Ultrafast Exciton Dephasing in PbS Colloidal Quantum Dots

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Lead salt (PbX, with X= Se, S) colloidal quantum dots (QDs) have recently attracted much interest both from the point of view of fundamental physics and for their possible application in optoelectronics, photonics, and biophysics. The exciton lifetime in these QDs can reach the µs range, promising for a long coherence time. Differently from conventional II-VI systems, PbX nanocrystals have a direct band gap at the L point of the Brillouin zone. Therefore, the ground state exciton is 64 fold degenerate [1], compared to the 8-fold degeneracy of excitons in spherical quantum dots with direct band gap at the Γ point. Moreover, the exciton Bohr radius is large (46 nm for PbSe and 18 nm for PbS) compared to the typical QD sizes, and PbX nanocrystals can be considered a model system for strong confinement. However, a direct measurement of the intrinsic exciton dephasing time in PbX dots is still missing.

In this work, we have measured the ground state excitonic dephasing in PbS QDs of sizes from 3.7nm to 5.7nm diameter in the temperature range from 5K to 100K by transient degenerate four-wave mixing (FWM) using 100fs pulses. A combination of heterodyne and **k**-selection detection was implemented [2] to increase sensitivity and enable 4 orders of magnitude dynamic range in the FWM field detection. We found that the intrinsic dephasing is ultrafast even at 5K with a sub-resolution (< 100fs) component followed by a sub-ps component (see Figure), far from the µs-long radiative lifetime. The sub-ps dephasing time decreases with increasing temperature and decreasing QD size. We also measured transient grating dynamics in co- and cross-polarisation configurations (similar to Ref. [3]) and found that exciton spin flip processes would give rise to dephasing times of a few picoseconds, hence they are not the limiting mechanism. We therefore suggest that the observed sub-ps decoherence is due to pure dephasing via phonon-assisted transitions as described theoretically by the so-called independent Boson model [4]. An estimate of the range of phonon wavevectors from the exciton-phonon coupling strength [4] and hence of the width of the phonon band using the LA phonon dispersion for bulk PbS is in good agreement with the measured dephasing. Furthermore due to the peculiar band-structure of PbS in which electron and hole wavefunctions contain contributions from all 4 L-valleys, phonon assisted transitions involve phonons near the Γ point but also near the difference between any two L points. Accordingly the absorption lineshape of a single excitonic level consists of a series of phonon assisted bands distributed over an energy range of about 30 meV. The dephasing between individual phonon bands which are excited simultaneously within the spectral width of the pulse thus accounts for the observed autocorrelation-like component. From the dynamic range in the FWM detection and the absence of an observable zero-phonon line (ZPL) we also estimate that the ZPL weight must be ≤ 7% assuming a 2.6ps ZPL coherence time given by the measured spin-flip time.

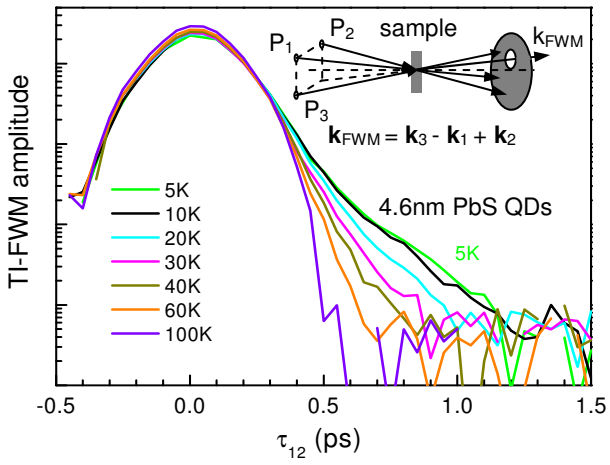

Fig.1 Transient four-wave mixing field amplitude versus delay between the first two exciting pulses measured in resonance with the ground-state excitonic transition in PbS colloidal quantum dots of 4.6nm diameter for different temperatures, as indicated. In the inset the directional geometry used for the FWM excitation/detection is sketched.

References

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