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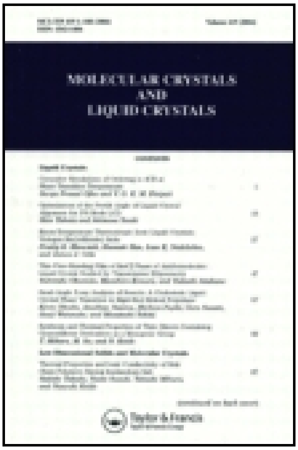

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Luminescence Properties of Indirect Bandgap Semiconductors: Nanocrystals of Silver Bromide

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Version of record first published: 24 Sep 2006.

To cite this article: Wei Chen, Julie M. Rehm, Claude Meyers, Michal Ilana Freedhoff, Alfred Marchetti & George Mclendon (1994): Luminescence Properties of Indirect Bandgap Semiconductors: Nanocrystals of Silver Bromide, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 252:1, 79-86

To link to this article: http://dx.doi.org/10.1080/10587259408038213

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Mol. Cryst. Liq. Cryst. 1994, Vol. 252, pp. 79–86
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LUMINESCENCE PROPERTIES OF INDIRECT BANDGAP SEMICONDUCTORS: NANOCRYSTALS OF SILVER BROMIDE

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Abstract Using a modified reverse micelle protocol with acetyl bromide as the bromide source, AgBr nanocrystals can be grown over a size range from 30 Å radius to bulk. These clusters exhibit quantum confinement indicated by an increasing blue shift of the free exciton emission peak as a function of size. As the cluster size decreases, a concomitant decrease occurs in the apparent radiative lifetime. This is predicted as the k selection rules break down at small crystal diameters. However, the effects are quite modest, indicating that even at these smallest sizes, the indirect character of the transition is largely retained.

Keywords: nanocrystals, silver bromide, exciton emission, indirect bandgap

INTRODUCTION

The photophysical properties of size restricted direct gap semiconductors have been extensively investigated. For such "nanocrystalline clusters," the optical properties are sensitive to size, with both emission and absorption shifting to higher energy with decreasing size of the crystal.[1-6] This is recognized as a "quantum confinement" effect.

The effect of size restriction on indirect gap semiconductors is interesting because it may be two-fold. First, the shift of the band edge toward higher energy as crystal size decreases is expected. Second, the shape of the bands and the selection rules governing the transitions between bands might also be affected. Brus and co-workers hypothesize that mixing of surface state wave functions into those of the bulk will cause the behavior of an indirect gap material to begin to resemble a direct gap material.[5] The confinement of the wavefunction in small crystals causes a breakdown in k(momentum) selection rules, and the ordinarily forbidden bandedge transition of the indirect gap material becomes "less forbidden". Therefore, the probability of the transition would increase with decreasing crystal radius and correspondingly the radiative lifetime would shorten. The indirect material, which typically exhibits radiative

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lifetimes on the order of milliseconds, could then exhibit lifetimes on the order of nanoseconds. Such questions have assumed particular importance for understanding luminescent (highly porous) silicon.

In earlier work[7] we showed that when the indirect gap material AgBr was prepared as 50 Å (radius) nanocrystals, a blue shift consistent with exciton confinement was observed. More interestingly, a concurrent large increase was observed in the (formally forbidden) exciton emission. Such an increase indeed suggests a change in the momentum selection rules of AgBr with the nanocrystal exciton developing more direct bandgap material character. This is quantitatively supported by an increase in the zero phonon line for smaller crystals. However, direct assignment of any band re-hybridization effect is complicated by other effects, including impurity exclusion and perhaps recursive recombination.

A more direct measure of $\underline{k}$ selection would be observation of the exciton absorption feature. Unfortunately this absorbance is obscured by scattering in the (frozen) reverse micelle solution. A formally equivalent alternative approach is to measure the radiative lifetime of the exciton. Preliminary measurements[7] for the 50 Å cluster suggested a surprisingly fast (nanosecond) lifetime, which, if correct, would suggest an almost complete breakdown of the selection rules.

To clarify the situation, we have developed a more general approach to synthesis and characterization of AgBr nanocrystals over a more extended size range. This synthetic procedure permits a more systematic examination of the dependence of the radiative lifetime on cluster size, as detailed below.

EXPERIMENTAL

Preparation of Size-Restricted Silver Bromide

Size restricted silver bromide crystallites were made using reverse micelles. Acetyl bromide (Aldrich) and silver nitrate (Fisher) was used as received. Dioctyl-sulfosuccinate, sodium salt (AOT, Aldrich) was first purified by stirring with activated charcoal for 24 h and then filtered repeatedly and dried under vacuum. All micelle solutions were made from a 0.2 M stock solution of AOT in HPLC grade n-heptane.

