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Solubility of Lanthanide Chlorides ($LnCl_3$) in Alkali Metal Chlorides (MCl): Thermodynamics and Electrical Conductivity of the M_3LnCl_6 Compounds

Marcelle Gaune-Escard[1,*] and **Leszek Rycerz**[2]

[1] École Polytechnique Universitaire de Marseille, Technopôle de Château Gombert, 13453 Marseille cedex 13, France
[2] Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wroclaw University of Technology, 50-370 Wroclaw, Poland

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Summary. Several compounds may exist in $LnCl_3$–MCl mixtures. Those corresponding to the M_2LnCl_5 and MLn_2Cl_7 stoichiometries are formed in a few systems only, with diverse stability strongly dependent on both the corresponding lanthanide and alkali metal. On the other hand, M_3LnCl_6 that occur in most systems have a far larger stability range and melt congruently. These latter compounds were investigated in the present work by differential scanning calorimetry and electrical conductivity measurements. The thermodynamic and transport properties were correlated to structural features and related to the mechanism of compound formation.

Keywords. Electrical conductivity; Enthalpy; Heat capacity; Lanthanide chlorides; Phase transitions.

Introduction

Lanthanide halides are used in a number of applications ranging from lighting to catalysis through pyrochemical reprocessing of nuclear fuel [1–18]. Much has been done to achieve fundamental insight [19–76] that is required by those many industrial processes still under development. In particular, efforts have been made to correlate macroscopic and microscopic properties [43, 49, 52, 55, 59, 60, 71].

The mutual solubility of molten lanthanide chlorides ($LnCl_3$) and alkali chlorides (MCl) has been investigated intensively over the past two decades [77–87]. Several experimental methods have been used complementarily in order to fully characterise the binary phase diagrams. They include DTA, X-ray, and electrochemical

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[*] Corresponding author. E-mail: Marcelle.Gaune-Escard@polytech.univ-mrs.fr

This paper is dedicated to Professor *H. Gamsjäger* on the occasion of his birthday techniques, the latter making it possible to identify the nature of phase transitions that take place in the solid state. They have allowed to distinguish between the formation of compounds in the solid state (reconstructive phase transition) and their structural transition (non-reconstructive phase transition).

The $Ln\mathrm{Cl}_3$–$M\mathrm{Cl}$ binary systems have relatively simple phase diagrams for the light alkali metal chlorides (LiCl and NaCl) while those including KCl, RbCl, and CsCl exhibit several compounds of stoichiometry $M_3Ln\mathrm{Cl}_6$, $M_2Ln\mathrm{Cl}_5$, and $M_2Ln_2\mathrm{Cl}_7$. All the $M_3Ln\mathrm{Cl}_6$ compounds melt congruently, whereas $M_2Ln\mathrm{Cl}_5$ and $MLn_2\mathrm{Cl}_7$ can melt congruently or decompose peritectically. Congruently melting $M_2Ln\mathrm{Cl}_5$ compounds exist only in the systems with lanthanum and cerium chlorides [77, 78], while $MLn_2\mathrm{Cl}_7$ happen to be congruently melting in the sequence $\mathrm{K}<\mathrm{Rb}<\mathrm{Cs}$ at increasing lanthanide atomic numbers, *i.e.* at decreasing lanthanide ionic radii [77–87]. Accordingly the congruently melting $\mathrm{Cs}Ln_2\mathrm{Cl}_7$ exists in all the chloride systems starting from cerium chloride, the $\mathrm{Rb}Ln_2\mathrm{Cl}_7$ starting from samarium chloride and $\mathrm{K}Ln_2\mathrm{Cl}_7$ from europium chloride. The LaCl_3–KCl system constitutes an exception to the previous description since it includes a single congruently melting compound, $\mathrm{K}_2\mathrm{LaCl}_5$ [77]. Systematic investigations of the $Ln\mathrm{Cl}_3$-based melts are conducted in our laboratory using different experimental, theoretical, and numerical techniques [39–76].

As far as thermodynamics is involved, we have paid much attention to the $M_3Ln\mathrm{Cl}_6$ stoichiometric compounds that exist in most of the $Ln\mathrm{Cl}_3$–$M\mathrm{Cl}$ systems and have a more extended stability range than those of different stoichiometry. Very little is available in literature in this respect and the present work reports these thermodynamic investigations performed in conjunction with electrical conductivity measurements.

