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Unusual nature of lanthanide chloride–alkali metal chloride M_3LnCl_6 compounds in the solid state

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Abstract

Thermodynamic and transport properties of M_3LnCl_6 compounds (M = K, Rb, Cs; Ln = La, Ce, Pr, Nd) were determined experimentally. The results obtained clearly show that the M_3LnCl_6 compounds can be divided into two groups, with compounds having only high temperature modification of cubic, elpasolite-type, crystal structure, in the first one, and compounds having both low-temperature (monoclinic, Cs_3BiCl_6-type) and high-temperature (cubic, elpasolite-type) modifications in the second one. Within the two groups, the thermodynamic and transport properties of M_3LnCl_6 compounds are well correlated with their crystal structure. These results suggest different order–disorder mechanisms of the alkali metal cation sublattice whereas the $LnCl_6$ octahedra, forming anionic sublattice, retain their normal lattice positions.

Keywords: Lanthanide chlorides; Alkali chlorides; M_3LnCl_6 compounds; Heat capacity; Ionic conductivity; Phase transition

1. Introduction

When combined to alkali chlorides, lanthanide(III) chlorides form a variety of stoichiometric compounds. They differ in number and stoichiometry and their stability range is quite various depending on the nature of both the alkali and lanthanide cations. However, most systems (with KCl, RbCl and CsCl) always include the M_3LnCl_6 (3:1) congruently melting compound. In order to characterize this interplay between those compounds with congruent melting which apparently form from others with a limited existence range, we have conducted systematic phase equilibrium investigations on the MCl–$LnCl_3$ systems (M = K, Rb, Cs; Ln = La, Ce, Pr, Nd, and Tb) [1–7]. The present work evidences systematic trends in the thermodynamic properties of these congruently melting compounds.

2. Results and discussion

The M_3LnCl_6 congruently melting compounds that the heavier alkali chlorides MCl (M = K, Rb, Cs) form with the $LnCl_3$ lanthanide chlorides (Ln = La, Ce, Pr, Nd, Tb) have been investigated by differential scanning calorimetry (DSC) [2,5–8]. Two endothermic effects were generally observed on heating DSC thermograms and identified as resulting from a solid–solid phase transition and congruent melting, respectively. The enthalpy data related to the phase transition clearly split into two groups characterized by unusually large values (group 1: 45–55 $kJ\,mol^{-1}$—K_3CeCl_6, K_3PrCl_6, K_3NdCl_6 and Rb_3LaCl_6), on the one hand, and by noticeably smaller values (group 2: only 7–9 $kJ\,mol^{-1}$—K_3TbCl_6, Rb_3CeCl_6, Rb_3PrCl_6, Rb_3NdCl_6, Rb_3TbCl_6 and all the Cs_3LnCl_6 compounds), on the other [2,8,9]. According to literature information [10–15], the large enthalpy effect in the first group corresponds to formation of M_3LnCl_6 compounds from MCl and M_2LnCl_5 and is described as a “reconstructive phase transition”. The M_3LnCl_6 compounds in this group have a single, high-temperature crystal modification. It is a cubic, elpasolite-type crystal structure.

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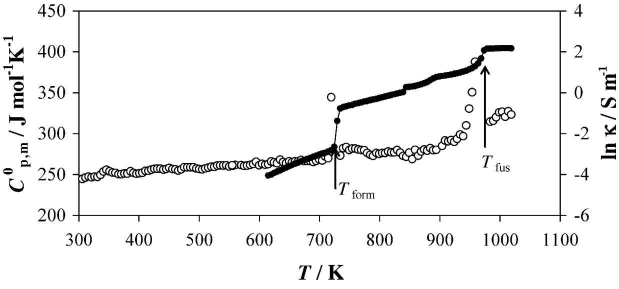

Fig. 1. Molar heat capacity and electrical conductivity dependence on temperature for K_3NdCl_6 compound: open circles—heat capacity, black circles and solid line—electrical conductivity.

