Institute of Low Temperature and Structure Research
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DOCTORAL DISSERTATION

The study of relaxation processes kinetics in silver indium sulphide nanoparticles

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Abstract

The optical properties of semiconductor nanoparticles – quantum dots (QDs) – can be tuned with their size. This property is known as the quantum size effect. Besides doping, it is one unique way to alter optical properties for a wide variety of binary QDs, e.g. CdSe, InP, ZnS etc. In the case of multinary compounds or semiconductor alloys, the size effect is often associated with the simultaneous control of the stoichiometry, introducing an additional degree of freedom in tuning the spectral characteristics. Deviations from stoichiometry are associated with several complications resulting from the formation of active defect levels. This frequently translates into complicated excited state relaxation kinetics, which is observed as significant deviations from the first-order luminescence decay law. These effects are very well exposed in I-III-VI semiconductor compounds like $AgInS_2$ (AIS) and $CuInS_2$ (CIS). Due to the high tolerance of the I-III-VI QDs for the presence of structural defects, their optical properties strongly depend on a wide class of point defects as well as defect clusters. Depending on the nature and activity of these defects, very strong suppression of exciton transitions and a dominant defect-related emission can be expected. Several models considering defect-related emission have been proposed in the literature, however the exact nature and kinetics of the excited state depopulation in ternary I-III-VI QDs remains an open question. The aim of this thesis was to gain a deeper understanding of the possible mechanisms and kinetics of the excited state relaxation in AIS QDs. The presented research was of an experimental and theoretical nature and included the synthesis of colloidal, semiconductor nanoparticles, their spectroscopic measurements and numerical calculations. The spectroscopic properties of I-III-VI QDs were analyzed on the basis of the measurements of colloidal systems as well as individual nanoparticles. A large variability of both the PL intensity and PL lifetime determined for individual counting intervals was observed, which has not been described in the literature so far. Based on numerical calculations in the framework of the density functional theory (DFT), a possible mechanism for the formation of surface trap states was determined, as a result of the reorganization of surface sulfur atoms aiming at minimizing their charge state. Further numerical calculations regarding the interaction of ligands with silver and indium metal ions, allowed us to observe a significant role of silver ions in the mechanism of the formation of surface defect states. As a result of the obtained numerical results, an attempt was made to control the spectroscopic properties of AIS QDs by intentionally introducing silver defects into the nanoparticle structure, as a result of the synthesis of non-stoichiometric QDs. Silver-rich samples were characterized by increased quantum yield and elongated photoluminescence decay times. DFT calculations of AIS clusters allowed us to link the observed spectral changes with the presence of excess silver atoms in the structure. The obtained experimental and computational results allowed us to propose kinetic models of excited state relaxation including defect-related transitions, in which defect-related optical transitions may be responsible for both the emission and formation of the dark state. Proposed models were simulated using Kinetic Monte-Carlo method. The obtained results were compliant with the experimental results from single-particle measurements of AIS and CIS QDs. A comparative study of the applicability of exchange-correlation functionals, alongside localized basis sets used in the computation of clusters of ternary I-III-VI semiconductors within the density functional theory was also performed. The selection of appropriate numerical methods is crucial to obtain the most accurate results that will be used in the future as an aid in understanding the experimental results.