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Thermodynamic and transport properties of M_3CeBr_6 compounds ($M = K, Rb, Cs$)

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Abstract Systematic trends in the thermodynamic properties of congruently melting M_3CeBr_6 compounds (molar enthalpies of the solid–solid phase transitions, molar heat capacity) following those found for another M_3LnX_6 compounds ($Ln =$ lanthanide; $X =$ halide, $M = Li$, Na, K, Rb, Cs) were evidenced. These data were complemented by electrical conductivity measurements over the wide temperature range. The results obtained clearly show that the M_3CeBr_6 compounds can be divided into two groups. The first one with K_3CeBr_6 compound having a single high temperature modification of cubic, elpasolite-type, crystal structure, and the second one with Rb_3CeBr_6 and Cs_3CeBr_6 compounds having both low- (monoclinic, Cs_3BiCl_6-type) and high-temperature (cubic, elpasolite-type) modifications. Transition from low- to high-temperature modification of these compounds is non-reconstructive phase transition. Within the two groups, the thermodynamic and transport properties of M_3CeBr_6 compounds are well correlated with their crystal structure. These results suggest different order–disorder mechanisms of the alkali metal cations whereas the $CeBr_6$ octahedra, forming anionic sublattice, retain their normal lattice positions.

Keywords Lanthanide(III) halides · Cerium(III) bromide · Alkali metal halides · Heat capacity · Phase transition · Electrical conductivity

Introduction

The LnX_3–MX binary systems ($Ln =$ lanthanide; $X =$ halide, $M = Li$, Na, K, Rb, Cs) have relatively simple phase diagrams for the light alkali metal halides (LiX and NaX) while those including KX, RbX, and CsX exhibit several compounds of the stoichiometry M_3LnX_6, M_2LnX_5, $M_3Ln_2X_9$, and MLn_2X_7 [1–4]. All the M_3LnX_6 compounds ($M = K$, Rb, Cs) melt congruently, whereas M_2LnX_5, $M_3Ln_2X_9$, and MLn_2X_7 can melt congruently, incongruently or decompose in the solid state. Detailed discussion of a quantitative relation between the LnX_3–MX phase diagram types (including nature of definite compounds) and the ionic potentials IP ($IP = z_i/r_i$, where $z_i =$ valency, $r_i =$ ionic radius) of components was given elsewhere [5]. As far as thermodynamics is involved, we have paid much attention to the M_3LnX_6 stoichiometric compounds that exist in most of the LnX_3–MX systems ($M = K$, Rb, Cs) and have a more extended stability range than those of different stoichiometry.

Additional structural and EMF measurements, performed on chloride and bromide systems [1, 2, 6, 7], indicated that all M_3LnX_6 compounds can be divided into two groups: compounds that are formed at higher temperatures from M_2LnX_5 and MX, and compounds which exist at lower temperatures as stable or metastable phases. Those compounds, which are formed at higher temperatures, have only one cubic, elpasolite-type, crystal structure or monoclinic, Cs_3BiCl_6-type, and cubic, elpasolite-type, crystal structures. Those compounds, which exist both at low

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temperatures and high temperatures, have monoclinic, Cs_3BiCl_6-type, and cubic, elpasolite-type, crystal structures, respectively [1, 2, 6]. Transition from low- to high-temperature modification is a non-reconstructive phase transition [7].

Our systematic calorimetric investigations lead to the conclusion that the formation enthalpy of M_3LnX_6 compounds from M_2LnX_5 and MX (45–55 kJ mol^{-1}) is significantly larger than the enthalpy related to that of the solid–solid phase transition (only 7–9 kJ mol^{-1}). In solid-state reactions the arrangement of the ions is drastically changed. Ions have to move from one site to another passing through strong potential walls of other ions. Accordingly enthalpy related to these reactions must be significantly larger.