Most silver bromide preparations were made from solutions of compositions of $\omega = 2$ to 10 (where $\omega = [H_2O]/[AOT]$). For an $\omega = 3$ reverse micelle solution, 0.27 mL of 0.1 M $AgNO_3$ solution was added to 25 mL of 0.2 M AOT in pure heptane. The solution was stirred for 30 min or until clear. The Ag^+ containing micelle solution was protected from the light at all times. A solution of 0.02 M acetyl bromide (CH_3COBr, AB) in heptane was freshly prepared. The AB concentration was varied from 0.02 M to 0.1 M.

To make the silver bromide crystallites, 2 mL of the 0.1 M Ag^+ reverse micelle solution was mixed with 1 mL of 0.02 M AB solution and was vortexed immediately for about 20 s. This solution was diluted to 8 mL with pure heptane and vortexed for 30 s. The sample was mounted and cooled to liquid helium temperatures within 4-5 min.

The sizes of the silver bromide clusters were determined by transmission electron microscopy (TEM). For an $\omega = 10$ solution, the mean particle diameter was 150 Å ± 70Å. A transmission electron micrograph of the crystallite resulting from an $\omega = 10$ preparation is given in Figure 1. For an $\omega = 3$ solution, the mean particle diameter was 70 Å ± 15Å. The low temperature luminescence apparatus used was previously described by Johannson et al.[7]

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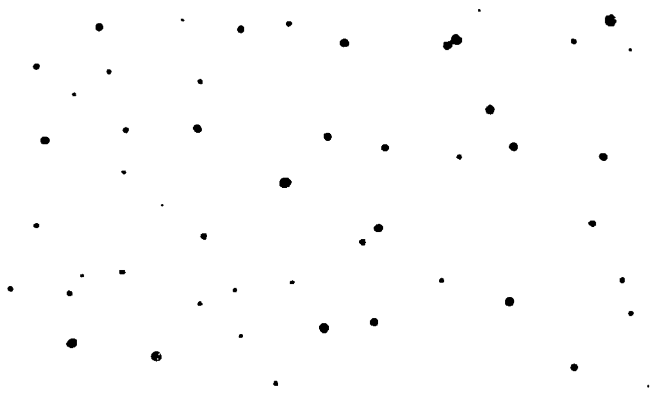

FIGURE 1 Transmission Electron Micrograph of ω=3 inverse micelle preparation of AgBr. The mean particle size is 70Å ± 15Å.

RESULTS AND DISCUSSION

Synthesis

As a rule, semiconductor clusters are thermodynamically unstable relative to the bulk and can thus only be prepared under kinetic control, e.g., "arrested precipitation." By varying the conditions (medium, temperature, and reactants) for nanocrystal formation, the cluster size can be varied. One popular approach has been synthesis in water in alkane "inverse micelles."[6-9] By varying the ratio (ω) of water to surfactant, the size of the water pool can be systematically varied. Crystal growth is then controlled in part by limiting the number of collisions which occur between the water pools. In this way, a range of cluster sizes has been obtained for II-VI materials.

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Such a procedure has been adapted with some success for the more ionic AgBr clusters by mixing micellar solutions which contain Ag^+ and Br^-, respectively. While this approach reproducibly produces 50 Å radius particles when $\omega = 3$, attempts to vary cluster size by variation of ω proved unsuccessful. To provide additional kinetic constraints in previous work on II-VI materials, alternate reagent sources have proved to be valuable (e.g., $(TMS)_2Se$ for synthesis of CdSe)[6].

We have therefore investigated a non-ionic bromide source: acetyl bromide (CH_3COBr). While acetyl bromide is stable in the heptane phase, it will hydrolyze on contact with the Ag^+ containing water pools, thereby releasing Br^- at a controlled rate. Thus the reaction proceeds via a three-step mechanism:

1. $CH_3COBr + H_2O \rightarrow CH_3COOH + HBr$
2. $HBr + AgNO_3 \rightarrow AgBr + HNO_3$
3. $AgBr + nAgBr \rightarrow (AgBr)_n$

This additional kinetic constraint in step 1 has indeed provided a route to a systematic range of $(AgBr)_n$ clusters, as desired. The optimal range of concentrations of CH_3COBr was 0.02-0.1M.

The size of the clusters was estimated indirectly by the emission frequency (vide supra) and directly by transmission electron microscopy (TEM). We believe that TEM somewhat overestimates both the mean cluster size and the size distribution, due to (limited) ripening that occurs as the solution is concentrated during preparation of the TEM samples.

