Second harmonic generation and two-photon luminescence upconversion in glasses doped with ZnSe nanocrystalline quantum dots

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Abstract

We report two-photon excited emission in borosilicate glasses doped with ZnSe nanocrystalline quantum dots. The emission, predominantly near the two-photon energy and detected in the direction of the excitation beam, is in the visible, and the fundamental excitation is the near-infrared output of a tunable femtosecond laser. Depending on the two-photon energy, time- and frequency-resolved measurements at room temperature reveal that the emission largely consists of second harmonic generation (SHG) and two-photon luminescence upconversion, and a much smaller luminescence from redshifted, low-lying trap states and other trap levels residing near the semiconductor band edge. We discuss the SHG origin in terms of bulk-like and surface contributions from the nanocrystals and the two-photon resonant enhancement near the excitonic absorption.

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1. Introduction

Optical second harmonic generation (SHG) in media doped with inorganic semiconductor nano-

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ZnSe quantum dots have received considerably less attention than others such as CdS and CdSe. In light of recent discoveries of SHG due to CdS nanocrystals in silicate glass [5] and CdSe nanocrystals in toluene [9,12], the possibility of producing SHG with ZnSe nanocrystals in a disordered medium such as glass is particularly appealing. Although their bulk second-order nonlinear susceptibilities are similar [16,17], the possible influence of differences in their underlying crystal structures at the nanoscale remains unexplored. While optically anisotropic CdS and CdSe are of hexagonal crystal structure, ZnSe is optically isotropic and exhibits a cubic crystal structure. Since ZnSe is noncentrosymmetric, SHG can either originate within the ZnSe nanocrystal or at the ZnSe nanocrystal–host interface. The bulk SHG susceptibility tensor components and the two-photon resonant enhancement [17,18] are expected to influence the bulk-like SHG contribution originating within the nanocrystals. However, preponderance of highly polarizable, noncentrosymmetric surface states due to imperfectly passivated nanocrystal surfaces in glass may also provide a source for the SHG mechanisms.

In this paper, we report measurements of the room temperature, two-photon excited emission in glasses doped with the ZnSe nanocrystals. The time-resolved emission is largely a fast component whose time resolution is limited by the instrument response of several nanoseconds. It also exhibits a much smaller, long multiexponential tail lasting several to hundreds of nanoseconds. Depending on the proximity of the two-photon energy to the excitonic absorption peak, the fast component is either largely due to SHG or a mixture of SHG and resonant luminescence. The slow component, on the other hand, is assigned to luminescence from redshifted, low-lying trap states and other trap levels residing near the band gap. Frequency-resolved measurements further confirm these findings. In particular, they indicate that the two-photon excited emission is largely centered near the two-photon energy and its spectral width is governed by the two-photon energy and its proximity to the excitonic absorption peak. When the two-photon energy of the fundamental excitation frequency is redshifted from the excitonic peak, the two-photon excited emission is centered at the two-photon energy and its spectral width corresponds to the coherence bandwidth of the fundamental excitation frequency. If, however, the two-photon energy of the fundamental excitation frequency is largely resonant with the excitonic peak, the spectrum exhibits broadening of the emission at the two-photon energy and a broad but much smaller redshifted emission beyond 500 nm. The enhancement of the SHG amplitude also is observed as the two-photon energy approaches the excitonic absorption peak. We discuss the SHG origin in terms of the bulk-like and surface contributions, and whether resonant enhancement influences the SHG component.

2. Experimental

The borosilicate glass sample doped with ZnSe nanocrystals was prepared at Corning’s Advanced Materials Processing Laboratory. The glass-melt recipe was based largely on a previous work [19]. The glass was annealed at 580 °C and exhibited a red-orange color. It was cut and polished into 2 mm thick, 10 mm × 10 mm samples of high optical quality. Fig. 1 shows the absorption spectrum taken at room temperature. The bulk ZnSe band gap energy is ~2.7 eV whereas the lowest excitonic transition peak position for the ZnSe-doped glass in Fig. 1 is near 400 nm or 3.1 eV. This blueshift of 0.40 eV implies that there are nanocrystals with an average radius ~2 nm [20]. The volume fraction of nanocrystals is estimated to be ~ 0.1%.

