Heat Capacity of the $\text{Rb}_3\text{LnCl}_6$ Compounds with $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$

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The heat capacities of the solid and liquid $\text{Rb}_3\text{LnCl}_6$ compounds, where $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$, have been determined by differential scanning calorimetry (DSC) in the temperature range 300 - 1100 K. The heat capacity shows a small decrease with increasing temperature from the temperature of phase transition up to 150 - 200 K above this transition for the $\text{Rb}_3\text{CeCl}_6$, $\text{Rb}_3\text{PrCl}_6$, and $\text{Rb}_3\text{NdCl}_6$ compounds. The measured heat capacities were used to calculate the formation enthalpy of the liquid phase. The results obtained compare satisfactorily with the known experimental data.

Key words: Lanthanum Chloride; Cerium Chloride; Praseodymium Chloride; Neodymium Chloride; Alkali Metals Chlorides; Heat Capacity; Differential Scanning Calorimetry.

Introduction

The lanthanide halides and their mixtures with alkali metal halides have been extensively investigated recently. Several multinstrumental techniques were used complementarily to characterise the macroscopic and microscopic behaviour of these mixtures [1 – 8]. The present paper reports heat capacity ($C_p$) measurements performed on $\text{Rb}_3\text{LnCl}_6$ compounds and is a continuation of our investigations on $K_2\text{LnCl}_6$ compounds [9]. These $\text{Rb}_3\text{LnCl}_6$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$) compounds form in all the ($\text{Rb}$, $\text{Ln}$)/Cl systems [10 – 13], but they do not exist at room temperature, as they form from $\text{RbCl}$ and $\text{Rb}_3\text{LnCl}_6$ at higher temperatures and then melt congruently. Earlier work suggested a limited temperature range of existence of these compounds [10 – 13]. However our recent differential scanning calorimetry (DSC) or differential thermal analysis (DTA) investigations did not confirm the temperatures of their formation [1]. Other effects at different temperatures were detected instead, which may be qualitatively related to formation / decomposition processes. The compounds investigated exhibit some specific features, rather unusual in stoichiometric binary halide compounds, i.e. a limited temperature range of existence and a tendency to the formation of metastable phases below the decomposition temperature [14, 15]. These facts, together with the occurrence of solid-solid phase transitions, give rise to rather complicated $C_p$ vs. $T$ curves with noticeable features related to the effects of compound formation and of phase transition, resulting in marked non-linearity. The polynomial

$$C_p = a + bT + cT^2$$  

was used to represent the experimental heat capacity as a function of temperature.

Experimental

The method used for the synthesis of lanthanide chlorides, the sample preparation and the procedure of $C_p$ measurements with a differential scanning calorimeter have been described in [1]. Samples with masses of 300 - 500 mg were sealed under low pressure of argon in quartz cells (15 mm long and 7 mm diameter). The cells were placed into the calorimeter and the measurements were carried out by the step method, each heating step (1.5 K/min) of 5 K being followed by a 400 s isothermal delay. The apparatus was calibrated by the Joule effect, and a secondary calibration was performed from time to time with NIST 720 alpha-alumina.

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Results

$Rb_3LaCl_6$

$Rb_3LaCl_6$ forms at 725 K from $RbCl$ and $Rb_2LaCl_5$, as reported in [10], while the decomposition temperature, determined from cooling curves, was 685 K [1h]. A similar effect of supercooling to a metastable phase was observed by Seifert et al. [10] and ascribed to a retarded rearrangement of ions. The formation enthalpy of $Rb_3LaCl_6$ from $RbCl$ and $Rb_2LaCl_5$ and the enthalpy of fusion were previously determined as $\Delta_{\text{form}}H_m = 48.4 \text{ kJ mol}^{-1}$ and $\Delta_{\text{fus}}H_m = 50.2 \text{ kJ mol}^{-1}$, respectively [1h].

Experimental heat capacity data are plotted against temperature in Figure 1. The $C_p$ values were slightly larger than reported in [17] at lower temperatures, but were nearly identical above 500 K. After compound formation, the heat capacity vs. temperature curve exhibited a very flat minimum at 860 K. Equation (1) was used for $Rb_3LaCl_6$ (and the stoichiometric mixture of $RbCl$ and $Rb_2LaCl_5$), and very good agreement between the experimental and calculated $C_p$ values was obtained. The parameters in (1) for the two solid phases and for the liquid are presented in Table 1. A constant heat capacity $C_p = 365.4 \text{ J mol}^{-1} \text{ K}^{-1}$ was determined for the liquid compound.