As mentioned above, cubic, elpasolite-type crystal structure is realized in the high temperature modifications of the M_3LnX_6 compounds [8]. The correct formula of these compounds should be written as $M_2M'LnX_6$. Lanthanide ions are surrounded by 6-X ions and form (LnX_6) octahedra. 1/3 of alkali metal cations (M′) occupy octahedral holes of the (LnX_6) sublattice, whereas remaining 2/3 (M) accommodate tetrahedral holes formed by (LnX_6) octahedra. So, each M′ cation is surrounded by 6 and each M by 12 halide ions. Monoclinic, Cs_3BiCl_6-type crystal structure can be derived from the cubic, elpasolite-type. At low temperatures the (LnX_6) octahedra are slightly deformed and have been markedly rotated from their ideal positions. In both types of structural modifications of M_3LnX_6 compounds, anionic sublattice is formed by (LnX_6) octahedra, whereas alkali metal cations constitute cationic sublattice. According to Seifert [8], due to enormously large temperature factors for all atoms except Ln, such a description can be considered only formally. The magnitude of these factors obtained from Rietveld analysis [8] means that alkali metal cations forming cationic sublattice can leave their ideal positions in the crystal structure. Thus, the disordering of cationic sublattice takes place. The increase in the intrinsic disorder in the crystal lattice with rising temperature means that more energy is required, and this in turn increases the heat content of the crystal. The specific heat must therefore contain a component due to the change in disorder with temperature. From other side increase of disorder in cationic sublattice means the increase in the number of current carrier ions and accordingly the increase of ionic conductivity. At sufficiently high temperature, the disordering of mobile sublattice can be complete with a random distribution of corresponding ions in the space of elementary cell. Such a state is referred to a "structural disorder" and the fully disordered sublattice can be assumed as quasi-liquid. 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 a defined temperature (first-order phase transition) [9].

Correlation of precise heat capacity data with transport properties would be of considerable interest with respect to disordering of crystal lattice in the compounds under investigation. Therefore, we have decided to investigate the transport properties of the M_3CeBr_6 compounds. This study reports the analysis of heat capacity of these compounds as well as electrical conductivity experimental results and their correlation with heat capacity.

Experimental

Sample preparation

Cerium(III) bromide was synthesized from the cerium(III) carbonate hydrate (Aldrich 99.9%). $Ce_2(CO_3)_3\cdot xH_2O$ was dissolved in hot concentrated HBr acid. Solution was evaporated, and $CeBr_3\cdot xH_2O$ was crystallized. Ammonium bromide was then added, and this wet mixture of hydrated $CeBr_3$ and NH_4Br was first slowly heated up to 450 K and then up to 570 K to remove the water. The resulting mixture was subsequently heated to 650 K for sublimation of NH_4Br. Finally the salt was melted at 1,100 K. Crude $CeBr_3$ was purified by distillation under reduced pressure (~0.1 Pa) in a quartz ampoule at 1,150 K. $CeBr_3$ prepared in this way was of a high purity, min. 99.9%. Chemical analysis was performed by mercurimetric (bromine) and complexometric (cerium) methods. The results were as follows: Ce, 36.91 ± 0.03% (36.89% theoretical); Br, 63.09 ± 0.04% (63.11% theoretical).

Potassium, rubidium, and cesium bromides were Merck Suprapur reagents (min. 99.9%). Prior to use, they were progressively heated up to fusion under gaseous HBr atmosphere. HBr in excess was then removed from the melt by argon bubbling.

The K_3CeBr_6, Rb_3CeBr_6, and Cs_3CeBr_6 stoichiometric compounds were prepared from $CeBr_3$ and appropriate alkali bromides, which were weighed in the molar ratio 1:3. All mixtures were prepared in a glove box filled with purified and water-free argon. For each compound, batches of several grams were synthesized in order to avoid deviation from stoichiometry. Stoichiometric mixtures of bromides were melted in vacuum-sealed quartz ampoules in an electric furnace. Melts were homogenized by shaking and solidified. These samples were ground in an agate mortar in a glove box. All chemicals were 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.

Measurements

Electrical conductivity measurements were carried out in the capillary quartz cells with cylindrical platinum electrodes, described in details elsewhere [10]. These cells were calibrated with pure molten NaCl [11]. The cell, filled with the substance under investigation, was placed into a furnace in a stainless steel block, used to achieve a uniform temperature. After salt melting, conductivity of the fused and solid salt was measured during increasing and decreasing temperature runs with the conductivity meter Tacussel CDM 230. Experimental runs were performed at heating and cooling rates equal to 1 K min^{-1}. The temperature was measured with a Pt/Pt–Rh thermocouple with 1 K accuracy. Temperature and conductivity data acquisition was made with PC computer, interfaced to the conductivity meter. All measurements were carried out under static argon atmosphere.