The excitation source was a tunable femtosecond laser, which emits linearly polarized, near-infrared, ~100 fs pulses at the 76 MHz pulse repetition frequency (PRF). This PRF was reduced to 3.8 MHz for the power-dependent measurements and 809 KHz for the time-resolved emission measurements. The spot size of ~21 μm was determined by measuring transmittance through precision pinholes of known sizes placed at the beam focus and using a Gaussian spatial beam profile. Two-photon excited emission measurements were made with the fundamental laser center wavelength tuned to 760, 800, and 853 nm.
The laser center wavelength and bandwidth (∼ 11 nm for each wavelength) were measured with an IST-Rees spectrum analyzer. The band pass filter was placed before the focusing lens and the sample to prevent the extraneous second harmonic light generated from optics placed before the sample from reaching the detector. The emitted photons were counted using a Hamamatsu R6358P photomultiplier tube (PMT) and a gated photon counter. The PMT gain was set to a constant value throughout the measurements. Interference and band pass filters were placed just before the PMT detector to ensure that mostly the two-photon excited emission was detected. The two-photon excited emission profile was measured by performing gated detection and scanning the gate with respect to the synchronous trigger from the pulse picker driver. The gate width was set to the minimum at 5 ns and each scan step was 3 ns. The instrument response in the time-resolved measurements was determined with a BBO doubling crystal (1 mm thick and ∼ 13% conversion efficiency) in place of the sample and measuring the instantaneous frequency-doubled light. The spectral measurements were made with a Jobin Yvon Triax 320 monochromator, its entrance slit width being set at about 0.5 mm. When calibrated against the SHG output of the BBO crystal measured with a calibrated power meter and attenuated with neutral density filters of known optical density, the apparatus is sensitive to SHG powers as low as $10^{-12}$ W.

3. Results and discussion

Fig. 2 is a logarithmic plot of the room-temperature power-dependence measurements taken with the fundamental excitation wavelength at 800 nm. The linear fit (solid line) whose slope of ∼ 2.1 indicates a quadratic power dependence. The quadratic power dependence also was obtained for the measurements taken with other center wavelengths at 760 and 853 nm. The quadratic dependence is characteristic of a two-photon process such as the two-photon excited emission.

Fig. 3 shows the room temperature, time-resolved two-photon excited emission measured with the 760, 800, and 853 nm fundamental wavelengths.
excitations. Each emission was detected with an interference filter having a bandwidth of several nanometers that passed only the second harmonic of the fundamental excitation frequency. In particular, Fig. 3a is a full-scale plot of the emission showing a fast component whose time resolution is limited by the instrument response. For the sake of clarity, we have chosen to display the instrument response function scaled to the peak amplitude of the 800 nm fundamental excitation only. Fig. 3b shows the same emission plotted on an expanded scale revealing a long, multiexponential decay obtained with the 760 and 800 nm fundamental excitations. The 853 nm fundamental excitation data, on the other hand, largely consist of the fast component. The tiny peaks seen between the gate delays of 10 and 150 ns are artifacts in the signal that are present at the current PMT gain setting, while the long multiexponential decay is reproducible and not associated with any particular PMT gain setting. The instrument response measured with the BBO frequency-doubling crystal also showed these peaks at the same temporal positions. The inset of Fig. 3b shows the 760 nm fundamental excitation data plotted on the logarithmic scale with a double-exponential decay fit (solid line) to the tail. The two decay times obtained are ~ 40 and 460 ns. The amplitudes of these components are less than 1% of the amplitude of the fast component. Fig. 4 shows the same two-photon excited emission decay now measured at 77 K, showing a multiexponential behavior similar to that indicated in Fig. 3b. Although there are differences in the actual decay times among the curves in Figs. 3 and 4 due to inhomogeneity of the sample and different locations of the excitation laser beam on the sample during the measurements, the nanosecond multiexponential behavior persists and is reproducible. Furthermore, decays measured without the narrow-band interference filters also exhibit the long, multiexponential decay behavior.

Fig. 5 shows the spectral contents of the two-photon excited emissions measured at room temperature. These spectral measurements were made with a band pass filter that transmitted
visible photons. The spectra have been scaled to achieve the same peak height for comparison. The spectral peaks for the 760, 800, and 853 nm fundamental excitations are located near the two-photon center wavelengths, respectively, at 380, 400, and 426.5 nm. The full-width at half-maximum (FWHM) of the 853 nm fundamental excitation is \( \frac{11}{C^2} \) nm, showing the excitation bandwidth limitation. The FWHM of the 800 nm fundamental excitation also is \( \frac{11}{C^2} \) nm, but the spectrum exhibits a small amplitude between 407 and 420 nm (making the main peak in the spectrum appear somewhat asymmetric) and also between 525 and 575 nm. On the other hand, the spectrum for the 760 nm fundamental excitation is highly asymmetric with the FWHM (\( \sim 30 \) nm) clearly being much greater than the laser pulse bandwidth. This spectrum most probably contains some amplitude near 550 nm, as observed for the 800 nm fundamental excitation, but the signal-to-noise ratio there is not sufficient to observe this emission. We discuss these and other aspects of the data below.