Table 1. Regression coefficients and standard error of estimation of $C_p$ (J mol$^{-1}$ K$^{-1}$) = $a + bT + cT^2$ for $Rb_3LnCl_6$ compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp. range</th>
<th>$a$</th>
<th>$b$</th>
<th>$c \times 10^4$</th>
<th>S.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>Jmol$^{-1}$</td>
<td>K$^{-1}$</td>
<td>Jmol$^{-1}$</td>
<td>K$^{-2}$</td>
</tr>
<tr>
<td>$Rb_3LaCl_6$ (s)</td>
<td>300 - 717</td>
<td>308.09</td>
<td>-0.16741</td>
<td>1.92</td>
<td>2.71</td>
</tr>
<tr>
<td></td>
<td>735 - 955</td>
<td>712.62</td>
<td>-1.0079</td>
<td>6.13</td>
<td>3.63</td>
</tr>
<tr>
<td></td>
<td>990 - 1025</td>
<td>365.38</td>
<td></td>
<td></td>
<td>2.43</td>
</tr>
<tr>
<td>$Rb_3CeCl_6$ (s)</td>
<td>300 - 390</td>
<td>274.83</td>
<td>0.01348</td>
<td>2.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>420 - 643</td>
<td>486.85</td>
<td>-0.74019</td>
<td>6.26</td>
<td>5.21</td>
</tr>
<tr>
<td></td>
<td>662 - 980</td>
<td>693.29</td>
<td>-0.99720</td>
<td>6.13</td>
<td>3.67</td>
</tr>
<tr>
<td></td>
<td>1016 - 1074</td>
<td>345.73</td>
<td></td>
<td></td>
<td>3.15</td>
</tr>
<tr>
<td>$Rb_3PrCl_6$ (s)</td>
<td>300 - 400</td>
<td>621.75</td>
<td>-2.12574</td>
<td>33.96</td>
<td>2.99</td>
</tr>
<tr>
<td></td>
<td>405 - 654</td>
<td>472.63</td>
<td>-0.75499</td>
<td>7.43</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>664 - 1000</td>
<td>794.60</td>
<td>-1.22287</td>
<td>7.23</td>
<td>3.15</td>
</tr>
<tr>
<td></td>
<td>1037 - 1097</td>
<td>329.89</td>
<td></td>
<td></td>
<td>2.48</td>
</tr>
<tr>
<td>$Rb_3NdCl_6$ (s)</td>
<td>300 - 380</td>
<td>360.46</td>
<td>-0.54373</td>
<td>8.77</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>400 - 660</td>
<td>391.21</td>
<td>-0.52122</td>
<td>5.53</td>
<td>1.40</td>
</tr>
<tr>
<td></td>
<td>675 - 1050</td>
<td>636.70</td>
<td>-0.79808</td>
<td>4.26</td>
<td>3.82</td>
</tr>
<tr>
<td></td>
<td>1060 - 1093</td>
<td>325.77</td>
<td></td>
<td></td>
<td>3.05</td>
</tr>
</tbody>
</table>

$Rb_3CeCl_6$

$Rb_3CeCl_6$ has been found to form from $RbCl$ and $Rb_2CeCl_4$ at 651 K [11] as confirmed by the endothermic effect at 650 K with a related enthalpy change of 8.5 kJ mol$^{-1}$ observed in [1h]. However an additional
effect at 411 K with an enthalpy of about 1.2 kJ mol\(^{-1}\) was also reported \([1h]\) together with congruent melting at 1016 K with \(\Delta_{\text{fus}} H_m = 52.4 \text{ kJ mol}\(^{-1}\).

The parameters of (1) for the three temperature ranges are presented in Table 1 and the \(C_p\) vs. \(T\) curve is given in Figure 2.

Over the existence range of Rb\(_3\)CeCl\(_6\) (from 650 K up to fusion), the heat capacity slowly decreases up to 860 K. A constant heat capacity \(C_p = 345.7 \text{ J mol}\(^{-1}\) K\(^{-1}\) was determined for liquid Rb\(_3\)CeCl\(_6\) in the temperature range 1016 - 1090 K.