Results and Discussion

We determined the temperatures and enthalpies of formation or solid–solid phase transition as well as of fusion of the $M_3Ln\mathrm{Cl}_6$ compounds ($Ln=\mathrm{La}$, Ce, Pr, Nd, Tb; $M=\mathrm{K}$, Rb, Cs). They are presented in Tables 1–3 together with almost all existing literature data.

All the $\mathrm{K}_3Ln\mathrm{Cl}_6$ compounds (Table 1) are not stable at low temperatures. They form at higher temperatures from $\mathrm{K}_2Ln\mathrm{Cl}_5$ and KCl. During cooling, they decompose back to the above components. Their formation is a ‘‘reconstructive’’ phase transition [88].

Results in Table 1 clearly show that the formation and fusion temperatures, T_{form} and T_{fus} are dependent on the ionic radius of the lanthanide. For the $\mathrm{K}_3Ln\mathrm{Cl}_6$ compounds, the smaller the ionic lanthanide radius, the lower the formation temperature and the higher the melting temperature.

Figure 1 shows the existence range, *i.e.* the stability of the $\mathrm{K}_3Ln\mathrm{Cl}_6$ compounds: the temperatures of fusion determined in the present work (Table 1) are plotted *vs.* the lanthanide ionic radii together with the temperatures of formation available from literature [81–83], that were obtained from DTA and e.m.f. measurements. The linear dependence of both T_{form} and T_{fus} on lanthanide ionic radius makes it possible to estimate the formation and fusion temperatures of the other $\mathrm{K}_3Ln\mathrm{Cl}_6$ compounds. Such an estimation was performed and indicated that all

Table 1. Temperatures and molar enthalpies of solid–solid and solid–liquid phase transitions of congruently melting K_3LnCl_6 compounds

Compound	T_{form}/K	T_{trs}/K	T_{fus}/K	$\Delta_{\mathrm{form}} H^0{}_{\mathrm{m}}$/ kJ mol^{-1}	$\Delta_{\mathrm{trs}} H^0{}_{\mathrm{m}}$/ kJ mol^{-1}	$\Delta_{\mathrm{fus}} H^0{}_{\mathrm{m}}$/ kJ mol^{-1}	Ref.
K_2LaCl_5	–	–	906	–	–	78.1	[40]
	–	–	913	–	–	–	[77]
	–	–	902	–	–	115.8	[90]
K_3CeCl_6	811	–	908	55.4	–	39.1	[40]
	807	–	905	–	–	–	[78]
K_3PrCl_6	768	–	944	52.6	–	48.9	[40]
	762	–	945	–	–	–	[79]
	–	–	1048	–	–	106.6	[91]
	–	–	938	–	–	84.0	[90]
K_3NdCl_6	724	–	973	46.3	–	48.0	[40]
	719	–	972	–	–	–	[80]
	–	–	961	–	–	94.5	[90]
K_3TbCl_6	–	641	1049	–	6.1	53.2	[92, 93]
	–	640DTA	1049	–	–	–	[85]
	394EMF	642EMF	–	–	8.1	–	[85]

Table 2. Temperatures and molar enthalpies of solid–solid and solid–liquid phase transitions of congruently melting Rb_3LnCl_6 compounds

Compound	T_{form}/K	T_{trs}/K	T_{fus}/K	$\Delta_{\mathrm{form}}H^0_{\mathrm{m}}$/ kJ mol^{-1}	$\Delta_{\mathrm{trs}}H^0_{\mathrm{m}}$/ kJ mol^{-1}	$\Delta_{\mathrm{fus}}H^0_{\mathrm{m}}$/ kJ mol^{-1}	Ref.
Rb_3LaCl_6	725	–	978	48.4	–	50.2	[40]
	725	–	989	–	–	–	[77]
Rb_3CeCl_6	–	411, 650	1016	–	1.5/8.5	52.4	[40]
	651	–	1012	–	–	–	[78]
Rb_3PrCl_6	–	398/658	1037	–	1.0/6.6	54.0	[40]
	598	659	1040	–	–	–	[79]
Rb_3NdCl_6	–	382/667	1060	–	0.9/6.7	58.8	[40]
	547	667	1060	–	–	–	[80]
Rb_3TbCl_6	–	686	–*	–	7.6	–*	[92, 93]
	–	681DTA	1049	–	–	–	[85]
	–	663EMF	–	–	8.1	–	[85]

* – not determined due to temperature limitation of apparatus

K_3LnCl_6 are not stable at 0 K, in agreement with *Seiffert's* conclusion from thermochemical calculations based on e.m.f. measurements [77–80, 85, 88].

