

EXPERIMENTAL EVALUATION AND THERMODYNAMIC MODELING OF THE LiF–GdF₃–LuF₃ PHASE DIAGRAM

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The phase diagram of binary systems LiF–LnF₃, where Ln is one of lanthanides elements or Y, were described by Thoma [1]. For the smaller rare earth ions, starting from Ln = Eu, the systems contain one intermediate phase LiLnF₄ that crystallizes in the scheelite structure, with *I4₁/a* space symmetry group. Among these systems, LiF–GdF₃ has been experimentally reevaluated by Ranieri *et al.* [2] resulting in the following data: a eutectic reaction at 25 mol% GdF₃ and 698°C and a peritectic reaction at 34 mol% GdF₃ and 755°C. The LiF–LuF₃ system was corrected by Harris *et al.* [3], it was proposed a eutectic reaction at 20 mol% LuF₃ and 700°C, a congruent melting point at 50 mol% LuF₃ and 850°C, and another eutectic reaction at 58 mol% LuF₃ and 832°C.

Since crystals of LiGd_{1-x}Lu_xF₄ solid solutions are interesting to be doped with other rare earths to develop new laser media, efforts were undertaken to study the phase relations on the ternary system LiF–GdF₃–LuF₃. Therefore, the experimental phase diagram of trifluorides compounds GdF₃–LuF₃ has been investigated and mutual miscibility was observed only for low temperatures, where the GdF₃ and LuF₃ present orthorhombic structure, and for the liquid solution [4]. The pseudo-binary section between the two scheelites LiGdF₄–LiLuF₄ was also investigated by thermal analysis, and it was shown that scheelite mixed crystals under equilibrium conditions are crystallizing first only from Lu-rich LiGd_{1-x}Lu_xF₄ melts $x \geq 0.6$ [5].

In this work thermodynamic simulation of binary sections belonging to LiF–GdF₃–LuF₃ ternary phase diagram has been performed. For calculation of LiF–GdF₃ section, *T-X* experimental points were taken from [2]. Capacity heat and other calorimetric constants were experimentally determined or were taken from Barin [6]. LiF–LuF₃ system was completely re-evaluated and both experimental and theoretical binary phase diagram has been set. And finally, the experimental points of trifluoride section GdF₃–LuF₃ was considered from [4]. Gibbs excess energy terms for the liquid phase, which describe the effects of interaction between the two fluorides in the liquid solution, were expressed by the Redlich-Kister polynomial function [7]. The same model was used to describe the solid solutions phases belonging to GdF₃–LuF₃ system. Afterwards, the solidification path at LiF–GdF₃–LuF₃ ternary phase diagram could be extrapolated according to the formalism of Kohler-Toop.

Keywords: Phase diagrams; Computer simulation; Rare earth compounds

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