Mid–IR spectroscopy of Fe:ZnSe quantum dots

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Abstract: We report spectroscopic characterization of Fe:ZnSe quantum dots (for 2% of Zn/Fe molar ratio) fabricated by microemulsion hydrothermal synthesis. Mid-IR photoluminescence of the \( ^5E \rightarrow ^2T_2 \) transition of Fe\(^{2+}\) ions over 3.5–4.5 \( \mu \)m spectral range was observed in Fe:ZnSe quantum dot samples and kinetics of luminescence have been characterized at temperatures of 30–300 K under direct (2.788 \( \mu \)m) mid–IR excitation and indirect (0.355 \( \mu \)m) photoionization excitation. The radiative lifetime (\( \tau_{rad} \)) was estimated from these measurements to be 48 \( \mu \)s while lifetime at room temperature was measured to be 440 ns. This agrees closely with the behavior of bulk material.

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References and links

1. Introduction

Transition metal (TM) doped and undoped wideband II–VI semiconductor nanoparticles and quantum dots (QDs) have attracted a great deal of interest. The ability to widen the bandgap through reducing the size of the QDs is promising for use in a variety of applications such as nano–bio application (due to wide absorption features and photo-stability superior to dyes), imaging, and laser spectroscopy [1–3]. In the case of ZnSe, crystals doped with TMs (such as Mn and Cu) have been characterized extensively and successfully with the stable and efficient imaging, and laser spectroscopy [1–3].
band-edge emission at energies slightly lower than the band-gap (580 to 600 nm for Mn:ZnSe [4–6], 350 to 500 nm for Cu:ZnSe [7–9]). These TM doped QDs exhibit high efficiency and high temperature stability as well as long photoluminescence lifetimes. Although successful experiments with doped II–VI QDs emitting in visible wavelengths have been reported [10,11], few have been performed in the mid–IR spectral range [12,13]. Works studying II–VI QDs doped with transition metals (such as Ni, Co, Fe, and Cr) prepared by chemical means have demonstrated poor optical characteristics in the mid–IR spectral region due to the high density of surface defects associated with most methods of synthesis resulting in the quenching of mid–IR luminescence [14–16]. Mid–IR luminescence in the 2–6 µm spectral range has been demonstrated in Co, Cr, and Fe doped II–VI nanocrystals produced by laser ablation, and laser oscillation has been achieved under direct excitation [12,17]; however, this laser ablation method is not readily scalable and offers poor control of particle size distribution.

On the other hand, recent developments in TM–doped II–VI bulk chalcogenides enabled significant progress in the performance of mid–IR laser systems based on these media [18–20]. For example, Fe:ZnSe crystals exhibit strong mid–IR photoluminescence of the $^5T_2 \rightarrow ^7E$ transition of Fe$^{2+}$ ions over the 3–6 µm spectral range with high emission cross–section ideal for broadly tunable laser systems. Laser oscillation has been demonstrated in several regimes of operation at cryogenic temperatures with free running pulse energies up to 2.1 J and continuous wave (CW) power up to 1.6 W. Gain–switched operation has been demonstrated at room temperature with pulse energies up to 30 mJ [18]. Various fabrication techniques have been employed in altering the optical and electronic properties of these semiconductors through the incorporation of various impurities, such as chemical vapor deposition (CVD) [21], physical vapor transport (PVT) [22,23], and post–growth thermal diffusion [24,25] among others. However, fabrication of large-scale, iron–doped laser materials with high dopant concentration and uniform dopant distribution remains problematic for these techniques. Hot–pressed ceramics show great promise for producing these highly–doped samples [26]. However, currently available hot-pressed ceramic materials exhibit strong scattering losses which reduce their effectiveness in laser applications. The large scale production of high quality optically active nanomaterials is an effective route to optimize the production of the pre-annealed green-bodies necessary for higher performance TM-doped II–VI mid-IR laser materials. TM-doped II–VI materials are also wide bandgap semiconductors, which have the potential for electrical excitation of the impurities. Quantum dot and quantum well structures can improve the efficiency of energy transfer to the impurities which can be advantageous for this direction of study [13,17,20].

In the present work, we report the synthesis of uniform Fe:ZnSe QDs using a reverse microemulsion with hydrothermal treatment in an autoclave for a simple-route chemical reaction. In addition, we demonstrate the first spectroscopic characterization of chemically synthesized Fe:ZnSe QDs in the mid-IR spectral range over a range of temperatures (30–300K).