Low Temperature Steady-State Luminescence Spectra

As detailed in earlier work, band edge luminescence provides insight into the exciton energies of the AgBr clusters[7]. This situation for AgBr contrasts with the better studied II-VI clusters (e.g., CdS, CdSe) where direct absorbance can provide elegant spectroscopic characterization of the clusters, while emission is, in general, dominated by mid-band trap states which may be reduced by chemical treatment but not eliminated[8]. For AgBr, direct absorbance spectroscopy is less helpful since the direct absorption is momentum forbidden and therefore weak. However, surface trapping appears to be far less important in the highly ionic AgBr than for the more covalent II-VI materials. Thus a peak which essentially corresponds to the free exciton can be readily observed in AgBr clusters. Following the simple particle in a box approach of Brus[12], the exciton energy of various AgBr cluster sizes can be estimated using the equation

$$E = \frac{h^2 n^2}{8R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] \frac{-1.8e^2}{\varepsilon R} + E_g \qquad (1)$$

where $m_e(m_h)$ is the effective mass of the electron(hole), R is the crystal radius, ε is the bulk dielectric constant and E_g the bulk bandgap.

The results of such a calculation when compared with experiment are shown in Figure 2. Both qualitative and semiquantitative agreement between the simple theory and experiment is clear. However, the observed energies are generally higher than predicted. Several explanations for such a discrepancy are possible. First, the theory is clearly approximate and should break down at very small R. However, in the weak confinement region ($R \geq R_{exciton}$) investigated here, the breakdown should be small. Secondly, the clusters show a range of sizes as expected for a kinetically controlled process. Since E increases rapidly with decreasing R, the observed position of the band will be preferentially weighted toward higher energy. Finally, this uncertainty will be exacerbated by crystal growth ("Ostwald ripening") which occurs during the time that the cluster solutions are being prepared for TEM measurements. (Such ripening is precluded in the low temperature frozen samples used for spectroscopy.) Given these various sources of experimental uncertainty, it seems inappropriate to attempt a more detailed theoretical analysis.

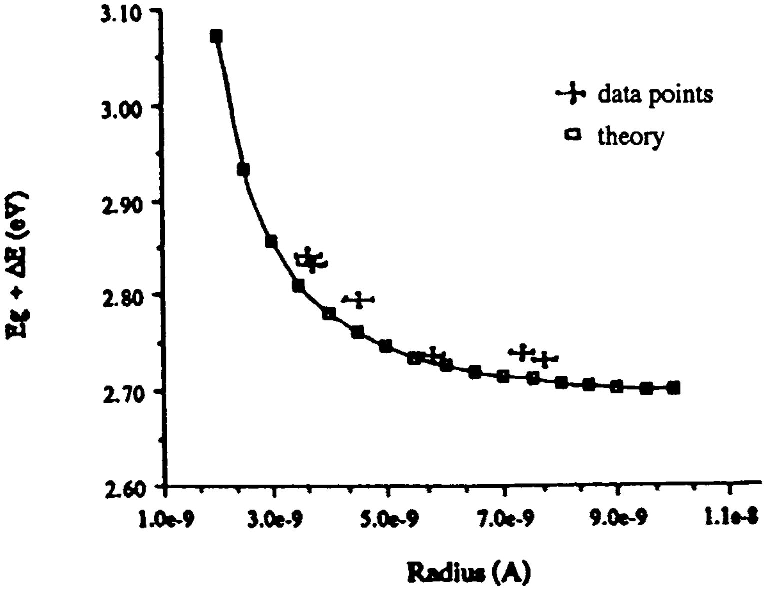

FIGURE 2 Calculation of the size dependence of the bandgap as per reference 12 and comparison to experimental results.

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Time-resolved Emission

While steady-state emission spectra can provide a measure of the energetics of quantum confinement in AgBr, they do not directly probe how the selection rules for this indirect band gap material are modified by confinement[10,11]. As noted above, confinement is predicted to relax the momentum k selection rules thereby making the forbidden transitions in an indirect gap material more "allowed." Previous theoretical treatments have suggested that the radiative lifetime will scale as a power of R, although there is disagreement over the precise R dependence, with estimates ranging from R^6 (13) to R^2 (14). The size effects are dominant when the particles are R ≈ 10 Å. When R > 70 Å, k is independent of R. This is referred to as the phonon assisted momentum conserving effect.