Results and discussion

K_3CeBr_6 forms at 775 K from KBr and K_2CeBr_5 and melts congruently at 879 K with the related enthalpies 54.5 ± 0.5 and 41.7 ± 0.3 kJ mol^{-1} [12, 13]. As discussed in details previously [14] Rb_3CeBr_6 forms from RbBr and Rb_2CeBr_5 at 614 K, undergoes a solid–solid phase transition at 695 K, and melts congruently at 966 K. The enthalpy of phase transition (8.0 kJ mol^{-1}) has a magnitude comparable to that observed in several M_3LnX_6 compounds (M = Rb, Cs; Ln = lanthanide) [5]. By analogy to other M_3LnX_6 compounds (M = K, Rb), the formation of Rb_3CeBr_6 from Rb_2CeBr_5 and RbBr should be associated to large enthalpy changes (45–55 kJ mol^{-1}) [14]. Surprisingly for pure Rb_3CeBr_6 no effect of formation was observable on the corresponding DSC thermograms, and another small endothermic effect appeared at 420 K instead. It is very likely that Rb_3CeBr_6 does not decompose upon cooling and that a metastable phase of this compound is formed instead. Such a behavior has been addressed in the literature for many M_3LnCl_6 chloride compounds, and it has been postulated that those compounds that form at temperatures below 700 K may exist as a metastable phase at lower temperatures [7]. In the solid-state reactions the arrangement of the ions is drastically changed. Ions have to move from one site to another passing strong potential walls of other ions. The resulting "kinetic hindrance" can cause great difference between the reaction temperatures measured in DSC heating and cooling runs (thermal hysteresis). In extreme cases during cooling experiments the "undercooling" can become so strong that the reaction does not occur in the DSC timescale. Due to kinetic reasons the decomposition during cooling does not occur and the compound still exists in a metastable form. This metastability was observed for several M_3LnX_6 compounds, and no decomposition was detected during cooling runs of Rb_3PrCl_6, Rb_3NdCl_6, K_3TbCl_6, and K_3TbBr_6 [5]. Additional experiments [14] performed on the Rb_3CeBr_6 compound fully confirmed the compound formation at 614 K and its existence at ambient temperature as a metastable phase. It is very likely that an additional thermal effect at 420 K with related enthalpy of 0.9 kJ mol^{-1} observed in this compound arises from low-temperature metastable phase.

The compound with cesium, Cs_3CeBr_6, is stable or metastable at ambient temperature. It undergoes a solid–solid state transition at 720 K and melts congruently at 1,034 K with the related enthalpies 9.0 and 57.6 kJ mol^{-1}, respectively [15].

Thus, M_3CeBr_6 compounds follow the behavior of all M_3LnX_6 compounds. Potassium compound belongs to the group of compounds that are formed at higher temperatures, whereas Rb_3CeBr_6 and Cs_3CeBr_6 belong to second group, i.e., compounds which exist at low temperatures as stable or metastable phases.

We have also determined in separate work [13, 16] the heat capacity of the same compounds and a detailed discussion of its temperature evolution was given. A global examination of these $C^0_{p,m}$ data (Figs. 1, 2, 3) indicates the same categorization. In first group (K_3CeBr_6), a normal heat capacity dependence on temperature can be observed with a smooth increase up to the temperature of formation. Then, K_3CeBr_6 compound (cubic, elpasolite-type crystal structure) shows a quite unusual behavior in that the heat capacity reaches a minimum before increasing again, as usual, with temperature up to anticipating melting temperatures. Temperature at which this minimum occurs (about 825 K) is about 50 K above the formation temperature T_{form}. In the second group of compounds (Rb_3CeBr_6 and Cs_3CeBr_6), i.e., those that can exist at low temperature and have two structural modifications (monoclinic,

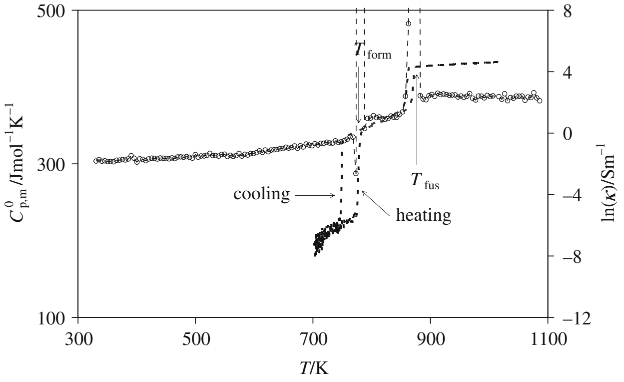

Fig. 1 Heat capacity and electrical conductivity of K_3CeBr_6: *open circles* heat capacity, *thin broken line* global evolution of heat capacity, *thick broken line* electrical conductivity