This behaviour has been addressed in literature and it has been postulated that those compounds that decompose at temperatures lower than 670 K can exist as a metastable phase at 0 K [89]. Indeed, we could not observe any decomposition of K_3TbCl_6 upon cooling during experimental DSC runs. In all the K_3LnCl_6 series, K_3SmCl_6 is the first compound that undergoes a ("non reconstructive") solid–solid

Table 3. Temperatures and molar enthalpies of solid–solid and solid–liquid phase transitions of congruently melting Cs_3LnCl_6 compounds

Compound	T_{form}/K	T_{trs}/K	T_{fus}/K	$\Delta_{form}H^0_m$/ kJ mol^{-1}	$\Delta_{trs}H^0_m$/ kJ mol^{-1}	$\Delta_{fus}H^0_m$/ kJ mol^{-1}	Ref.
Cs_3LaCl_6	–	670	1055	–	7.5	58.7	[40]
	–	674	1053	–	–	–	[77]
Cs_3CeCl_6	–	676	1078	–	7.8	67.4	[40]
	–	674	1077	–	–	–	[78]
Cs_3PrCl_6	–	676	1093	–	7.6	61.1	[40]
	–	677	1093	–	–	–	[79]
Cs_3NdCl_6	–	678	1103	–	7.4	66.4	[40]
	–	678	1108	–	–	–	[80]
Cs_3TbCl_6	–	672	–*	–	7.0	–*	[92, 93]
	–	673DTA	1153	–	–	–	[85]
	–	661EMF	–	–	7.2	–	[85]

* – not determined due to temperature limitation of apparatus

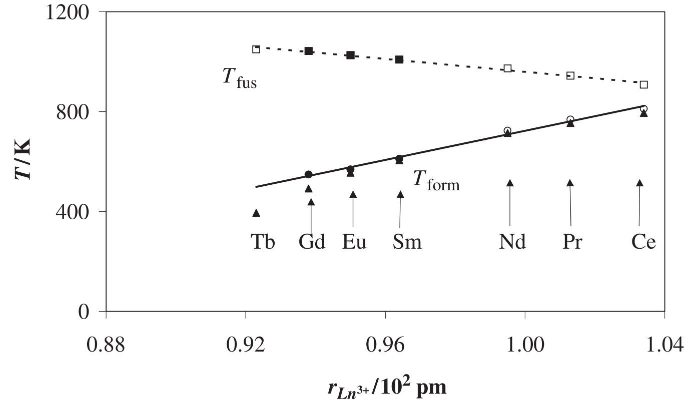

Fig. 1. Existence range of the K_3LnCl_6 compounds: temperatures of formation and fusion are plotted against ionic radius of lanthanide: open circles – T_{form} (this work), black circles – T_{form} (literature DTA [81–83]), black triangles – T_{form} (literature emf [94]), open squares – T_{fus} (this work), black squares – T_{fus} (literature DTA [81–83])

phase transition at 627 K [81] after forming at 611 K. For K_3TbCl_6, the transition occurs at 641 K.

From the results in Table 1, it may be concluded that the formation of the K_3LnCl_6 compounds is associated to large enthalpy changes (45–55 kJ mol^{-1}) for a so-called “reconstructive” phase transition while it corresponds to more modest enthalpies for structural (“non reconstructive”) phase transitions.

Figure 2 shows the existence range, *i.e.* the stability of the Rb_3LnCl_6 compounds: the temperatures of fusion determined in the present work (Table 2) are plotted *vs.* the lanthanide ionic radii together with the temperatures of formation available from literature [94], that were obtained from e.m.f. measurements. The linear dependence of both temperatures of formation and of fusion on these ionic

