The $NdBr_3$-MBr Ionic Mixtures: A Case Discussion of Thermodynamics and Transport Properties of Lanthanide (III) - Alkali Metal Halide Systems

M. Gaune-Escard[C, S]
Ecole Polytechnique, France
Marcelle.Gaune-Escard@polytech.univ-mrs.fr

L. Rycerz and E. Ingier-Stocka
Chemical Metallurgy Group, Faculty of Chemistry, Wroclaw University of Technology, Wroclaw, Poland

S. Gadzuric
Faculty of Natural Science, Department of Chemistry, University of Novi Sad, Novi Sad, Serbia

W. Gong
Department of Physics, Institute of Huizhou University, Huizhou, Guangdong, China

All the $NdBr_3$-MBr liquid binary systems (M = Li, Na, K, Rb, Cs) are characterized by a negative enthalpy of mixing, with a minimum shifted towards alkali bromide-rich compositions. The corresponding interaction parameter λ, which represents the energetic asymmetry in the melt, is negative. Its absolute value increases significantly with alkali cationic radius and is more negative in the alkali halide-rich composition range. The composition dependence of this interaction parameter depends on the nature of the alkali metal cation. Practically linear in the lithium and sodium bromide systems, the $\lambda=f(x)$ plots exhibit a more and more marked minimum for the heavier alkali halide systems. This minimum can be undoubtedly ascribed to the formation of $NdBr_6^{3-}$ octahedral complexes in the systems under investigation. This conclusion, suggested by earlier structural investigations, is further supported by the electrical conductivity measurements performed in the present work. In the solid state, the $NdBr_3$-MBr mixtures are characterized by the M_3NdBr_6 congruently melting compounds (M = K, Rb, Cs), which all undergo a solid-solid transition. Temperatures and molar enthalpies of phase transitions and fusion were determined and compared to those obtained previously for the analogous chloride and bromide compounds of other lanthanides. This comparison showed that the M_3NdBr_6 compounds fall into two categories: compounds, which form only at high temperatures from M_2NdBr_5-MBr and MBr, and compounds, which are stable or metastable at ambient temperature. Moreover, those high temperature-forming compounds can exist at ambient temperature as metastable phases upon fast cooling. Heat capacity and electrical conductivity determinations were performed on all M_3NdBr_6 compounds and consistently indicate a disordering mechanism of the cationic sublattice formed by alkali metal ions.