**Rb\(_3\)PrCl\(_6\)**

Rb\(_3\)PrCl\(_6\) is the first Rb\(_3\)LnCl\(_6\) compound to undergo a phase transition \([12]\). This compound was reported to form at 598 K from RbCl and Rb\(_2\)PrCl\(_5\), while a solid-solid transition and fusion occurred at 659 K and 1040 K, respectively. We confirmed the transition and fusion temperatures and also determined the related enthalpy changes. The phase transition and fusion were observed at \(T_{\text{trs}} = 658 \text{ K}\) and \(T_{\text{fus}} = 1037 \text{ K}\) with the corresponding enthalpies \(\Delta_{\text{trs}} H_m = 6.6 \text{ kJ mol}\(^{-1}\) and \(\Delta_{\text{fus}} H_m = 54.0 \text{ kJ mol}\(^{-1}\), respectively \([1h]\). However we did not observe any compound formation at 598 K. An additional effect was observed instead at 396 K with an enthalpy of 1.0 kJ mol\(^{-1}\).

The experimental heat capacity data are presented in Figure 3. \(T_1\) denotes the temperature of a small endothermic effect of unknown origin. The heat capacity dependence on temperature was approximated by (1) for the three temperature ranges \((300 \text{ K} - T_1),\) \((T_1 - T_{\text{trs}})\) and \((T_{\text{trs}} - T_{\text{fus}})\). The calculated values were compared with the experimental heat capacities in Fig. 3, the parameters of (1) being listed in Table 1. A constant heat capacity \(C_p = 329.9 \text{ J mol}\(^{-1}\) K\(^{-1}\) was found for the liquid phase.

**Rb\(_3\)NdCl\(_6\)**

In \([13]\) Rb\(_3\)NdCl\(_6\) was found to form from RbCl and Rb\(_2\)NdCl\(_5\) at 547 K, to show a solid phase transition at 667 K and congruent melting at 1060 K. Later \([1h]\) we determined the corresponding enthalpies of phase transition \(\Delta_{\text{trs}} H_m = 6.7 \text{ kJ mol}\(^{-1}\) and of fusion \(\Delta_{\text{fus}} H_m = 58.8 \text{ kJ mol}\(^{-1}\) and also found an excellent agreement with the higher two temperatures \((T_{\text{trs}} = 667 \text{ K} \text{ and } T_{\text{fus}} = 1060 \text{ K})\). Our observations did not support, however, the temperature reported for Rb\(_3\)NdCl\(_6\) formation. Our DSC experiments \([1h]\) showed reproducibly that no thermal effect took place at 547 K either on heating or on cooling. Actually, in \([13]\) that temperature was extrapolated from e.m.f. vs. \(T\) measurements, while the same authors postulated a metastable phase as they did not observe any thermal
evidence for formation / decomposition of Rb$_3$NdCl$_6$, unless the mixture had been annealed with some water.

We did observe an endothermic effect in Rb$_3$NdCl$_6$ at a lower temperature, obtained consistently on heating as 382 K by DSC in [1h] and by heat capacity measurements in the present work. The reverse exothermic effect also occurred at the same temperature on cooling.

The only structural information available so far on solid Rb$_3$NdCl$_6$ was obtained from X-ray powder diffraction experiments. Two, low- and high-temperature modifications were reported, monoclinic and cubic, respectively [13]. It seems unclear, however, whether the low temperature modification was observed below or above 382 K, the temperature at which we observed a thermal phenomenon. New structural investigations by neutron diffraction are in progress [7] in order to determine whether this can be related to a phase transition in solid Rb$_3$NdCl$_6$.

Heat capacity measurements were performed on the solid and liquid compound. The experimental heat capacity data are presented in Figure 4. ($T_1$ denotes the temperature of a small endothermic effect of unknown origin). The heat capacity dependence on temperature was again described by (1) for the three temperature ranges : (300 K - $T_1$), ($T_1$ - $T_{trs}$) and ($T_{trs}$ - $T_{fus}$). The calculated values are compared with the experimental heat capacities in Fig. 4, the parameters of (1) being listed in Table 1. A constant heat capacity $C_p$ = 325.8 J mol$^{-1}$ K$^{-1}$ was found for the liquid phase.

**Discussion**

No heat capacity data were available in literature on the Rb$_3$LnCl$_6$ compounds excepted for solid Rb$_3$LaCl$_6$ in the range 200 - 250 K [17]. These results are in fairly good agreement with ours with a maximum deviation less than 4 percent.

In order to assess the consistency of these original $C_p$ data with other thermodynamic data on solid and liquid compounds, they were used in the calculation of the enthalpy of formation $\Delta_{form}H_m$ (Rb$_3$LnCl$_6$,l,T) of the liquid Rb$_3$LnCl$_6$ and compared with the experimental enthalpy measured previously by direct calorimetry for the (Rb,Ln$_{1/3}$)Cl melts [1c, 18, 19].