2. Experimental procedures

Iron-doped ZnSe QDs were synthesized using a reverse microemulsion with hydrothermal treatment in autoclave based on Lin Yang et al. [27]. This group indicated that the properties of ZnSe QDs can be controlled with the surfactants polyoxyethylene lauryl ether and Triton X–100. In the current study, Triton X–100 was introduced as a surfactant, producing enhanced band–edge luminescence and a lower density of surface defects as well as high crystallinity. First, a sodium hydrogen selenide (NaHSe) aqueous solution was prepared by mixing selenium (Se) powder and sodium borohydride (NaBH₄) with molar ratio of 1:2. The mixture solution was then intensively stirred for 30 minutes at 100 °C under a N₂ treatment until the color turned dark brown. A precursor mixture of zinc acetate (Zn(AC)₂) was dissolved in deionized water while Iron (II) sulfate Heptahydrate (Fe(SO₄)₂) in deionized water
was prepared separately. Four of Teflon-lined stainless steel autoclave (M1) and four vials (M2) as a reverse microemulsion were prepared. A surfactant (Triton X–100) and cosurfactant (isopropl alcohol) were mixed with cyclohexane (C6H12) as the oil phase to obtain reverse micelles with a volume ratio of 3:6:20. Next, the prepared NaHSe solution was added to the mixture M1 to form a precursor solution. Meanwhile, M2 containing Zn(AC)2 solution and iron sulfate (FeSO4) solution were selectively added. Four feeding ratios of Zn/Fe were prepared as 0 %, 0.2 %, 2 %, and 5% in M2. For hydrothermal treatment, the resultant mixture was put into a Teflon-lined stainless steel autoclave (100 mL in volume), which heated to 120 °C for 12 hours to enable the reaction to occur, and subsequently allowed to cool naturally to room temperature. Finally, ZnSe and Fe:ZnSe nanocrystals were precipitated and the samples separated from the reaction media using a centrifuge. Samples were then washed with ethanol and deionized water, and after a couple of extractions, dried in vacuum to get the solid particles. These ZnSe and Fe:ZnSe nanocrystals were transferred for spectroscopic characterization and structural analysis.

The X–ray diffraction (XRD) analysis was conducted to study the structural properties of as–synthesized freshly dried ZnSe QDs and Fe:ZnSe QDs using PANalytical X’Pert PRO X–ray diffractometer of Cu K–α1 radiation (λ=1.5406 Å) with a scanning rate of 0.02 degree/s operated at 40 kV and 30 mA. The shapes and sizes of ZnSe and Fe:ZnSe QDs were measured using a field emission transmission electron microscope (FE–TEM, JEM–2100F, JEOL) operated at 200 kV. In addition, the elemental properties of the QDs were investigated by energy–dispersive X–ray spectroscopy (EDS, Oxford Instruments).

For a spectroscopic characterization, Fourier transform infrared spectroscopy (FTIR) spectra were measured, using a FTIR–4200 spectrophotometer (JASCO) to identify and characterize the organic species on the surface. For mid–IR photoluminescence (PL) spectra and kinetics of luminescence measurements, an electro–optically Q-switched Cr:Er:YSGG laser operating at 2.78 µm with 80 ns pulse duration was used as an excitation source. Furthermore, PL spectra and kinetics were studied under 355 nm excitation – third harmonic radiation of the Nd:YAG laser (Spectra Physics, GCR–230). Nd:YAG operated with pulse duration 10 ns, repetition rate 10 Hz, and maximum output energy of 0.4 J (at 355 nm). The temperature dependence of lifetime was measured for the studied QDs and mechanically ground Fe:ZnSe powders were used for reference. QDs and powder samples were enclosed in ZnSe container and placed in a closed cycle refrigeration system (Janis Research Co., Inc., Model CCS–450). Sample temperature was adjusted over 30 to 300 K ranges. A low pass filter was placed before the sample to eliminate fundamental frequency from the pump beam. The signal was observed through a low–pass Si–Ge filter combination, focused by a CaF3 lens, and detected by Thorlabs PDA 20H PbSe detector (λ=1.5–4.8 µm) as well as PVI–3TE–5 (HgCdTe, VIGO systems, λ=2–12 µm) with response time less than 200 ns. The photoluminescence spectra were collected by a monochromator (Acton Research ARC–300i), with data acquisition performed using a boxcar integrator (Standard Research Systems Models SR250).