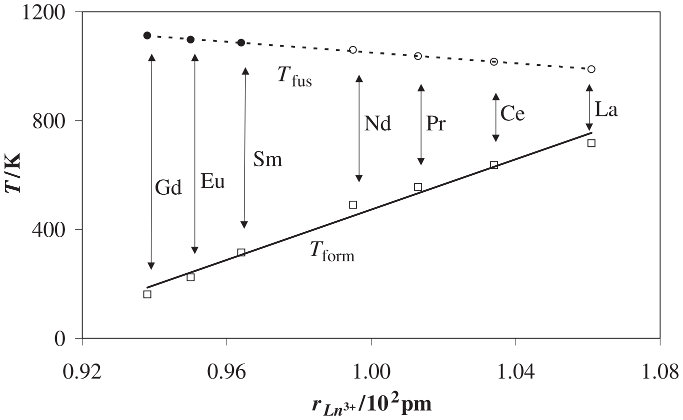

Fig. 2. Existence range of the Rb_3LnCl_6 compounds: temperatures of formation and fusion are plotted against ionic radius of lanthanide: open circles – T_{fus} (this work), black circles – T_{fus} (literature DTA [81–83]), open squares – T_{form} (literature emf [94])

radii is also to be noted. It indicates that the existence range of the $Rb_3\mathit{Ln}Cl_6$ decreases as the lanthanide ionic radius increases. However, it should be stressed that our measurements do not confirm that the temperatures reported as formation temperatures in literature always correspond to the formation of the compound. Indeed, this was confirmed only for Rb_3LaCl_6 (Table 2) but not for the other Rb_3CeCl_6, Rb_3PrCl_6, and Rb_3NdCl_6 rubidium compounds in which an additional thermal effect, not reported in literature, was observed for the first time at significantly lower temperatures. No explanation can be offered so far, but it is likely that this effect may arise from low temperature metastable phase. For the heavier lanthanides (starting from Pr) the corresponding compounds also undergo a structural phase transition with a related enthalpy change of 7–8 kJ mol^{-1}.

Among the $Cs_3\mathit{Ln}Cl_6$ compounds, Cs_3LaCl_6, Cs_3CeCl_6, and Cs_3PrCl_6 are the only ones to exist at temperatures above 0 K. They form from $Cs_2\mathit{Ln}Cl_5$ and CsCl at 462, 283, and 143 K [94]. Due to these moderate formation temperatures, decomposition doesn't occur upon cooling down from high temperature and metastable phases are formed. All $Cs_3\mathit{Ln}Cl_6$ compounds undergo a structural phase transition at a nearly identical temperature of about 670–680 K (Table 3). The melting temperature increases as the lanthanide ionic radius decreases. The melting temperature of the $M_3\mathit{Ln}Cl_6$ also increases as the ionic radius of the M alkali metal, *i.e.* in the sequence $K < Rb < Cs$.

Heat capacity determinations were performed on the same compounds: a normal temperature dependence was observed for those compounds that formed at higher temperatures and correspond to a "reconstructive" phase transition (K_3CeCl_6, K_3PrCl_6, K_3NdCl_6, Rb_3LaCl_6) [66]. No other structural phase transition takes place before melting and the crystal structure is of the elpasolite-type. Figure 3 gives an example for K_3NdCl_6.

Two different crystal structures characterize the other group of compounds, *e.g.* those that form at lower temperatures (K_3TbCl_6, Rb_3PrCl_6, Rb_3NdCl_6, Rb_3TbCl_6, and all $Cs_3\mathit{Ln}Cl_6$): monoclinic Cs_3BiCl_6-type and cubic elpasolite-type [94]. Heat capacity also exhibits different features: both an unusual *C*p increase before

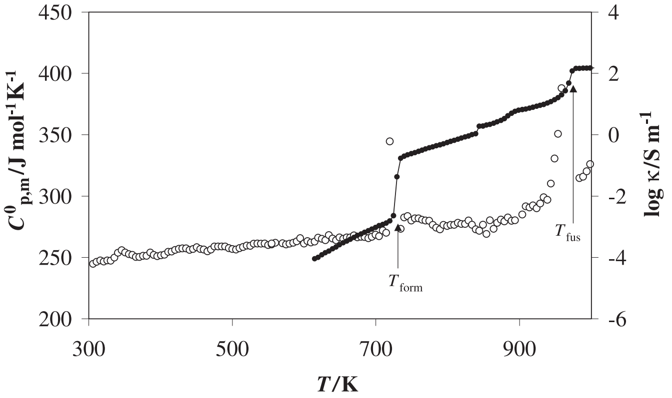

Fig. 3. Dependence of molar heat capacity and electrical conductivity of K_3NdCl_6 on temperature: open circles – heat capacity, black circles – electrical conductivity

