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Thermodynamic and transport properties of K_3TbX_6 congruently melting compounds formed in TbX_3-KX binary systems (X = Cl, Br)

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Abstract

Thermodynamic (temperatures and enthalpies of phase transitions, heat capacity) and transport (electrical conductivity of solid phase) properties of K_3TbX_6 compounds are well correlated with their crystal structure. Specific dependence of heat capacity and electrical conductivity of solid phase of K_3TbX_6 compounds can be explained as a result of disordering of cationic sublattice formed by potassium cations. The state of 'complete disorder' of cationic sublattice is obtained in high temperature modification. In this state potassium cations are randomly distributed between TbX_6 octahedra, which form anionic sublattice.

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1. Introduction

Several technologically important processes are related to lanthanide chemistry. Whatever the field of application (lanthanide or lanthanide-based alloys production, reprocessing of nuclear wastes, recycling of spent nuclear fuel, lighting industry,...) fundamental knowledge, which is very scarce in literature, is needed. Thermodynamic data for instance, even if they are included in thermodynamic tables, mostly come from estimation. In addition, when experimental data are available from different sources, they are often in poor agreement. The present work is a part of a general research program focused on lanthanide halides and the systems they form with alkali halides.

We have previously measured and reported the enthalpy of fusion and heat capacity of $TbBr_3$ as well as phase diagrams of $TbBr_3$–NaBr and $TbBr_3$–KBr binary systems [1–3]. This work deals with the thermodynamic and transport properties of the congruently melting K_3TbBr_6 compound, which are compared to those of K_3TbCl_6 chloride analogue [4].

2. Experimental

Samples preparation and experimental procedures used were described in detail previously [1–3,5–9].

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3. Results and discussion

K_3TbBr_6 is the only congruently melting compound in the $TbBr_3$–KBr binary system [2]. It undergoes a solid–solid phase transition at 691 K with related enthalpy 8.0 kJ mol^{-1}, and melts at 983 K with enthalpy 48.0 kJ mol^{-1}. As no information on the structure of the above compound could be found in literature, the nature of the solid–solid phase transition was concluded on the basis of comparative studies for analogous chloride and bromide compounds.

M_3LnX_6 congruently melting compounds (M = K, Rb, Cs; Ln = lanthanide; X = Cl, Br, I) exist in almost all lanthanide halide-alkali metal halide systems [10,11]. Additional structural and emf measurements, performed on chloride and bromide systems [12,13], indicated that all M_3LnX_6 compounds can be divided into two groups: with, firstly the compounds that are formed at higher temperatures from M_2LnX_5 and MX, and secondly the compounds which exist at low temperatures as stable or metastable phases. Those compounds, which are formed at higher temperatures have only one cubic, elpasolite-type crystal structure. Those compounds, which exist both at low temperatures and high temperatures – have monoclinic, Cs_3BiCl_6-type, and cubic, elpasolite-type, crystal structures, respectively [12,13]. We have measured the formation or transition enthalpies of many of these compounds [4,6,10,14,15]. These systematic 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 higher than the enthalpy related to the solid–solid phase transition (only 7–9 kJ mol^{-1}). Thus it can be inferred that the enthalpy increment 8.0 kJ mol^{-1} observed at 691 K in the K_3TbBr_6 compound is undoubtfully related to a solid–solid phase transition. Moreover, taking into account analogies between all the M_3LnX_6 compounds one can assume that the low temperature phase is monoclinic, Cs_3BiCl_6-type, and transforms into the cubic, elpasolite-type, structure at high temperature. The same features were also observed previously for K_3TbCl_6 [4], e.g. a structural phase transition from low-temperature monoclinic, Cs_3BiCl_6-type, to high-temperature cubic, elpasolite-type, with the same enthalpic effect (8.1 kJ mol^{-1}).

Fig. 1 displays the experimental heat capacity data obtained on solid and liquid K_3TbBr_6 on the temperature range 300–1100 K. The characteristic temperatures observed on this plot match well the transition and melting temperatures, which were previously determined by DSC. However, an additional effect, not visible on DSC thermograms, can be observed at about 370 K in Fig. 1(a). No explanation of the nature of this effect can be given at the present time. It is hoped that structural measurements, which are in project in the near future, will bring more insight. Starting from 550 K a significant increase of heat capacity is observed up to the phase transition temperature (Fig. 1(a)), then heat capacity increases smoothly with temperature and no minimum can be observed, as previously found for the K_3TbCl_6 compound [4] (Fig. 2(a)).

It is likely that the characteristic dependence of heat capacity on temperature (unusual increase before phase transition) in K_3TbBr_6 and K_3TbCl_6 may result from a second-order transition (λ transition). One of the reasons of second-order transition appearance can be disordering of cationic or anionic sublattice. If this disordering takes place, it should reflect in the electrical conductivity of the compound. Thus, we decided to perform measurements of electrical conductivity of the solid phase of these compounds. The results are presented in Figs. 1(b) and 2.

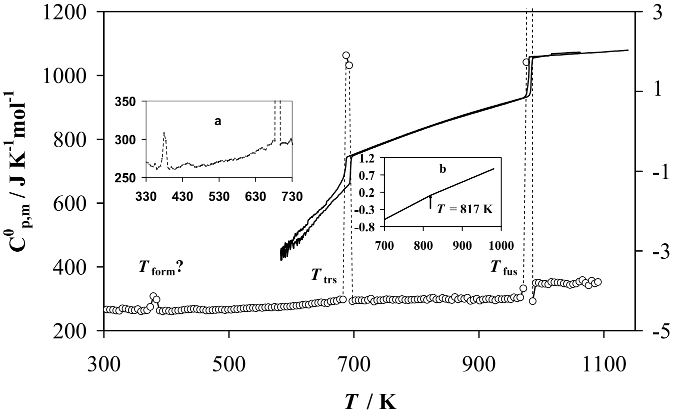

Fig. 1. Molar heat capacity and electrical conductivity of K_3TbBr_6 vs. temperature: open circles – heat capacity experimental results, solid lines – electrical conductivity; insert a – molar heat capacity dependence on temperature before solid–solid phase transition; insert b – evolution of ln κ in temperature range 700–1000 K.

