High Pressure Steady State Photoluminescence and Time-Resolved Photoluminescence Study of MnS/ZnS Core/Shell Quantum Dots

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Mn doped ZnS quantum dots (QDs) is a kind of simple, non-toxic material with excellent luminescent properties, which can be used in chemo/bio-sensing, electroluminescence devices, etc. The MnS/ZnS core/shell QDs used in this work were synthesized via a nucleation doping method. XRD and HRTEM results showed that the QDs were of mono-phase zinc-blende structure with average size of about 3.5nm. To further understand the energy transfer paths and luminescence mechanisms, steady state photoluminescence (SSPL) and time-resolved photoluminescence (TRPL) studies under high pressure were performed using a diamond anvil cell (DAC). From SSPL results, a weak blue PL centered at about 490nm and a strong red PL centered at about 600nm were observed with excitation energy (3.8eV) exceeding the band gap of ZnS (3.5eV). The red emission is widely accepted to be the $4T^1 \rightarrow 6A^1$ transition of Mn^{2+} ions in a ZnS crystal while the blue one can be attributed to trapped states emission. With increasing pressure, the Mn^{2+} emission showed typical red shift due to the strengthened crystal field. After 6GPa, the red shift became unobvious and the intensity showed remarkable decrease until disappeared after 16GPa, which could be attributed to changes of band gap and energy transfer paths. The blue trapped states emission showed little shift and the intensity gradually decreased, much less insensitive to pressure. A bluer peak centered at about 370nm emerged with increasing pressure and showed obvious blue shift, which might be related to some high-lying energy levels. Its intensity increased until 7GPa and then decreased until disappeared after 16GPa. The changing pressure points were similar to those of the Mn^{2+} emission， showing that the emerged bluer peak might be related to the Mn^{2+} ions. With sub-band gap excitation (2.4eV), the red Mn^{2+} emission could also be seen and showed similar trend as with 3.8eV excitation. TRPL with a pulsed laser (3.5eV, 7ns) excitation showed that the Mn^{2+} emission, the trapped states emission and the bluer peak could be almost included in time range of about hundreds of μs, hundreds of ns and less than 10ns, respectively. After the initial hundreds of μs, a red PL could also be seen with integrating time of 10ms, but showed a little blue shift, which could be attributed to the emission of the single isolated Mn^{2+} ions in a cubic site, while the former faster redder Mn^{2+} emission could be attributed to the emission of exchange coupled Mn^{2+} ion pairs. With increasing pressure, the TRPL showed similar shifting and intensity changing trend as their corresponding SSPL and the time constants became shortened. Decay curves of the Mn^{2+} emission and the trapped states emission were also measured, both showed shortening trend with increasing pressure. The Mn^{2+} emission showed single-exponential dynamics until disappeared, while the trapped states emission showed more complex high-density-defects like dynamics, indicating widely spreaded energy level distribution and energy transfer paths. The changes of the SSPL and TRPL properties of the MnS/ZnS core/shell QDs under high pressures revealed some detailed aspects about the electronic structure and energy transfer paths of the material and might give some insight on luminescence mechanism studies and better luminescent properties designing.

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