The thermal effect at about 650–680 K for the M_3LnCl_6 compounds in the second group also corresponds to a solid–solid phase transition [10–15], from low-temperature modification (monoclinic, Cs_3BiCl_6-type) to high-temperature (cubic, elpasolite-type) modification. This structural phase transition was described as a “non-reconstructive phase transition”. All the compounds of this group may exist as stable, or for kinetic reasons, as metastable at room temperature. An additional thermal effect at about 380–410 K (with molar enthalpy of about 0.9–1.5 kJ mol^{-1}) is observed only in some compounds of this group (Rb_3CeCl_6, Rb_3PrCl_6 and Rb_3NdCl_6), but thus is not a characteristic feature of the whole group. Its nature is unclear so far. It is hoped that more insight would be provided by structural investigations at different temperatures which are in project.

We have also determined in a separate work [5–7,9] the heat capacity of the same compounds and a detailed discussion of the temperature evolution was given. A global examination of these C_p data (Figs. 1 and 2) indicates the same categorization. In group 1, a normal heat capacity dependence on temperature can be observed with a smooth increase up to the temperature of formation. Then, these cubic, elpasolite-type, M_3LnCl_6 compounds show a quite unusual, and not explained so far behaviour in that the heat capacity reached a minimum before increasing again, as usual, with temperature up to anticipating melting temperatures. For all compounds, it is also interesting that the temperature at which this minimum C_p occurs is about 150 K above the formation temperature T_{form}. In the second group of compounds, i.e. those that can exist at low temperature and have two structural modifications (monoclinic, Cs_3BiCl_6-type, and cubic, elpasolite-type) (Fig. 2) heat capacity exhibited a mixed behaviour. In the high-temperature range associated to a cubic, elpasolite-type modification, heat capacity also goes through a minimum value at temperature about 150 K above the transition temperature T_{trs}, which is almost identical for all compounds. In the lower temperature range, below the transition temperature, in which compounds have monoclinic structure, an unusual, and not previously reported in literature, heat capacity increase is observed with a characteristic λ-shape, thus suggesting a second order transition. Classical examples of ionic crystals undergoing a second order phase transition indicate order–disorder reaction in cationic or anionic sublattice. In order to verify it the features observed for the thermodynamic properties would tinge from this mechanism, we initiated electrical conductivity measurements on all these M_3LnCl_6 solid (and liquid) compounds [8,9]. Indeed, electrical conductivity in ionic crystals proceeds by jumps of ions (either cation or anion) in the respective sublattice. Extreme and classical examples of enhanced ionic superconductor are AgI or $RbAg_4I_5$, with the Ag^+ cation conductor, or PbF_2 and earth-alkali fluorides, with the F^- anion conductor.

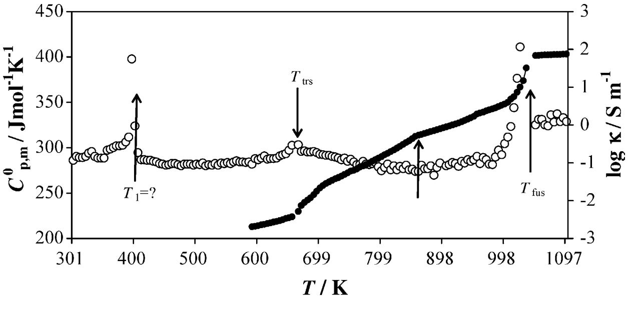

Fig. 2. Molar heat capacity and electrical conductivity dependence on temperature for Rb_3PrCl_6 compound: open circles—heat capacity, black circles and solid line—electrical conductivity.

Typical examples of the electrical conductivity of the M_3LnCl_6 compounds are given for K_3NdCl_6 and Rb_3PrCl_6 in Figs. 1 and 2.