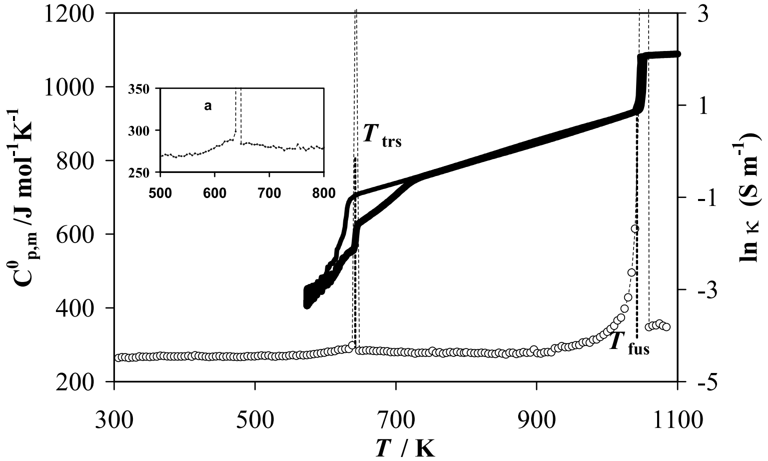

Fig. 2. Molar heat capacity and electrical conductivity of K_3TbCl_6 vs. temperature: open circles – heat capacity experimental results, solid lines – electrical conductivity; insert a – molar heat capacity dependence on temperature before and after solid–solid phase transition.

Electrical conductivity of K_3TbBr_6 rises sharply with temperature (4.78×10^{-2} S m^{-1} at 594 K and 2.72×10^{-1} S m^{-1} at 694 K). At 694 K a significant conductivity jump up to 5.47×10^{-1} S m^{-1} is observed, followed by a further and smooth increase of conductivity up to 9.14 S m^{-1} at 982 K. Careful examination of results in the range 694–982 K showed however, that this smooth increase can be divided into two ranges where conductivity varies linearly with temperature (Fig. 1(b)). These two straight lines cross at about 817 K. Another jump in electrical conductivity up to 69.6 S m^{-1} takes place at 987 K and corresponds to melting.

A similar behaviour was observed for K_3TbCl_6 (Fig. 2). It increases sharply with temperature (5.46×10^{-2} S m^{-1} at 600 K and 1.26×10^{-1} S m^{-1} at 641 K). At 643 K a significant jump in conductivity up to 2.12×10^{-1} S m^{-1} is observed in correspondence with the solid–solid phase transition. This jump is followed by a further, smooth increase of conductivity up to 5.41×10^{-1} S m^{-1} at 731 K where again a change in the slope of the conductivity plot is observed, more marked than for K_3TbBr_6.

These modifications of the conduction regime correlate well with heat capacity dependence on temperature. In ionic solids, a significant increase of electrical conductivity corresponds to a significant increase of current carriers number. It is likely that a solid electrolyte phase appears in the K_3TbX_6 compounds. O'Keeffe and Hyde [16] proposed a simple model of solid electrolyte based on the existence of disordered phase with ionic conductivity. Changes in ionic conductivity correlate well with characteristic changes of other properties, such as, for example, heat capacity. These evolutions result from the gradual disordering of sublattice with ionic conductivity, which causes an increase in the number of current carrier ions. O'Keeffe and Hyde [16] 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 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 occurring at a characteristic temperature (first-order phase transition). In the temperature range where the disordering becomes significant, heat capacity reaches unusually high values, consistently with the fact that disorder increase requires additional energy. Clearly marked heat capacity increase with 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 slope change in electrical conductivity plot. These features describing the different types of order–disorder transitions can be retrieved in the K_3TbX_6 compounds.

In both types of structural modifications of K_3TbX_6 compounds, the anionic sublattice is formed by (TbX_6) octahedra, whereas potassium cations constitute the cationic sublattice [17]. The significant electrical conductivity jumps that follow the phase transitions in these compounds must be due to the increase of mobile ions number. These mobile ions can be only the potassium cations. Thus, it is very likely that the cationic sublattice undergoes gradual order–disorder transition. At sufficiently high temperature, this disordering can be complete and potassium cations are randomly distributed between (TbX_6) octahedra in the space of elementary cell. This disordering of cationic sublattice takes place in a continuous way. It starts in the low temperature modification at temperatures significantly lower than temperature of phase transition (T_{trs}). Unusual heat capacity increase with temperature (Figs. 1(a) and 2(a)) is the result of this disordering. The state of complete 'structural disorder' is obtained in the high temperature modification. Thus, heat capacity dependence on temperature exhibits a typical λ shape. This heat capacity evolution correlates very well with electrical conductivity changes. The end of λ effect on heat capacity plot (state of complete 'structural disorder' of cationic sublattice) corresponds well to the kink in electrical conductivity plot vs. temperature. Continuous disordering of cationic sublattice is overlapped by the discontinuous disordering resulting from the first-order (low temperature–high temperature) transition, which takes place in the K_3TbX_6 compounds.

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