

## **Abstract of doctoral dissertation**

„Thermodynamic properties of binary systems  
 $LnBr_3$ -TlBr ( $Ln = La, Ce, Pr, Nd$ )”

The main aim of the doctoral thesis was the thermodynamic characterization of a series of bromide systems for the first four lanthanides(III), La, Ce, Pr, Nd, with thallium bromide.

An important factor influencing the phase equilibria in binary systems involving lanthanide halides is the purity of the compounds used in the research. Therefore, the first stage of work was the synthesis of anhydrous lanthanide(III) bromides with high purity (min. 99.9%), the so-called "wet method".

Phase diagrams of  $LnBr_3$ -TlBr binary systems ( $Ln = La-Nd$ ) were established in the full range of compositions by differential scanning calorimetry (DSC). The  $LaBr_3$ -TlBr and  $CeBr_3$ -TlBr diagrams were determined for the first time in the presented work, while the literature data on phase relationships in the  $PrBr_3$ -TlBr and  $NdBr_3$ -TlBr systems were verified by us and some information turned out to be incorrect. The topology of the determined  $LnBr_3$ -TlBr ( $Ln = La-Nd$ ) phase diagrams is very similar to each other. The presence of  $Tl_2LnBr_5$ , congruently melting intermediate compound, was found in all the investigated systems, while another  $TlNd_2Br_7$  intermediate compound melting incongruently exists in the  $NdBr_3$ -TlBr system. Both the temperature and the melting enthalpy of  $Tl_2LnBr_5$  compounds ( $Ln = La-Pr$ ) depend linearly on the atomic radius of the lanthanide(III). Due to the different crystal structure of neodymium(III) bromide, the system formed by this compound does not follow these trends. The heat capacity temperature dependences determined by the step method for the compounds  $Tl_2LnBr_5$  ( $Ln = La-Nd$ ) in the solid state is linear. The measured value of the molar heat for  $Ln = La, Ce, Pr$  increases slightly with increasing temperature. By contrast, the dependence of molar heat on temperature determined for  $Tl_2NdBr_5$  shows a negative deviation from the dependence determined as a rule by Neumann-Kopp. However, no dependence of molar heat on temperature was found for the liquid phase of all the discussed compounds.

All the data obtained experimentally were used to optimize the phase diagrams by the CALPHAD method. The coupled phase diagrams of the  $LnBr_3$ -TlBr systems were compared with the thermodynamic properties of the studied  $LnBr_3$ -MBr systems ( $Ln = La-Nd$ ,  $M = Li-Cs$ ). For this purpose, the process of optimizing the systems of lanthanide(III) bromides with alkali bromides by the CALPHAD method was also carried out. The analysis of the thermodynamic properties of  $LnBr_3$ -MBr systems ( $Ln = La-Nd$ ,  $M = Li-Cs$ , Tl) showed that the relative stability of  $M_3LnBr_6$  and  $MLn_2Br_7$  intermediate compounds increases with the atomic number of lanthanides, while the relative stability of  $M_2LnBr_5$  compounds decreases.

The results of calculations obtained by the CALPHAD method enabled the evaluation of thermodynamic properties and structure of the liquid phase in  $LnBr_3$ -MBr systems ( $Ln = La-Nd$ ,  $M = Li-Cs$ , Tl). Based on the calculated course of mixing entropy on the composition  $x(LnBr_3)$ , the contents of the  $\{3M^+ + LnBr_6^{3-}\}$  associate in the liquid phase were estimated for each system. For the systems with lithium and sodium bromides ( $M = Li, Na$ ,  $Ln = La-Nd$ ), the estimated content of the  $\{3M^+ + LnBr_6^{3-}\}$  associate in the liquid phase is negligibly small, whereas in the other systems ( $Ln = La-Nd$ ,  $M = K-Cs$ , Tl) it increases with increasing both the lanthanide ion radius and the monovalent metal ion radius. This implies that the value of ionic potential of the monovalent metal has a decisive influence on the formation and abundance of associates in the liquid phase.

In conclusion, research of great cognitive importance was carried out within the framework of the dissertation. Some of the experimental results presented in this dissertation have been published in peer-reviewed international journals.

Beata Salamou-Baran