This calculation included the enthalpy of formation at 298 K, ($\Delta_{form}H_m$ (Rb$_3$LnCl$_6$,s,298), where Ln = La

**Table 2. Literature values of the enthalpy of formation of Rb$_3$LnCl$_6$'s and Rb$_3$NdCl$_6$ at 298 K.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta_{form}H_m$ (s, 298)/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb$_3$LaCl$_6$</td>
<td>-33.3 [10]</td>
</tr>
<tr>
<td>Rb$_3$CeCl$_6$</td>
<td>-37.4 [11]</td>
</tr>
<tr>
<td>Rb$_3$NdCl$_6$</td>
<td>-21.9 [13]</td>
</tr>
</tbody>
</table>
and Ce, and $\Delta_{\text{form}} H_m(\text{Rb}_3\text{NdCl}_6, s, 298)$ (Table 2), and the enthalpies relative to the solid-solid and solid-liquid phase transitions occurring in the temperature range 298 K - $T$:

$$
\Delta_{\text{form}} H_m(\text{Rb}_3\text{LnCl}_6, l, T) = \Delta_{\text{form}} H_m(\text{Rb}_3\text{LnCl}_6, s, 298) + [\Delta H_m(\text{Rb}_3\text{LnCl}_6, s, (T_{\text{trs}} - 298)) + \Delta_{\text{trs}} H_m(\text{Rb}_3\text{LnCl}_6, s, T_{\text{trs}}) + \Delta H_m(\text{Rb}_2\text{LnCl}_5, s, (T_{\text{fus}} - T_{\text{trs}})) + \Delta_{\text{fus}} H_m(\text{Rb}_2\text{LnCl}_5, T_{\text{fus}})]
$$

Since $\text{Rb}_3\text{LaCl}_6$ and $\text{Rb}_2\text{LaCl}_5$ form from $\text{RbCl}$ and $\text{Rb}_2\text{LaCl}_5$ or $\text{Rb}_2\text{CeCl}_5$ at $T_{\text{form}}$, this extra contribution was accordingly incorporated on the right-hand side of (2):

$$
\Delta_{\text{form}} H_m(\text{Rb}_3\text{LaCl}_6, l, T) = \Delta_{\text{form}} H_m(\text{Rb}_2\text{LaCl}_5, l, 298) + [\Delta H_m(\text{Rb}_2\text{LaCl}_5+\text{RbCl}, s, (T_{\text{form}} - 298)) + \Delta_{\text{form}} H_m(\text{Rb}_2\text{LaCl}_5, s, T_{\text{form}}) + \Delta H_m(\text{Rb}_3\text{LaCl}_6, s, (T_{\text{fus}} - T_{\text{form}})) + \Delta_{\text{fus}} H_m(\text{Rb}_3\text{LaCl}_6, T_{\text{fus}})]
$$

The enthalpies of formation $\Delta_{\text{form}} H_m(\text{Rb}_3\text{LnCl}_6, s, T_{\text{form}})$ and phase transitions $\Delta_{\text{trs}} H_m(\text{Rb}_3\text{LnCl}_6, s, T_{\text{trs}})$ of $\text{Rb}_3\text{LnCl}_6$ were determined in [1h]. The thermodynamic quantities relative to $\text{RbCl}$ were taken from [20]. The data relative to the lanthanide chlorides were also previously determined.

The heat capacity of solid LaCl$_3$ is given by

$$
C_{p,s} = 82.51 + 3.816 \cdot 10^{-2} T, \quad (300 - 1100 \text{ K}) [16].
$$
The heat capacity of the liquid is reported contradictorily by Dworkin and Breding [21] (158 J mol\(^{-1}\)K\(^{-1}\)) and Savin [22] (350 J mol\(^{-1}\)K\(^{-1}\)). It seems that the latter value is not very reliable as it was obtained by a discutable extrapolation method. Therefore heat capacity of [21] was used in the calculations. Different values of the melting enthalpy were reported: 39.1 kJ mol\(^{-1}\) [22] and 54.3 kJ mol\(^{-1}\) [21]. Our own experimental determinations [21] were carried out on heating and on cooling. Though the value (55.7 kJ mol\(^{-1}\)) obtained on heating seems to confirm the value of [21], a reproducible and substantially larger value was obtained on cooling (64.2 k J mol\(^{-1}\)). This difference of about 15%, which does not exist for the other lanthanide chlorides, obtained reproducibly on several heating / cooling cycles is beyond the experimental accuracy. It has already been addressed [21] and, from the "post-fusion" effect reported by Savin [22], it was concluded that the value of the crystallisation enthalpy had to be preferred in the calculation.

