

# Enthalpies of phase transition in the lanthanide chlorides $\text{LaCl}_3$ , $\text{CeCl}_3$ , $\text{PrCl}_3$ , $\text{NdCl}_3$ , $\text{GdCl}_3$ , $\text{DyCl}_3$ , $\text{ErCl}_3$ and $\text{TmCl}_3$

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## Abstract

The enthalpies of phase transition in the lanthanide chlorides have been measured with a differential scanning calorimeter and also with a Calvet-type microcalorimeter to within an experimental error of  $\pm 2\%$ . The molar enthalpies of fusion of  $\text{LaCl}_3$ ,  $\text{CeCl}_3$ ,  $\text{PrCl}_3$ ,  $\text{NdCl}_3$ ,  $\text{GdCl}_3$ ,  $\text{DyCl}_3$ ,  $\text{ErCl}_3$  and  $\text{TmCl}_3$  are 55.7, 55.5, 52.1, 48.1, 40.6, 22.8, 31.1 and 35.6  $\text{kJ mol}^{-1}$  respectively. The existence of a solid–solid phase transition was found in  $\text{DyCl}_3$  and  $\text{ErCl}_3$  at 611 and 1025 K with a molar enthalpy of transition of 1.4 and 5.3  $\text{kJ mol}^{-1}$  respectively. A significant difference (8.5  $\text{kJ mol}^{-1}$ ) between the absolute values of molar enthalpies of crystallization and fusion was found for  $\text{LaCl}_3$  at  $1124 \pm 3$  K; this unusual behaviour was explained by an “after-fusion” effect. The entropies of fusion are discussed in terms of structural types of the lanthanide chlorides.

## 1. Introduction

The lanthanide chlorides may be used as intermediate compounds for preparation of the rare earth metals. Also, a process of anodic dissolution in molten salts of nuclear spent fuel from fast nuclear reactors was considered recently [1] since lanthanides form part of this spent fuel; thermochemical data on the lanthanide chlorides are very useful from this point of view too.

Published thermodynamic data are often contradictory; for example, the enthalpy of melting has been reported as 50.2 [2] and 33.5  $\text{kJ mol}^{-1}$  [3] for  $\text{NdCl}_3$  and as 53.6 [4] and 33.5  $\text{kJ mol}^{-1}$  [3] for  $\text{CeCl}_3$ . At low temperatures (5–350 K) precise heat capacity data have been obtained by adiabatic calorimetry [5, 6]. At high temperatures (solid and liquid state) heat capacity data are either non-existent [7] or derived from enthalpy measurements [2, 8–10] or only estimated [11]. This may lead to some inconsistencies in thermodynamic calculations, especially for melts involving quantities referred to the liquid state.

A systematic study is in progress to determine the thermodynamic and transport properties of rare earth halide melts, both pure and mixed with alkali metal halides [12], in order to contribute to the understanding of the structure and behaviour of ionic species [13] in

these melts. The present work deals with the experimental enthalpies of solid–solid and solid–liquid transitions in the lanthanide chlorides  $\text{LaCl}_3$ ,  $\text{CeCl}_3$ ,  $\text{PrCl}_3$ ,  $\text{NdCl}_3$ ,  $\text{GdCl}_3$ ,  $\text{DyCl}_3$ ,  $\text{ErCl}_3$  and  $\text{TmCl}_3$ .

## 2. Experimental details

### 2.1. Materials

Rare earth chlorides of 99.9% purity were prepared from rare earth oxides in a manner similar to that described previously [14]. No insoluble matter was found on dissolving them in water or alcohol. Great care has been taken in conditioning the very moisture-sensitive samples. Quartz cells were filled with the chlorides (about 300 mg) in an argon-filled glove-box and sealed under a reduced pressure of purified argon. In all experiments quartz cells 7 mm in diameter and 15 mm long were used.

### 2.2. Techniques

#### 2.2.1. Differential scanning calorimetry (DSC)

The instrument used in this technique was a Setaram DSC 121 differential scanning calorimeter coupled to a CS controller, the whole arrangement being connected to a PC92 computer. Two cylindrical (reference and

laboratory) quartz cells, identical in so far as possible, are located in a metallic block provided with a heater and temperature sensors. As the temperature is increased or decreased, an endothermic or exothermic transition, such as melting or crystallization, occurs in the sample. The power required to keep the sample cell at the same temperature as the reference cell during a transition is recorded; this signal is equivalent to the rate of energy absorbed or evolved and is read directly in millijoules per second. This apparatus can be operated between 298 and 1100 K. Enthalpy-of-transition measurements were carried out at rates between 1 and 5 K min<sup>-1</sup> to within an experimental error of about 2%.