Past measurements on glasses doped with ZnSe nanocrystalline quantum dots of the size employed here revealed a broad single-photon excited luminescence (width \( \sim 250 \) meV) in the blue-ultraviolet region [20]. Its decay time due to recombination at the band edge was estimated to be several nanoseconds. Furthermore, two-photon microscopy measurements on different II–VI nanocrystals of CdSe also showed a broad luminescence [21]. We therefore expect the two-photon excited luminescence from ZnSe nanocrystals to be much broader than the excitation laser bandwidth. The two-photon excited emission here instead resembles previous measurements on CdSe nanocrystals in toluene [9, 12] and CuCl nanocrystals in an NaCl matrix [6, 7]. It was observed in those measurements that the emission upon two-photon excitation at or above the band gap consisted of a component at the two-photon energy whose resolution was limited by the laser bandwidth and a broad luminescence component at an energy much less than the two-photon energy. Furthermore, two-photon excitation below the band gap generally resulted in second harmonic scattering at the two-photon energy [6, 7, 9, 12]. We make similar observations here except that much of the emission is near the two-photon energy. The inhomogeneous glass samples contained randomly oriented ZnSe nanocrystals. Therefore they were effectively centrosymmetric, and the SHG produced by all the dots should average to zero. However, a random partial alignment perhaps achieved during processing also should produce a weak SHG, as observed in our measurements. The observed SHG emission was directional and depended on the orientation of the sample and the polarization of the pump beam. These are characteristics of the coherent SHG emission. On the other hand, photoluminescence is incoherent, and should be isotropic and unpolarized. Although our time resolution may not have been sufficient, based on the past results, our frequency-resolved measurements, and the above observations, we conclude that the two-photon excited emission obtained with the fundamental tuned to 853 nm is largely due to SHG and that the fast component, whose time resolution is limited by the instrument response, is predominantly of the SHG origin. However, the excitations with higher two-photon energies whose fundamentals are tuned to 800 and 760 nm result in emissions

![Fig. 5. Two-photon excited emission spectra measured at room temperature.](image-url)
that most likely contain, in addition, a luminescence component. We further discuss emissions at 400 and 380 nm and the origin of luminescence below.

Since the emission at 400 nm (the 800 fundamental in Fig. 5) is essentially bandwidth-limited, we conclude that the fast component in the time-resolved measurement (Fig. 3a) is largely of the SHG origin. On the other hand, the emission at 380 nm (the 760 nm fundamental in Fig. 5), which is much broader than the laser bandwidth, appears to be of both the SHG and luminescence origins. We attribute this photoluminescence portion of the fast component to the recombination near the band edge. The weak, but measurable, long multiexponential tail in the time-resolved emissions though appears to be of a different origin. In bulk semiconductors, time-resolved luminescence measurements had revealed a complex, multiexponential decay lasting several to hundreds of nanoseconds. Its origin was assigned to donor–acceptor pair transitions and relaxation from other trap states [22–25]. Similarly, single-photon excited acceptor pair transitions and relaxation from other trap states [22–25].

We further assume that the effective SHG susceptibility and the effective coherence length for the ZnSe nanocrystals remain essentially the same as the bulk values. We further assume that all the nanocrystals are aligned. Using the average fundamental intensity of \( \sim 2 \times 10^7 \text{W/m}^2 \), \( n \sim 2.5 \) [28], and \( \eta = 0.001 \), we obtain a “rough” conversion efficiency of \( \sim 5 \times 10^{-14} \), which is much smaller than the measured value of \( \sim 6 \times 10^{-8} \). Our motivation for using Eq. (1) to arrive at the above “rough” conversion efficiency estimate is the \( L^2 \) (square of sample thickness) dependence observed in the case of a phase-matched SHG for glasses doped with the II–VI semiconductor nanocrystals [1,2]. Here, we have instead used not the total thickness but the much smaller bulk coherence length. The much smaller calculated value compared to the measured value suggests a more prominent surface contribution to the overall second-order nonlinearity in our

\[ \frac{I_{2\omega}}{I_{\omega}} \sim 8 \left( \frac{\mu_0}{\varepsilon_0} \right)^{3/2} \eta^2 \frac{L_{\text{eff}}^2}{L_{\text{coherence}}^2} I_{\omega}, \]

where \( \eta \) is the volume fraction of nanocrystals, \( \mu_0 \) is the free-space permeability, \( \varepsilon_0 \) is the free-space permittivity, \( I_{\omega} \) is the fundamental intensity at the focus inside the nanocrystal sample, and \( n_{\text{eff}} \) and \( L_{\text{eff}} \) are, respectively, the refractive index and the coherence length of the effective medium consisting of the glass host and the ZnSe nanocrystals. For the purpose of estimating the upper limit to the SHG emanating inside the nanocrystals, we assume that the effective SHG susceptibility and the effective coherence length for the ZnSe nanocrystals remain essentially the same as the bulk values.