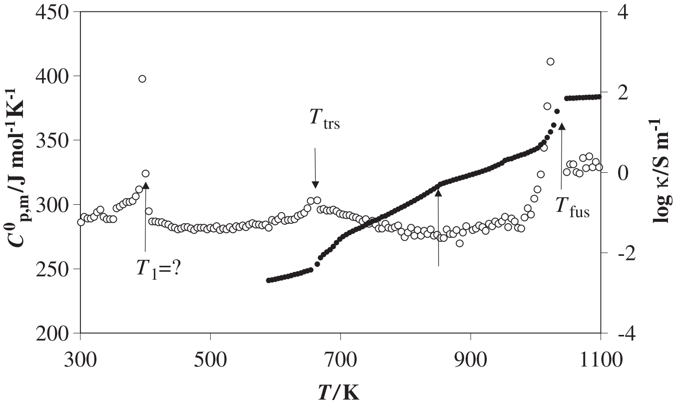

Fig. 4. Dependence of molar heat capacity and electrical conductivity of Rb_3PrCl_6 on temperature: open circles – heat capacity, black circles – electrical conductivity

the structural phase transition and the occurrence of a *C*p minimum are observed as exemplified in Fig. 4.

The electrical conductivity evolution with temperature follows the same pattern: in the first group of compounds a significant (two orders of magnitude) conductivity jump is observed at the same temperature determined for the "reconstructive" phase transition. A second, but smaller jump happens approximately at an identical temperature for all compounds (835–845 K). This effect was not observable in the DSC thermograms (Fig. 3).

In the second group of lower temperature-forming compounds, two conductivity regimes can also be observed but the e.c. jumps differ noticeably from what was observable for the other compounds. The first conductivity break appears at a different temperature for each compound, has a smaller magnitude, and also spreads over a 40–50 K temperature range.

A second effect can be observed which, as described above, remains undetected in the DSC thermogram. This kink in the electrical conductivity plot *vs.* temperature corresponds very well to the minimum in the $Cp = f(T)$ curve (Fig. 4).

Conclusion

No in depth conclusions can be given on the various phenomena observed in this work from the observation of macroscopic properties. The validation of postulated order–disorder transitions would require information on the microscopic level. Powder diffraction investigations at different temperatures were recently performed at the ILL in Grenoble and are currently being refined. Also cross-linked information is expected from high temperature X-ray diffraction investigations that are in progress.

Experimental

Synthesis of $LnCl_3$ and M_3LnCl_6 compounds has been described in details elsewhere [40, 42, 92]. Great care has been taken in conditioning the very moisture-sensitive samples. All the manipulations were carried out in an Ar-filled glove box with H_2O and O_2 content less than 2 ppmV. Although only a small amount of sample (300–500 mg) was used for differential scanning calorimetry (DSC) experiments, about 10 g of each compound were synthesised in order to avoid deviation from stoichiometry.

The experimental procedure for enthalpy of phase transitions and heat capacity measurements with a differential scanning calorimeter SETARAM DSC 121 has been described in Refs. [40, 42, 54, 96]. The experimental quartz cells, 7 mm diameter and 15 mm long, were filled with the required amount of sample and sealed under reduced pressure of Ar. The DSC experiments were conducted at heating and cooling rates ranging 1–5 K $\min^{-1}$.

Heat capacity measurements were carried out with the same SETARAM DSC 121 calorimeter by the so called step method. In this method, small heating steps are followed by isothermal equilibration. Each heating step of 5 K was being followed by a 400 s isothermal delay. The apparatus was calibrated by the *Joule* effect, and some experiments were carried out with NIST 720 α-alumina for secondary calibration, to monitor the *C*p measurements.

Electrical conductivity measurements were performed in a capillary quartz cell by the method described in detail elsewhere [47]. The conductivity of the compounds was measured with conductivity meter Tacussel CD 810. Experimental runs were conducted both upon heating and cooling regimes at rates of 1 K $\min^{-1}$. Temperature and conductivity data acquisition was made with a PC interfaced to the conductivity meter. Temperature was measured by means of a Pt/Pt-Rh thermocouple within the accuracy of 1 K. Experimental cells were calibrated with NaCl melt [95]. The resulting cell constant ranged from 950 to 1900 m^{-1}. All measurements were carried out under static Ar atmosphere.

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