Such a change might be monitored by an increase in the extinction coefficient of the exciton transition, or, equivalently, by the decrease in radiative lifetime of the exciton. When $R > R_{exc}$, the effects of confinement on the transition matrix element $|S|$ are small and thus may be difficult to observe in direct absorbance but may still be observable in measurements of the emission lifetime. However, several caveats should be noted. First, it is the radiative rate, k_r, which is related to $|S|$. However, one does not directly measure k_r but $k_{obs} = k_r + k_{nr}$ where k_{nr} includes all non-radiative rate contributions (trapping, phonon assisted decay, etc.). In the simplest case, k_r can be obtained by combining measurements of k_{obs} and quantum yield: $\phi_r = \frac{k_r}{k_r+k_{nr}}$. Thus $k_{obs}/\phi = k_r$.

For AgBr emission, such an analysis is complicated by the branching of the excitation energy between exciton formation and other channels, e.g., free electrons and holes. These branching ratio(s) are not known exactly and might change with size. However, earlier calculations suggest that free electrons and holes in these nanocrystals will rapidly collapse (by the multiple encounters resulting from the restricted space) to produce free excitons. This effect will minimize the effect of such branching. If significant branching occurs, then the apparent quantum yield ϕ_{obs} will be less than the actual radiative quantum yield ϕ_r. Thus the estimates of k_r reported here represent maximum values. In the absence of more exact knowledge, we assume that the measured quantum yield is unbiased by branching, or, at least, that any branching ratio does not change with cluster size. With these caveats, the measurements of time resolved exciton emission are discussed below.

In earlier work, quite rapid (ns) emission was observed. This appeared to correspond to the lifetime of a near direct transition suggesting a significant change in selection rules was associated with confinement of the exciton in the AgBr lattice.

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However, these results seemed inconsistent with the absorption (or equivalently excitation hole burning) spectra which are more consistent with an indirect transition, with no evidence of an exciton peak. With a new range of cluster sizes available, we have re investigated the time-resolved emission. A fast (ns) component is indeed observed in all samples, but its lifetime is essentially invariant with cluster size. More importantly, detailed single photon counting studies showed that over 95% of the emission had not decayed within the 100 nanosecond window of the photon counting apparatus. We therefore repeated the previous pulsed excitation time-resolved emission decay studies over a broader time window. Consistent with the photon counting results, a small amplitude nanosecond component is observed, but primary excitation decay occurs at a much longer lifetime. Depending on cluster size, this lifetime ranges from 200 μs (R = 35 Å) to 1000 μs (R ≥ 150 Å).(Figure 3)

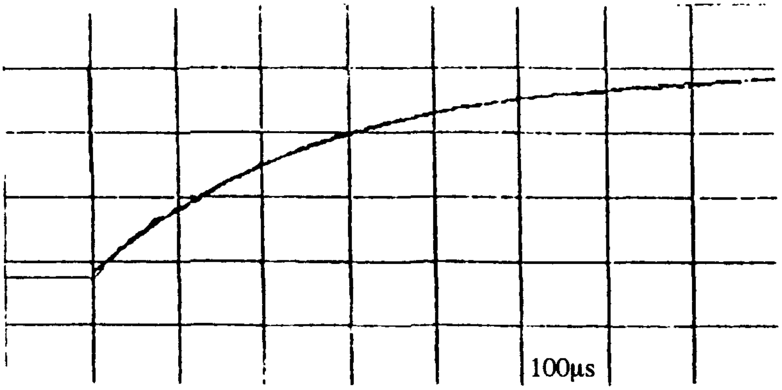

FIGURE 3 Luminescence Decay of 40Å AgBr.

Two points emerge from these data. First, and perhaps most important, the observed lifetimes are all quite long, suggesting that over this range of cluster size, quantum confinement of the AgBr exciton has not had a major effect on momentum selection rules: absorbance and emission in 35 Å AgBr nanocrystals is still highly forbidden. Thus these new emission measurements are consistent with the absorbance data already discussed. The noted uncertainties in quantum yield can only increase the radiative lifetime, which will not change this conclusion. Second, although the observed lifetime effects are modest, the lifetimes clearly decrease systematically with decreasing size. This is in qualitative agreement with the preceding analysis. It is possible to analyze the results more quantitatively by accounting for the fact that the observed emission includes both the phonon assisted emission rate which is independent of size and the zero phonon emission which is expected to show an R^6 dependence. Such an approach is presented elsewhere.

TABLE I Free Exciton Luminescence Lifetimes

R_{calc} (Å)[a]	Lifetime (μs)
29.8	350
32.7	390
38.3	480
40.4	520
46.1	620
50.0	780
61.4	920

[a] estimated from Brus' particle in a spherical box formalism. Similar values were observed by transmission electron microscopy.

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ACKNOWLEDGEMENT

Financial support of this work from the National Science Foundation
(Grant No. CHE-9120001) is gratefully acknowledged.

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