The electrical conductivity evolution with temperature follows the same pattern as described above, i.e. division of M_3LnCl_6 compounds into two groups. In the first group (Fig. 1) a significant (two order of magnitude) conductivity jump is observed at temperature of compound formation (T_{form}), i.e. temperature of reconstructive phase transition. A second but smaller jump happens approximately at a temperature identical for all compounds (835–845 K) while this effect was not observable in DSC curves. The temperature of this jump corresponds well to that of the heat capacity minimum. In the second group of M_3LnCl_6 compounds (stable or metastable at room temperature), a significant electrical conductivity increase takes place in low-temperature modification and matches very well the unusual heat capacity increase (Fig. 2). It is followed by jump in electrical conductivity at the temperature of solid-solid phase transition T_{trs} (from low- to high-temperature modification). This conductivity jump is however significantly smaller in comparison with that in the first group of compounds that takes place at the formation temperature T_{form} (Fig. 1). And finally a kink in electrical conductivity is observed in the high-temperature modification, while it remained undetected in the DSC thermogram. It corresponds well to the minimum on heat capacity dependence on temperature. Significant electrical conductivity increase results from significant increase of current carriers number in the solid phase of M_3LnCl_6 compounds, indicating a likely electrolyte phase.

Crystals with solid electrolyte phases pass, either gradually or through a series of phase transitions, from normal ionic conductivity (about 10^{-2} S m^{-1}) to liquid-like values while still solid [16]. It has been stated that the superionic phase is a result of “sublattice melting” [17]; i.e., atoms on a certain set of lattice positions become mobile, almost liquid-like, while the remaining atoms retain their normal lattice positions. O’Keeffe and Hyde [17] have created a simple model of solid electrolyte based on the assumption that solid electrolyte properties are the result of existing disordered phase with ionic conductivity. They divided ionic solids into three classes characterised by their phase transitions. Class I contains “normally melting” salts such as alkali halides which show large discontinuities in ionic conductivity at the melting point, with low conductivities in the solid phase. Crystals showing first-order solid electrolyte transitions belong to class II. O’Keeffe and Hyde place those salts that show a large, discontinuous change in ionic conductivity and a change in the lattice symmetry of both mobile and nonmobile sublattices in a subclass IIa. Those crystals for which the changes in the immobile sublattice are minor are placed into a subclass IIb. Finally, class III includes materials in which the change from low to high ionic conductivity is spread over a wide temperature range and which have no change in the symmetry of nonconducting sublattice.

The continuous changes in ionic conductivity are followed by characteristic changes of other properties, for example, changes of heat capacity. These changes are the result of gradual disordering of sublattice with ionic conductivity, which causes increase of number of current carrier ions. O’Keeffe and Hyde [17] have defined this type of transition as gradual order–disorder transition. At sufficiently high temperature, the disordering of mobile sublattice can be complete and ions forming this sublattice are distributed randomly in the space of elementary cell. Such a state is called as “structural disorder” and the fully disordered sublattice can be assumed as quasi-liquid [16]. The state of “structural disorder” can be reached in a continuous process spread over a wide temperature range (second-order phase transition) or in a discontinuous way at defined temperature (first-order phase transition). The discontinuous disordering of one of ionic sublattices can be exemplified by the $\beta \rightarrow \alpha$ transition in AgI at temperature 422 K. Anionic sublattice formed by iodide ions obtains the cubic symmetry, whereas silver cations are randomly distributed in the space of elementary cell between iodide anions [18]. The transition in CaF_2 and $SrCl_2$ [16] can be given as an example of continuous disordering spread over a wide temperature range. Continuous disordering of one of ionic sublattices is followed by characteristic heat capacity behaviour. In the temperature range where this disordering becomes significant, heat capacity reaches unusually high values, consistent with the fact that disorder increase requires additional energy. Clearly marked heat capacity increase with increase of temperature takes place even at relatively low temperatures, indicating continuous transition to the state of “structural disorder”. The heat capacity dependence on temperature exhibits a characteristic λ-shape, very well correlated to electrical conductivity changes. The end of this λ transition (complete “structural disorder”) corresponds well to the kink in electrical conductivity plot. These features describing the different types of order–disorder transitions can be retrieved in the M_3LnCl_6 compounds.

