PHASE EQUILIBRIUM IN THE $LnCl_3$-MCl MIXTURES (Ln=LANTHANIDE ; M=ALKALI) : THERMODYNAMICS AND ELECTRICAL CONDUCTIVITY OF THE M_3LnCl_6 COMPOUNDS

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Phase equilibrium in the systems formed by $LnCl_3$ lanthanide chlorides and MCl alkali chlorides have been investigated intensively [1]. Several experimental methods were used complementarily in order to fully characterize the binary phase diagrams. They include DTA, X-ray and electrochemical techniques, the latter making it possible to identify the nature of phase transitions that take place in the solid state. They allowed to distinguish between the formation of compounds (reconstructive phase transition) and their structural transition (non-reconstructive phase transition).

The $LnCl_3$-MCl binary systems have relatively simple phase diagrams for the light alkali metal chlorides (LiCl and NaCl) while those including KCl, RbCl and CsCl exhibit several compounds of stoichiometry M_3LnCl_6, M_2LnCl_5 and $M_2Ln_2Cl_7$. All the M_3LnCl_6 compounds melt congruently, whereas M_2LnCl_5 and MLn_2Cl_7 happen to melt congruently or to decompose peritectically.

Systematic investigations of the $LnCl_3$-based melts are conducted interactively using different experimental, theoretical and numerical techniques [2-35]. The present work is focused on the M_3LnCl_6 stoichiometric compounds . They exist in most of the $LnCl_3$-MCl systems and have generally a more extended stability range than those of different stoichiometry. Very little is available in literature in this respect and the present work reports thermodynamic investigations performed in conjunction with electrical conductivity measurements over an extended temperature range.

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