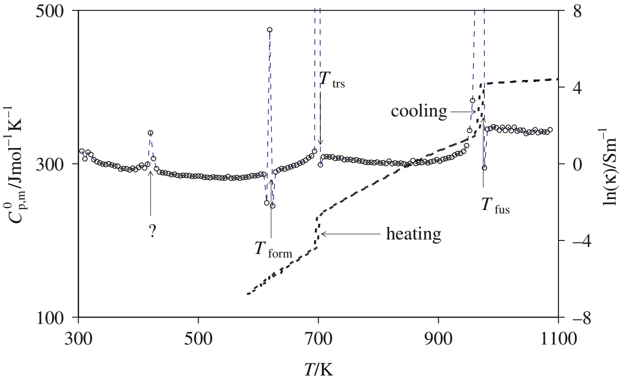

Fig. 2 Heat capacity and electrical conductivity of Rb_3CeBr_6: *open circles* heat capacity, *thin broken line* global evolution of heat capacity, *thick broken line* electrical conductivity, *?* effect of unknown origin

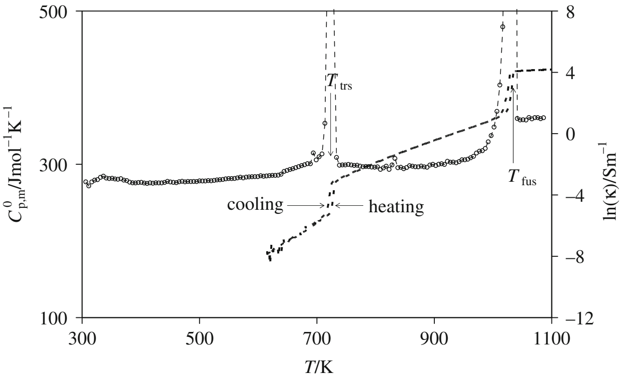

Fig. 3 Heat capacity and electrical conductivity of Cs_3CeBr_6: *open circles* heat capacity, *thin broken line* global evolution of heat capacity, *thick broken line* electrical conductivity

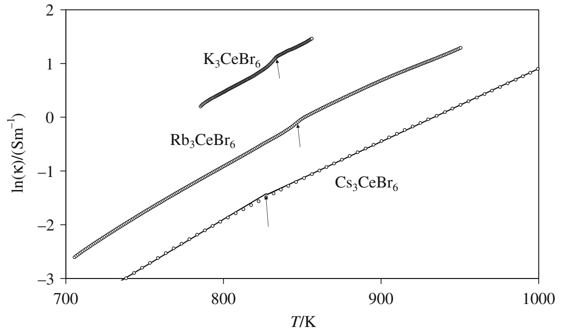

Fig. 4 Electrical conductivity of high-temperature modification of M_3CeBr_6 compounds (heating curves): *open circles* experimental results, *solid lines* linear fitting the results on Cs_3CeBr_6 (in order to keep clarity of the figure only selected by 5 K points are presented for Cs_3CeBr_6)

Cs_3BiCl_6-type, and cubic, elpasolite-type) (Figs. 2, 3), unusual increase of heat capacity is observed in the low-temperature modification with a characteristic λ-shape, thus suggesting a second-order transition. High-temperature modification of these compounds show, similarly like K_3CeBr_6, unusual heat capacity dependence on temperature, i.e., minimum at temperatures of about 850 K.

Classical examples of ionic crystals undergoing a second-order phase transition indicate order–disorder reaction in cationic or anionic sublattice. 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 superconductors are AgI or $RbAg_4I_5$, with the Ag^+ cation conductor, or PbF_2 and earth-alkali fluorides, with the F^- anion conductor [9]. In order to verify if the features observed for the thermodynamic properties would tinge from this mechanism, electrical conductivity measurements were performed.