### 2.2.2. Calvet high temperature microcalorimetry

The instrument used was a Calvet high temperature microcalorimeter. It is based on the heat flow principle of Calvet and Prat [15] and has two compartments, one for the sample and the other for the reference substance, which are surrounded by a Pt/Pt-10%Rh thermopile for measuring the heat flux between them. The temperature of the calorimeter can be kept constant or can be programmed to scan from ambient temperature to a maximum temperature of 1273 K. Two identical quartz tubes closed at one end (the first with

TABLE 1. Temperatures and enthalpies of fusion of the rare earth chlorides

Compound	Melting point (K)		Enthalpy of fusion (kJ mol <sup>-1</sup> )	
	Heating	Cooling	Heating	Cooling
LaCl <sub>3</sub>	1127	1122	55.7	64.2
CeCl <sub>3</sub>	1086	1088	55.5	54
PrCl <sub>3</sub>	1061	1055	52.1	52.1
NdCl <sub>3</sub>	1032	1009	48.1	47.9
GdCl <sub>3</sub>	873	833	40.6	38.1
DyCl <sub>3</sub>	909	911	22.8	23.3
ErCl <sub>3</sub>	1046	1050	31.1	31
TmCl <sub>3</sub>	1092	1091	35.6	38.4

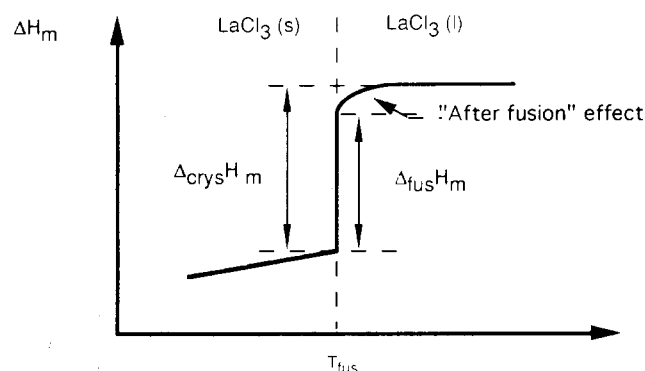


Fig. 1. Enthalpies of fusion and crystallization for LaCl<sub>3</sub>.

TABLE 2. Molar enthalpies of fusion of the lanthanide chlorides

Compound	$T_{fus}$ (K)	$\Delta_{fus}H_m$ (kJ mol <sup>-1</sup> )	$\Delta_{fus}S_m$ (J mol <sup>-1</sup> K <sup>-1</sup> )	Reference
LaCl <sub>3</sub>	1127	55.7	49.4	This work
	1128	54.3	48.1	17
	1131	54.3	48.0	2
	1150			18
	1192			22
	1119			19
	1135	30.9	27.2	20
	1130	37.6	33.3	3
CeCl <sub>3</sub>	1086	55.5	51.1	This work
	1078	33.5	31.1	21
	1090	53.5	49.1	10
	1104			23
PrCl <sub>3</sub>	1061	52.1	49.1	This work
	1051			23
	1059	50.6	47.8	2
	1043	28.8	27.6	20
NdCl <sub>3</sub>	1032	48.1	46.6	This work
	1033	33.5	32.4	21
	1032	50.2	48.6	2
	1013			24
GdCl <sub>3</sub>	873	40.6	46.5	This work
	875	40.5	46.3	10
TmCl <sub>3</sub>	1092	35.6	32.6	This work
	1094	37.6	34.4	17

an empty quartz cell and the second with the quartz cell containing the sample under investigation) are introduced into the two compartments. The temperature of the calorimeter is increased to the desired temperature at a rate of 0.2 K min<sup>-1</sup>. The signal from the thermopile, which is the result of the thermal effect of the transition, is amplified and fed to a recorder. Temperatures are measured with a calibrated Pt/Pt-10%Rh thermocouple and the calorimeter is calibrated against enthalpies and temperatures of fusion of pure metals. Additionally, a known mass of NBS 720 (synthetic sapphire, Al<sub>2</sub>O<sub>3</sub>) is dropped into the compartment of the calorimeter with the sample under investigation at a temperature close to the transition for the purpose of calibration. Enthalpies of transition were obtained to within an experimental error of about 2%.

### 3. Results and discussion

The enthalpy measurement data obtained from both heating and cooling curves are given in Table 1. The results for LaCl<sub>3</sub> and TmCl<sub>3</sub> were obtained only by Calvet high temperature microcalorimetry, since the high temperatures of melting were beyond the experimental range of the DSC equipment.