3. Results and discussions

3.1 Characterization of Fe:ZnSe QDs

X-ray diffraction measurements for four feeding ratios of Zn/Fe (0 %, 0.2 %, 2 %, and 5%) were performed to investigate the structure and composition of the QDs. Fig. 1 shows XRD patterns of ZnSe QDs and Fe:ZnSe QDs of three different Fe2+ concentrations. The positions of the prominent peaks correspond to (111), (220), (311), and (400) lattice planes of the cubic zinc blende ZnSe structure with corresponding angle positions of 27.3°, 45.2°, 53.6°, and 66°, respectively, consistent with the standard card (JCPDS Card No. 65-9602) [28]. All samples exhibit dominant Bragg reflection at 27.3°. No other impurity phases are observed in the XRD pattern of Fe:ZnSe QDs, indicating the formation of a pure cubic zinc blende ZnSe phase only.
The average QDs’ sizes (~6 nm) were estimated from the full-width at half maximum (FWHM) using Debye-Scherrer’s formula [29]. A small increase of FWHM was observed with increasing concentration of the iron ions from 0 % to 2 % but this small increase is within the error of our measurement. However, the FWHM was slightly reduced in highly doped ZnSe (5% Fe). This behavior could be explained by two competing processes. At small concentrations, the addition of iron to ZnSe quantum dots can result in reduced crystallinity which can result in the broadening of XRD bands. However higher concentrations of iron could stimulate growth of larger nanoparticles, which would lead to a narrowing of the XRD bands. Composition analysis of Fe:ZnSe QDs was performed using the energy dispersive X-ray spectroscopy (EDS) built into the field emission transmission electron microscope (FE–TEM), providing a measurement of the zinc/iron molar ratio in Fig. 1(b). The EDS spectrum of Fe:ZnSe QDs indicates the presence of Fe, Zn and Se in the synthesized QDs. The detection of strong O and C signals is mainly due to the surfactant binding to the Fe:ZnSe QDs facilitating presence of C=O radicals [30].

The morphology and size distribution of the Fe:ZnSe QDs were confirmed using the FE–TEM images depicted in Fig. 2. These images reveal highly crystalline nanostructures with spherical morphology [Fig. 2(a)]. In the case of the nearly spherical Fe:ZnSe QDs, the measured interplanar spacing (0.327 nm) matched that of the (111) plane of zinc blende ZnSe phase [Fig. 2(b)] and the QD sizes were approximately 5–6.5 nm, which is consistent with XRD data [Fig. 2(c)-2(f)]. The particle size distribution was determined using software (Gatan Microscopy Suite 2.0). Approximately 70-120 particles were manually collected for each sample. The slightly inhomogeneous size distributions are likely the result of the small sample size, however we feel that these particles were representative of the overall sample. As one can see from Fig. 2, samples with higher concentration exhibit a shift of the average particle size toward larger radii. This is consistent with XRD data.
3.2 Mid-IR photoluminescence of $^5E\leftrightarrow^3T_2$ transition of Fe:ZnSe QDs under direct and photoionization excitations

Figure 3(a) shows the absorbance spectrum of ZnSe QDs. The absorbance spectrum of polycrystalline Fe:ZnSe fabricated by post–growth thermal diffusion technique is shown as an insert for comparison [Fig. 3(b)]. Absorbance was measured through samples drop casted onto sapphire substrates. The absorbance spectrum of QDs shows a significant blue–shift of band gap with respect to the spectrum of bulk at room temperature [inset Fig. 3(b)]. An excitonic absorption band is clearly visible in the absorption of Fe:ZnSe QDs [Fig. 3(a)] with a peak near 410 nm. The corresponding average particle size was fit according to the Brus equation,

$$\Delta E(r) = E_{gap} + \frac{\hbar^2}{8r^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\varepsilon_0\varepsilon r},$$

