.98	256.23	149.97	−856.5	−736.7
1200	151.12	396.00	263.24	159.34	−853.1	−730.0
1300	151.12	408.09	273.93	174.45	−847.6	−719.6

Table 2. Thermodynamic functions of LaBr₃ at selected temperatures from 298.15 to 1300 K.

The above equations were used to calculate the thermodynamic functions of LaBr₃ formation. The formation of LaBr₃ from the elements can be described by the equation:

$$\mathrm{La(s) + 1.5Br_2(l,g) = LaBr_3(s,l).} \qquad (2)$$
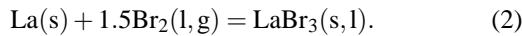
Related thermodynamic functions of LaBr₃-formation depend on the thermodynamic functions of metallic La and bromine Br_2. The latter were calculated using literature data for $C_{\mathrm{p.m}}^0$ and $S_{\mathrm{m}}^0(298.15$ K) [26]. The enthalpy of LaBr₃ formation at 298.15 K, $\Delta_{\mathrm{form}}H_{\mathrm{m}}^0(\mathrm{LaBr_3, s, 298.15\ K}) = -904.4$ kJ mol⁻¹, also required in this calculation, was taken from Cordfunke and Konings recent work [27].

Five phase changes occur in the system described by (2): boiling of bromine at 331 K (enthalpy of 29.56 kJ mol⁻¹), melting of LaBr₃ at 1058 K, $\alpha \to \beta$ solid-solid phase transition of La at 583 K (with enthalpy of 3.0 kJ mol⁻¹), $\beta \to \gamma$ solid-solid phase transition of La (with enthalpy 3.1 kJ mol⁻¹), and melting of La at 1191 K (enthalpy of 6.2 kJ mol⁻¹) [26]. Accordingly, the formation enthalpy $\Delta_{\mathrm{form}}H_{\mathrm{m}}^0$ (kJ mol⁻¹) and Gibbs formation energy $\Delta_{\mathrm{form}}G_{\mathrm{m}}^0$(kJ mol⁻¹) are described by the equations:

LaBr₃ solid, 298.15 K < T < 331 K:

$$\Delta_{\mathrm{form}}H_{\mathrm{m}}^0 = -43.37 \cdot 10^{-3}T + 8.805 \cdot 10^{-6}T^2$$
$$+ 0.18 \cdot 10^2 T^{-1} - 892.3,$$

$$\Delta_{\mathrm{form}}G_{\mathrm{m}}^0 = -188.22 \cdot 10^{-3}T - 8.805 \cdot 10^{-6}T^2$$
$$+ 0.09 \cdot 10^2 T^{-1} + 43.372 \cdot 10^{-3}T \ln T - 892.3.$$

LaBr₃ solid, 331 K < T < 583 K:

$$\Delta_{\mathrm{form}}H_{\mathrm{m}}^0 = 14.18 \cdot 10^{-3}T + 8.460 \cdot 10^{-6}T^2$$
$$- 1.77 \cdot 10^2 T^{-1} - 940.3,$$
$$\Delta_{\mathrm{form}}G_{\mathrm{m}}^0 = 291.47 \cdot 10^{-3}T - 8.460 \cdot 10^{-6}T^2$$
$$- 0.885 \cdot 10^2 T^{-1} - 14.183 \cdot 10^{-3}T \ln T - 940.3.$$

LaBr₃ solid, 583 K < T < 1058 K:

$$\Delta_{\mathrm{form}}H_{\mathrm{m}}^0 = 22.96 \cdot 10^{-3}T + 2.115 \cdot 10^{-6}T^2$$
$$+ 2.12 \cdot 10^2 T^{-1} - 939.2,$$
$$\Delta_{\mathrm{form}}G_{\mathrm{m}}^0 = 350.02 \cdot 10^{-3}T - 2.115 \cdot 10^{-6}T^2$$
$$+ 1.06 \cdot 10^2 T^{-1} - 22.963 \cdot 10^{-3}T \ln T - 944.3.$$

LaBr₃ liquid, 1058 K < T < 1138 K:

$$\Delta_{\mathrm{form}}H_{\mathrm{m}}^0 = 77.42 \cdot 10^{-3}T - 7.855 \cdot 10^{-6}T^2$$
$$+ 1.94 \cdot 10^2 T^{-1} - 931.5,$$
$$\Delta_{\mathrm{form}}G_{\mathrm{m}}^0 = 711.43 \cdot 10^{-3}T + 7.855 \cdot 10^{-6}T^2$$
$$+ 0.97 \cdot 10^2 T^{-1} - 77.422 \cdot 10^{-3}T \ln T - 936.6.$$

LaBr$_3$ liquid, 1138 K $<$ T $<$ 1191 K:

$$\Delta_{\text{form}}H_{\text{m}}^0 = 55.54 \cdot 10^{-3}T - 0.345 \cdot 10^{-6}T^2$$
$$-1.95 \cdot 10^2 T^{-1} - 919.0$$

$$\Delta_{\text{form}}G_{\text{m}}^0 = 555.25 \cdot 10^{-3}T + 0.345 \cdot 10^{-6}T^2$$
$$-0.975 \cdot 10^2 T^{-1} - 55.542 \cdot 10^{-3}T \ln T - 924.2.$$

LaBr$_3$ liquid, 1191 K $<$ T $<$ 1300 K:

$$\Delta_{\text{form}}H_{\text{m}}^0 = 60.77 \cdot 10^{-3}T - 0.345 \cdot 10^{-6}T^2$$
$$-1.95 \cdot 10^2 T^{-1} - 931.4,$$

$$\Delta_{\text{form}}G_{\text{m}}^0 = 602.32 \cdot 10^{-3}T + 0.345 \cdot 10^{-6}T^2$$
$$-0.975 \cdot 10^2 T^{-1} - 60.72 \cdot 10^{-3}T \ln T - 936.55.$$

These thermodynamic functions of LaBr$_3$ are given at selected temperatures from 298.15 to 1300 K in Table 2.

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