TABLE 3. Molar enthalpies and entropies of phase transitions in DyCl<sub>3</sub> and ErCl<sub>3</sub>

Compound	$T_{\text{trs}}$ (K)	$\Delta_{\text{trs}}H_m$ (kJ mol <sup>-1</sup> )	$\Delta_{\text{trs}}S_m$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$T_{\text{fus}}$ (K)	$\Delta_{\text{fus}}H_m$ (kJ mol <sup>-1</sup> )	$\Delta_{\text{fus}}S_m$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta_{\text{trs}}S_m + \Delta_{\text{fus}}S_m$ (J mol <sup>-1</sup> K <sup>-1</sup> )	Reference
DyCl <sub>3</sub>	611	1.4	2.3	909	22.8	25.1	27.4	This work
				898				24
				928				18
				924				25.5
ErCl <sub>3</sub>	1025	5.3	5.2	1046	31.1	29.7	34.9	This work
				1049				32.6

The values of enthalpies of fusion and crystallization obtained from the heating and cooling curves are almost the same, with the exception of LaCl<sub>3</sub>. Several measurements for this compound always gave the same result: the enthalpy of crystallization determined from the cooling curve is larger than the enthalpy of fusion obtained from the heating curve. This result is quite unusual but can be explained. According to Savin [16], the formation of a "chain structure" takes place during the melting of LaCl<sub>3</sub>; the destruction of this structure with increasing temperature is connected with very high values of the heat capacity (up to 350 J mol<sup>-1</sup> K<sup>-1</sup>). Taking into account this so-called "after-fusion" effect, it is possible to explain the larger values of  $\Delta_{\text{cryst}}H_m$  obtained from the cooling curves (see Fig. 1). During cooling there is no formation of a "chain structure" of LaCl<sub>3</sub>. It is likely that a metastable liquid phase is formed instead and that the value obtained for  $\Delta_{\text{cryst}}H_m$  is the sum of  $\Delta_{\text{fus}}H_m$  and the "after-fusion" effect.

Supercooling was observed for a few chlorides (greatest for NdCl<sub>3</sub> (23 K) and GdCl<sub>3</sub> (40 K)). The melting points and enthalpies of fusion for all chlorides were obtained from the heating curves.

Tables 2 and 3 list the enthalpies and entropies of transition and fusion of the lanthanide chlorides together with the literature data. Transitions were found in DyCl<sub>3</sub> and ErCl<sub>3</sub> for the first time; the temperatures and enthalpies of transition for these compounds were measured. The transition effects are relatively minor in comparison with the effects of fusion.

The results obtained (*i.e.* melting points, enthalpies of melting and entropies of melting) are in good agreement with the data given by Dworkin and Bredig [2, 8, 10], with the exception of DyCl<sub>3</sub> and ErCl<sub>3</sub>. For DyCl<sub>3</sub> a solid–solid transition, not reported in the literature, was found. The temperature of this transition is 611 K and the enthalpy about 1.4 kJ mol<sup>-1</sup>. The temperature of melting of DyCl<sub>3</sub> is lower by about 13 K than that reported by Dworkin and Bredig [10]. The sum of the entropies of transition and of fusion,  $\Delta_{\text{trs}}S_m + \Delta_{\text{fus}}S_m = 27.4$  J mol<sup>-1</sup> K<sup>-1</sup>, is almost identical

to that reported by Dworkin and Bredig. The phase transition in ErCl<sub>3</sub> is very close to fusion; it occurs at 1025 K with an enthalpy of transition of 5.2 kJ mol<sup>-1</sup>.

For the lanthanide chlorides with the Y(OH)<sub>3</sub>-type structure (LaCl<sub>3</sub>, CeCl<sub>3</sub>, PrCl<sub>3</sub>, NdCl<sub>3</sub> and GdCl<sub>3</sub>) the entropy of melting is about  $50 \pm 4$  J mol<sup>-1</sup> K<sup>-1</sup>.

The lanthanide chlorides with the AlCl<sub>3</sub>-type structure (DyCl<sub>3</sub>, ErCl<sub>3</sub> and probably TmCl<sub>3</sub>) have significantly lower entropies  $\Delta_{\text{fus}}S_m$  or  $\Delta_{\text{trs}}S_m + \Delta_{\text{fus}}S_m$  equal to  $31 \pm 4$  J mol<sup>-1</sup> K<sup>-1</sup>.

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