where $\Delta E$ represents the energy of this absorption band, $E_{gap}$ is the bandgap energy, $r$ is the particle radius, $m_e^*$ and $m_h^*$ are the effective masses of electrons and holes within the crystal lattice respectively, $e$ is the fundamental charge constant, and $\varepsilon_0\varepsilon$ is the relative permittivity of the material multiplied by the permittivity of free space. Taking $E_{gap} = 2.71$ eV, $m_e^* = 0.21m_e$, $m_h^* = 0.6m_e$ and $\varepsilon = 9.2$, [31–33] an absorption peak centered near 410 nm corresponds to an average particle radius of ~2.5 nm. This agrees very well with the measurements made by TEM.
Fe$^{2+}$ in a tetrahedral field possesses a $^5$D level split by the crystal field into $^5$E ground state and first excited state of $^5$T$^2$. The absorption and emission spectra for this transition are located in the mid-IR spectral region near 3 $\mu$m. A typical evolution of the transmission spectra of Fe:ZnSe QDs are shown in Fig. 4. The QDs of 0.25%, 2%, and 5% are examined by measuring their FTIR spectra over 1000–4000 cm$^{-1}$ range. All samples exhibit a broad $^5$E$\leftrightarrow$$^5$T$^2$ transition at 2700–3700 cm$^{-1}$. A shifting of the absorption maximum from approximately 3200 cm$^{-1}$ to 3400 cm$^{-1}$ can be partly due to the overlap of the $^5$E$\leftrightarrow$$^5$T$^2$ Fe$^{2+}$ absorption with the absorption associated with stretching vibration of hydroxyl groups on the surface. FTIR measurements do not directly indicate that the surface of QDs is covered with the organic ligands being intercalated by a surfactant (Triton X–100). This can be explained by the fact that typical vibration bands (such as 2923 and 2848 cm$^{-1}$ in CH$_2$ stretching mode [8]) could not be observed due to their overlap with the broad and strong absorption bands at the laser active $^5$E$\leftrightarrow$$^5$T$^2$ transition in Fe:ZnSe QDs.

Mid–IR emission of Fe$^{2+}$ in ZnSe QDs was studied with the use of two regimes of excitation: direct excitation of $^5$T$^2$ triplet excited state of Fe$^{2+}$ and 355nm (3$^\text{rd}$ harmonic of the Nd:YAG laser) radiation.
Fig. 5(a) shows the temperature dependence of PL spectra at the $^5T_2 \rightarrow ^5E$ transition of Fe$^{3+}$ ions in Fe:ZnSe QDs over 3400–4500 nm spectral range. The sample is excited with 2.78 µm radiation, and the Fe concentration of the QDs is 2%. The absorption feature around 4300 nm is caused by atmospheric absorption of CO$_2$. The intensity of the PL band at 200 K is almost an order of magnitude weaker than that at low temperatures. A decrease in the PL is the result of temperature quenching. Above 200 K, the luminescence signal was too weak to effectively measure spectra.

The PL kinetics of the QDs are shown in Fig. 5(b) and 5(c). As one can see, the luminescence decay curves exhibit single exponential behavior through all temperatures and the PL kinetics at low temperatures remain unchanged (48 µs) up to 120 K and then decrease with temperature up to approximately 440 ns at room temperature (RT) due to thermally activated non-radiative decay analogous to the low iron concentration (0.1×10$^{18}$ cm$^{-3}$) doped ZnSe polycrystals [34].

Fig. 5(d) shows the dependence of lifetime on temperature for QD samples compared to bulk [34]. Measured temperature dependence is due to the involvement of nonradiative processes causing thermal quenching of luminescence. A qualitative approach of thermally activated nonradiative transition should be considered. The luminescence lifetime as a function of temperature can be expressed by [35],

$$\frac{1}{\tau(T)} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{nonrad}} \exp\left(\frac{-\Delta E_a}{k_B T}\right),$$

where $\tau_{rad}$ is radiative lifetime, $\tau_{nonrad}$ is nonradiative lifetime (with $1/\tau_{nonrad}$ being the nonradiative relaxation rate), $\Delta E_a$ is the activation energy, and $k_B$ is the Boltzmann constant. The radiative lifetime estimated as a low temperature limit was measured to be 48 µs. A fit to the data in Fig. 5(d) using Eq. (2) yields $\tau_{nonrad}=0.14$ ns and the behavior of the QDs with an activation energy of 1690 cm$^{-1}$ which is close to that obtained from bulk Fe:ZnSe crystal. The results of these fitting parameters for the bulk and QD samples are summarized in Table 1. The smaller radiative lifetime in QD’s can result from concentration quenching which was reported for bulk Fe:ZnSe crystals [34].

<table>
<thead>
<tr>
<th>Crystals</th>
<th>$\tau_{rad}$ [µs]</th>
<th>$\tau_{nonrad}$ [ns]</th>
<th>$\Delta E_a$ [cm$^{-1}$]</th>
<th>$\tau$ [ns]$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Fe:ZnSe</td>
<td>57±4</td>
<td>0.1</td>
<td>2500</td>
<td>382</td>
</tr>
<tr>
<td>Fe:ZnSe QDs</td>
<td>48±2</td>
<td>0.14</td>
<td>1690</td>
<td>437</td>
</tr>
</tbody>
</table>

$^a$Measured at 300 K.
Fig. 5. Photoluminescence (a), luminescence lifetime at 35 and 175 K (b) and at 250 and 298 K (c), and luminescence lifetime (black square: experimental) & the fitting curves (black dashed line) (d) as a function of temperature for Fe:ZnSe QDs (2%) excited by Cr:Er:YSGG laser at 2.78 µm.

