Energy transfer processes in rare earth doubly doped lead borate glasses

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Among the different oxide and mixed oxyfluoride glass compositions, lead borate glasses doped with rare earth ions seem to be very attractive systems for optical applications. Lead borate glasses belong to the unique amorphous solid-state materials, which are thermally stable and are formed over a wide region of PbO concentration. The large glass-forming region is advantageous for manufacture of structurally and optically different systems, which strongly depend on B_2O_3/PbO ratios. On the other hand, the introduction of a heavy metal oxide component such as PbO to the borate glass strongly influences its radiative parameters and, consequently, the luminescence peculiarities of rare earth ions. Luminescence properties of lead borate based glasses singly doped with rare earth ions are well documented in literature, in contrast to the same glass-host doubly doped with rare earth ions.

The aim of the PhD thesis was to study energy transfer processes between rare earth ions in lead borate glasses. The following glass systems co-doped with rare earth ions were examined: Yb^{3+}/Tm^{3+} , Dy^{3+}/Tb^{3+} and Tb^{3+}/Ln^{3+} (where Ln = Eu, Sm). In particular, the energy transfer processes and their mechanisms between rare earth ions in lead borate glasses were investigated. The energy transfer efficiencies as a function of donor and acceptor concentrations were determined.

The presence of the excitation energy transfer processes between rare earth ions in lead borate glasses was confirmed by luminescence measurements. The detailed spectroscopic analysis lead to the following conclusions:

- 1. The energy transfer from Yb³⁺ to Tm³⁺ ions in lead borate glass was observed. The energy transfer is quite efficient. However, near-infrared emission at about 1800 nm and blue up-conversion of Tm³⁺ under Yb³⁺ excitation was not observed due to the relative high energy phonon of the glass host.
- 2. The energy transfer from Dy³⁺ to Tb³⁺ ions in lead borate glass was observed. The energy transfer mechanism is electric dipole–dipole interaction for glass samples with lower activator concentrations (up to 3% Tb³⁺). Above 3% Tb³⁺ concentration-dependent luminescence quenching is observed. Further increasing activator concentration (above 5% Tb³⁺) lead to the partial crystallization of lead borate glass host. X-ray diffraction analysis confirmed the presence of crystalline phase TbBO₃.
- 3. The energy transfer from Tb^{3+} to Ln^{3+} ions (Ln = Eu, Sm) in lead borate glass was observed. The relative intensities of the main emission bands of trivalent rare earth ions as a function of donor (Tb³⁺) and acceptor (Eu³⁺) concentration were determined. The energy transfer process in direction Tb³⁺ \rightarrow Eu³⁺ was verified by various experimental methods. The energy transfer from Tb³⁺ to Sm³⁺ in lead borate glass is limited. It is due to the presence of cross-relaxation processes in glass samples containing higher acceptor (Sm³⁺) concentrations.