Cubic, elpasolite-type crystal structure is realised in the high temperature modifications of the M_3LnCl_6 compounds [19]. The correct formula of these compounds should be written as $M_2M'LnCl_6$. Lanthanide ions are surrounded by 6-Cl ions and form $(LnCl_6)$ octahedra. One-third of alkali metal cations (M′) occupy octahedral holes of the $(LnCl_6)$ sublattice, whereas remaining two-third (M) accommodate tetrahedral holes formed by $(LnCl_6)$ octahedra. So, each M′ cation is surrounded by 6 and each M—by 12 chloride ions. According to Seifert [19], due to enormously large temperature factors for all atoms except Ln, such a description can be considered only formally.

Monoclinic, Cs_3BiCl_6-type crystal structure can be derived from the cubic, elpasolite-type. At low temperatures the $(LnCl_6)$ octahedra are slightly deformed and have been markedly rotated from their ideal positions. These rotations reduce the difference in coordination between M′ and M cations. In the Cs_3BiCl_6-type structure one of the alkali metal cations (M′) is coordinated by 11, and the remaining two (M) by 8 chloride ions.

In both types of structural modifications of M_3LnCl_6 compounds, anionic sublattice is formed by $(LnCl_6)$ octahedra, whereas alkali metal cations constitute cationic sublattice. Significant jumps in electrical conductivity that follow the phase transitions must result from increase of mobile ions number. These mobile ions can be only alkali metal cations. Thus, it is very likely that cationic sublattice undergoes gradual order–disorder transition. At sufficiently high temperature, this disordering can be complete and alkali metal cations are randomly distributed between $(LnCl_6)$ octahedra in the space of elementary cell.

It seems that in the group of M_3LnCl_6 compounds, which have only high temperature, elpasolite-type modification (K_3CeCl_6, K_3PrCl_6, K_3NdCl_6 and Rb_3LaCl_6) disordering of cationic sublattice takes place in a discontinuous way at temperature T_{form}. The compound formation from M_2LnCl_5 and MCl is a reconstructive phase transition. As the result of this transition M_3LnCl_6 compound with cubic, elpasolite-type crystal structure is formed. In this phase, the anionic sublattice constituted by $(LnCl_6)$ octahedra has the cubic symmetry, whereas alkali metal cations (cationic sublattice) become mobile, almost liquid-like. Large discontinuous change in ionic conductivity (Fig. 1) at the temperature of compound formation ($T_{form)}$ is undoubtedly related to the increased possibility of migration of alkali metal cations in the space of elementary cell. Additional jump in electrical conductivity of high temperature modification, which takes place at temperature corresponding to the minimum of heat capacity (Fig. 1), can be ascribed to the state of the complete “structural disorder”. Alkali metal cations are randomly distributed between $(LnCl_6)$ octahedra and become mobile, almost liquid-like.

In the group of M_3LnCl_6 compounds that have both high temperature and low temperature modifications (K_3TbCl_6,

Rb_3CeCl_6, Rb_3PrCl_6, Rb_3NdCl_6, Rb_3TbCl_6, and all the Cs_3LnCl_6 compounds) disordering of cationic sublattice, formed by alkali metal cations, takes place in a continuous way. It starts in low temperature modification at temperatures significantly lower than temperature of non-reconstructive phase transition (T_{trs}). Unusual increase of heat capacity at increasing temperature (Fig. 2) is the result of this disordering. The state of complete "structural disorder" is obtained in high temperature modification. Thus, heat capacity dependence on temperature exhibits a λ-shape. Behaviour of heat capacity correlates very well with changes in electrical conductivity. The end of λ effect on heat capacity dependence on temperature (state of complete "structural disorder" of cationic sublattice) corresponds well to the kink in electrical conductivity plot versus temperature (Fig. 2). Different in that from the compounds of the first group, in which the first order transition (compound formation) initiates the order–disorder transition, the second group of M_3LnCl_6 compounds includes the superimposition of order–disorder and first order (low–high-temperature) transitions.

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