In the course of this study the mid-IR photoluminescence of Fe:ZnSe QDs under photoionizing excitation by third harmonic of the Nd:YAG laser at 355 nm was also examined. Several excitation mechanisms by UV radiation are depicted in Fig. 6 [36].

Fig. 6. Possible energy route in Fe:ZnSe QDs excited by 355 nm and 2.78 µm lasers.

The fastest process (τ<1 ns) is direct non–radiative relaxation from the excited complex (Fe³⁺+e*) to the ²T₂ (³D) level [37]. This excitation mechanism is faster than ²T₂ (³D) level decay–time (440 ns) at RT. This level can also be populated by cascade relaxation through higher lying Fe²⁺ ion levels, in which case the rate of population is limited by the lifetime of the metastable ³T₁(³H) state. Finally, in the case of ionization of Fe²⁺ ions, the electron can be
localized at a shallow donor. The large distance between localized electrons and iron ions could result in slow recombination process. These recombination processes have been thoroughly studied via EPR by Godlewski and co-authors [37,38]. The variation of the distances between iron ions and shallow donor (or donor–acceptor pair participation in Auger–type recombination) results in non-exponential behavior [39]. In the case of dipole–dipole interaction, reaction rates depend strongly on the separation of DAP and ions as $R^{-6}$ [36]. In addition to ionization of iron, a 355 nm photon has sufficient energy to create electron hole pairs in bulk and QDs (see Fig. 6). After fast thermalization, electrons and holes localize at DAPs. Subsequent recombination of DAP can provide an additional route for excitation of $\text{Fe}^{2+}$ ions. As shown in Fig. 3, the bandgap in QD is shifted with respect to the bulk and this may result in a change in the ratios between different excitation routes.

In our experiments, kinetics of mid–IR PL at $(5T_2 \rightarrow 5E)$ transition of Fe:ZnSe QD, microsize powder, and bulk under UV excitation were studied. Figure 7 shows decay of the PL signal of Fe:ZnSe QD, and bulk samples measured at RT. The decay curve of the Fe:ZnSe microsize powder was indistinguishable from that measured in Fe:ZnSe bulk samples. The curve (a) shows decay of the PL of Fe:ZnSe QDs measured under direct excitation of the $5T_2$ state for comparison. As one can see from the Figure 7, after excitation all curves reveal similar decay time equal to the decay time from the $5T_2$ level under direct excitation. This indicates fast excitation mechanism of the $5T_2$ level in all samples. However, the tail of the decay curve of bulk samples has longer time constant (3.4 $\mu$s) than that in Fe:ZnSe QDs samples (2.2 $\mu$s). This could be explained by the limit on distance between iron ions and shallow donors in the QDs. While in QDs, this distance is limited by QD size, the large distance in the bulk samples could be responsible for a slow decay process. In addition, in the case of QDs, the charge transfer process may become more effective than photoionization, and this may also result in a shortening of PL tail. The branching ratio for the “fast” excitation route of the $5T_2$ level could be estimated as a ratio of area under the “fast” exponential decay component to the total area under PL decay curve. In our experiments the signal–to–noise ratio limits our measurements by 10 $\mu$s decay time. Using these data, the upper limit of branching ratio for fast excitation route were estimated as 43% and 31% for Fe:ZnSe QDs and bulk samples, correspondingly.

7. Conclusions

The first demonstration of mid-IR photoluminescence in the 3.7–4.5 $\mu$m spectral range from chemically synthesized Fe:ZnSe QDs under mid-IR (2.78 $\mu$m) and UV (355 nm) excitation is reported. The combined procedure of microemulsion and hydrothermal synthesis
to prepare ZnSe QDs and Fe doped ZnSe QDs can be utilized for the large-scale fabrication of Fe:ZnSe QDs optically active in the mid-IR spectral region. The radiative lifetime (τ_{rad}) in 5 nm QDs was estimated from these measurements to be 48 µs while lifetime at RT was measured to be 440 ns. This agrees with the behavior of bulk material. Measurement of the temperature dependence of luminescence decay times can be fitted to the Mott model of thermally activated nonradiative processes and the activation energy was estimated to be ΔE_{a}=1690 cm⁻¹. It was demonstrated that this fabrication technique is a viable method for large–scale production of green body material for hot-pressed ceramic mid–IR laser gain elements.

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