\[ C_{p,s} = 89.05 + 1.790 \times 10^{-2} T, \quad (300 - 1040 \text{ K}) [16]. \]

The heat capacity of solid CeCl\(_3\) is given by

The heat capacity of the liquid is reported contradic-
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and cooling. Though the value (55.7 kJ mol\(^{-1}\)) ob-
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thanide chlorides, obtained reproducibly on several
heating / cooling cycles is beyond the experimen-
tal accuracy. It has already been addressed [21] and,
from the "post-fusion" effect reported by Savin [22],
it was concluded that the value of the crystallisation
enthalpy had to be preferred in the calculation.

\[ C_{p,s} = 89.05 + 1.790 \times 10^{-2} T, \quad (300 - 1040 \text{ K}) [16]. \]

The heat capacity of solid LaCl\(_3\) is given by

\[ C_{p,s} = 102.27 + 2.170 \times 10^{-2} T, \quad (300 - 980 \text{ K}) [16]. \]

\[ C_{p,s} = 102.27 + 2.170 \times 10^{-2} T, \quad (300 - 980 \text{ K}) [16]. \]

The heat capacity of solid NdCl\(_3\) is given by

\[ C_{p,s} = 102.27 + 2.170 \times 10^{-2} T, \quad (300 - 980 \text{ K}) [16]. \]

\[ C_{p,s} = 102.27 + 2.170 \times 10^{-2} T, \quad (300 - 980 \text{ K}) [16]. \]

Our experimental determination [16] (149.5 J mol\(^{-1}\) K\(^{-1}\)) used in the following calculation was in agree-
ment with the heat capacity of the liquid (146 J
mol\(^{-1}\)K\(^{-1}\)) reported by Dworkin and Breding [21].
Different values of melting enthalpy were reported:
33.5 kJ mol\(^{-1}\) [24] and 50.2 kJ mol\(^{-1}\) [21]. Our own
experimental determinations [11] were carried out on
heating and on cooling. The value obtained (48.1 kJ
mol\(^{-1}\)) confirms that in [21] and was used here.

Table 3 shows the excellent agreement between cal-
culated and experimental enthalpies of formation of
liquid Rb\(_3\)NdCl\(_6\) and Rb\(_3\)CeCl\(_6\). The value calculated
for Rb\(_3\)LaCl\(_6\) deviates more from the calorimetric
result.

**Conclusions**

No heat capacity data have been previously
reported on the 3:1 stoichiometric compounds
Rb\(_3\)LaCl\(_6\) formed by RbCl and LnCl\(_3\) lanthanide
chlorides (Ln = La, Ce, Pr, Nd), excepted Seifert's
[17] on solid Rb\(_3\)LaCl\(_6\), which are in quite good agree-
ment with the results obtained in the present work.
The other heat capacity values reported here were ob-
tained for the first time. They were fitted by an equa-
tion that provided a satisfactory representation up to
the temperature of \( C_p \) discontinuity. These heat capac-
ity data were checked for thermodynamic consistency
by calculating the enthalpy of Rb\(_3\)LaCl\(_6\), Rb\(_3\)CeCl\(_6\),
and Rb\(_3\)NdCl\(_6\) formation in the liquid phase, which
had been previously measured. An excellent agree-
ment between calculated and experimental values was
found for Rb\(_3\)CeCl\(_6\) and Rb\(_3\)NdCl\(_6\) while a small dis-
crepancy was observed for Rb\(_3\)LaCl\(_6\).

The heat capacity dependence on temperature of
the Rb\(_3\)LnCl\(_6\) compounds is rather unusual. After
compound formation or a solid phase transition, the
heat capacity decreases with temperature over about
150 - 200 K, and then increases up to the melting
temperature. Structure investigations are planned to
explain this phenomenon in more detail and also to
identify the lower temperature effect which occurs
in Rb\(_3\)CeCl\(_6\), Rb\(_3\)PrCl\(_6\), and Rb\(_3\)NdCl\(_6\). Though the
structure of these compounds, investigated by X-ray,
has been determined as monoclinic and cubic before
and after the phase transition, when it occurs (Pr, Nd),
or cubic only when it does not occur (La, Ce), a more
detailed characterisation of the structure by neutron
diffraction of powder, at several temperatures before
and after the characteristic temperature reported in
this work is in progress.