Assuming that all of the emission near 426 nm is due to SHG, we obtain a conversion efficiency of \( \sim 6 \times 10^{-8} \) for the fundamental excitation at 853 nm with the 32 mW average power and the 3.8 MHz PRF. ZnSe is a cubic crystal with only three nonvanishing but equal second-order nonlinear susceptibility tensor components, namely, \( d_{xyz}, d_{yzx}, \) and \( d_{zxy} \). The \( d \) value (dropping subscripts for clarity) in the near infrared is \( \sim 1.5 \times 10^{-21} \) in MKS units [17]. The coherence length for ZnSe is \( \sim 3 \mu \) [17]. The SHG conversion efficiency can be approximated as [16,18]

\[ \frac{I_{2\omega}}{I_{\omega}} \sim 8 \left( \frac{\mu_0}{\varepsilon_0} \right)^{3/2} \eta^2 \frac{L_{\text{eff}}^2}{L_{\text{coherence}}^2} I_{\omega}, \]

\( 1 \) We use the convention \( P_{(2)}^{(2)} = d_{ik}E_iE_k \) instead of \( P_{(2)}^{(2)} = \varepsilon_0 d_{ik}E_iE_k \), where \( P_{(2)}^{(2)} \) is a nonlinear polarization component. Therefore the cited value of \( d \) has absorbed \( \varepsilon_0 \) [27].
measurement. A prominent surface contribution is entirely possible in a glass host where there is a preponderance of noncentrosymmetric surface states at the nanocrystal–glass interface. To rigorously quantify the bulk and surface contributions, size-dependent SHG measurements similar to those of references [9,12] and precise coherence length measurements are necessary. The measurements of references [9,12] indicated enhancement of the first hyperpolarizability of noncentrosymmetric CdSe nanocrystals as the nanocrystal radius decreased. The authors attributed this observation to a more prominent surface contribution at smallest radii, where the total SHG contribution no longer scales with the nanocrystal volume as observed for large nanocrystal radii.

As outlined in the theoretical treatment of SHG in centrosymmetric nanoparticles, both surface and bulk SHG sources may be incorporated into the total susceptibility as a sum [8]. In a similar fashion, we now treat the susceptibility $d$ in Eq. (1) as the sum of the bulk and surface contributions. Therefore, if we instead calculate $d$ using the same values for the remaining parameters in Eq. (1) except for the conversion efficiency of $2 \times 10^{-7}$ measured at 800 nm and assuming that the two-photon excited emission here is largely of the SHG origin, we find that the $d$ value obtained with the 800 nm fundamental excitation is about twice as large as the $d$ value obtained with the 853 nm fundamental excitation. Regardless of the physical origin (surface or bulk) of SHG, this finding suggests the possibility of two-photon resonant enhancement in the nonlinear susceptibility as the fundamental wavelength is blueshifted from 853 to 800 nm. The resonantly enhanced SHG of interfacial or bulk origin has been either deemed possible or demonstrated [8,17].

4. Summary

We have observed two-photon excited emission as a function of the near-infrared excitation frequency in the vicinity of the band gap in glasses doped with ZnSe nanocrystals. Depending on the fundamental excitation frequency and the proximity of the two-photon energy to the excitonic absorption peak, the emission consists of SHG, photoluminescence upconversion, and relaxation from the traps residing near the band gap and the low-lying traps. Time- and frequency-resolved measurements reveal that the emission is largely due to SHG when the nanocrystals are excited with 800 and 853 nm wavelengths. At the 758 nm fundamental excitation wavelength, the emission consists of resonant photoluminescence and SHG. Furthermore, a much smaller component assigned to luminescence from the trap states residing near and in the band gap is observed in the time-resolved emissions measured with the 758 and 800 nm fundamental wavelengths. This component exhibits a multieponential decay lasting several to hundreds of nanoseconds. This component is reminiscent of long luminescence decay times previously observed in bulk semiconductors.

We have measured SHG conversion efficiencies of $6 \times 10^{-8}$ and $2 \times 10^{-7}$, respectively, at the 853 and 800 nm fundamental excitations. We also have estimated the conversion efficiency at the 853 nm fundamental excitation using a bulk nonlinear susceptibility value and a coherence length of a few microns. The resultant conversion efficiency is much smaller than the measured value, suggesting a prominent contribution arising from a nonvanishing nonlinear susceptibility source associated with surface states. To ascertain the origin of the increase in the SHG intensity as the two-photon energy is tuned towards the excitonic absorption peak, we have estimated the second-order nonlinear susceptibilities from the measured conversion efficiencies. We found that the susceptibility is twice as large at the resonance, when the fundamental excitation wavelength is 800 nm. Although this enhancement in the second-order nonlinear optical susceptibility is reminiscent of the two-photon resonant enhancement observed in bulk semiconductors, the resonant enhancement originating in the nonlinear susceptibility arising from surface states is also possible.

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