

Abstract

Research on novel luminescent materials applicable in efficient mercury-free discharge lamps has been motivated in line with a joint cooperation between industry and universities. In the framework of this BMBF project photoluminescence spectroscopy of rare earth (RE) and transition metal ion doped fluoride crystals has been performed in order to characterize luminescence and energy transfer processes.

LiCaAlF₆ (LiCAF) single crystals, singly and co-doped with Tm³⁺ and Mn²⁺, have been successfully grown by Czochralski technique and investigated spectroscopically in the vacuumultraviolet (VUV) to visible spectral region using synchrotron radiation, F2 operated excimer laser, and supplementary techniques. The iso-structural LiSrAlF₆ (LiSAF) compounds have been obtained by solid state reaction. However, the doping concentrations of the Tm³⁺ and Mn²⁺ doped LiCAF and LiSAF compounds are surprisingly low (of the order 0.01%), being close to the detection limit of the trace analysis. This fact imposes severe restraints on the prospective energy transfer in these hosts.

On the other hand, the optically thin crystals are well suited for absorption and excitation spectroscopy of the (partially) allowed inter-configurational 4f¹¹5d - 4f¹² transition of Tm³⁺. A rich fine structure, mainly consisting of electronic and vibronic lines, is observed in high resolution emission spectra due to transitions to the Stark levels in the crystal field. The splitting of the ground state is determined, and zero-phonon lines of f - f transitions are assigned. Supplementary results have been obtained for BaY₂F₈:Tm³⁺. Fine structure in d - f emission spectra has been revealed in the respective hosts for the first time. The substitutional lattice sites and corresponding charge compensation of Tm³⁺ in LiCAF and LiSAF were investigated by analyzing the fine structure in emission as well as in excitation, being in agreement with the theoretical results of defect and rare earth doping studies in the respective hosts. Drastic differences have been observed in high resolution emission spectra due to f - f transitions excited via the 4f¹¹ 5d states (with excimer laser) compared to those excited via the F - Tm³⁺ charge transfer state at our setup.

A series of Mn²⁺ doped fluoride samples, namely LiCAF, LiSAF, BaMgF₄, KMgF₃, and MgF₂, has been analyzed in terms of 3d⁵ - 3d⁵ transitions and intense absorption bands due to 3d⁵ - 3d⁴ 4s transitions in the VUV spectral region. The oscillator strengths of these bands in LiCAF:Mn²⁺ are determined from absorption spectroscopy in good agreement with sparse values from the literature.

For the first time a systematic analysis of Mn²⁺ in fluorides using synchrotron radiation is presented, associating the observed peaks due to 3d⁵ - 3d⁴ 4s transitions with the corresponding sub-levels of the crystal field splitted ground state. The influence of the local symmetries of different substitutional lattice sites is demonstrated.