The electrical conductivity evolution with temperature follows the same pattern as described above, i.e., division of M_3CeBr_6 compounds into two groups. In the first group (Fig. 1) a significant (two order of magnitude) conductivity jump is observed at the temperature of K_3CeBr_6 compound formation (T_{form}). A kink in electrical conductivity happens approximately at a temperature of about 825 K (Fig. 4), which corresponds well to that of the heat capacity minimum. In the second group of M_3CeBr_6 compounds (stable or metastable at room temperature Rb_3CeBr_6 and Cs_3CeBr_6), a significant electrical conductivity increase takes place in low-temperature modification and matches very well the unusual heat capacity increase (Figs. 2, 3). 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 jump in K_3CeBr_6 that takes place at the formation temperature T_{form} (Fig. 1). And finally a kink in electrical conductivity (Rb_3CeBr_6) at about 850 K or change of slope in dependence $\ln\kappa = f(T)$ (Cs_3CeBr_6) at about 830 K is observed in the high-temperature modifications (Fig. 4). Significant electrical conductivity increase realized in high-temperature modification of compounds under investigation results from significant increase of current carriers number in the solid phase of M_3CeBr_6 compounds, thus indicating a solid 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 [9]. It has been stated that the superionic phase is a result of "sublattice melting," i.e., atoms or ions on a certain set of lattice positions become mobile, almost liquid-like, while the remaining atoms (ions) retain their normal lattice positions. The changes in ionic conductivity correspond to related changes of other properties, as for example, heat capacity. These changes result from the gradual disordering of the sublattice responsible for ionic conductivity, i.e., the increase in the number of current carrier ions. This type of transition has been defined as gradual order–disorder transition [9]. At sufficiently high temperature, the disordering of mobile sublattice can be complete with a random distribution of corresponding ions in the space of elementary cell. Such a state is referred to a "structural disorder" and the fully disordered sublattice can be assumed as quasi-liquid. 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 a defined temperature (first-order phase transition). The discontinuous disordering of one ionic sublattice can be exemplified by the $\beta \rightarrow \alpha$ transition in AgI at the temperature 422 K. The 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 [9]. The transition in CaF_2 and $SrCl_2$ [9] can be given as an example of continuous disordering spread over a wide temperature range. Continuous disordering of ionic sublattice is followed by characteristic heat capacity behavior. In the temperature range where this disordering becomes significant, heat capacity reaches unusually high values, consistently with the fact that disorder increase requires additional energy. Clearly marked heat capacity rise with temperature takes place even at relatively low temperatures, indicating continuous transition to the state of "structural disorder." The heat capacity plot versus temperature exhibits a characteristic λ-shape, in close correspondence with electrical conductivity changes. The end of this λ transition (complete "structural disorder") corresponds well to the kink in the electrical conductivity plot. These characteristic features of the different types of order–disorder transitions can be retrieved in the M_3CeBr_6 compounds.

Significant jumps in electrical conductivity that follow the phase transitions must result from increase in the number of mobile ions. 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 $(CeBr_6)$ octahedra in the space of elementary cell.

In the case of K_3CeBr_6 compound which has only high temperature modification, elpasolite-type, possible disordering of cationic sublattice takes place in a discontinuous way at the temperature T_{form}. In this K_3CeBr_6 compound, possibly with cubic, elpasolite-type crystal structure, the anionic sublattice would be constituted by $(CeBr_6)$ octahedra and the cationic sublattice with mobile, almost liquid-like potassium cations. The 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 potassium cations in the space of elementary cell. The kink in conductivity of high temperature modification (Fig. 4), which takes place at the same temperature as the minimum of heat capacity (Fig. 1), can be ascribed to a complete "structural disorder" with potassium cations randomly distributed between $(CeBr_6)$ octahedra and becoming mobile, liquid-like.

In the group of M_3CeBr_6 compounds that have both high-temperature and low-temperature modifications (Rb_3CeBr_6 and Cs_3CeBr_6) disordering of cationic sublattice, formed by alkali metal cations, takes place in a continuous way. It starts in the low temperature modification at temperatures significantly lower than the temperature of non-reconstructive phase transition (T_{trs}). The unusual heat capacity rise with temperature (Figs. 2, 3) proceeds from this disordering. The state of complete "structural disorder" is obtained in the high temperature modification. Thus, heat capacity dependence on temperature exhibits a λ-shape. Behavior 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 or change the slope of the plot $\ln(\kappa)$ versus temperature (Fig. 4). Different in that from the K_3CeBr_6 compound, in which the first-order transition (compound formation) initiates the order–disorder transition, the second group of M_3CeBr_6 compounds includes the superimposition of order–disorder and first-order (low-temperature–high-temperature) transitions.

Conclusions

1. Characteristic dependence of heat capacity and electrical conductivity of solid phase of M_3CeBr_6 compounds on temperature is a result of disordering of cationic sublattice formed by alkali metal cations.
2. Disordering of cationic sublattice in K_3CeBr_6compound that is formed at higher temperature takes place in a discontinuous way at compound formation temperature.
3. Disordering of cationic sublattice of compounds that have low- and high-temperature modifications (Rb_3CeBr_6 and Cs_3CeBr_6) takes place in a continuous way. It starts in the low-temperature modification and is finished in high-temperature modification.
4. The state of complete disordering of cationic sublattice in both types of compounds is obtained in high-temperature modifications (minimum in heat capacity and kink in electrical conductivity dependencies on temperature).

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