Optical Properties and Local Structure of Ag(I) Dopant in ZnSe:Ag Nanoparticles

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Ag(I) doped ZnSe nanoparticles were synthesized using molecular cluster precursors. In the emission spectrum at 390 excitation, three emission bands, centered at 432 nm, 517 nm, and 484 nm, respectively were observed. The 432 nm and 517 nm bands can be assigned to ZnSe band-edge emission and donor-accepter emission from the vacancies and trap states in the ZnSe lattice to the Ag(I) dopant, respectively. Similarly the 484 nm band could be the result of ZnSe trap state or vacancies to Ag(I) acceptor emission or simply ZnSe trap state emission. X-ray Absorption Fine Structure (XAFS) data were collected at the Ag K–edge of the Ag(I) doped ZnSe nanoparticles. From these data it was concluded that the Ag(I) dopant occupied a variety of different environments in the ZnSe lattice.

Keywords: ZnSe, nanoparticles, Ag, doped nanoparticles, XAFS

1. Introduction

Semiconductor nanomaterials have attracted considerable attention in recent years because of their many novel properties derived from the spatial confinement of charge carriers and large surface-to-volume ratio[1-6]. These properties are potentially useful in emerging technologies such as advanced sensors, large area displays, solar cells, detectors, lasers, and other opto-electronic devices[7, 8]. The strong, size-dependent optical emission of many semiconductor nanoparticles also makes them promising candidates for use as fluorescent tags in the study of biological systems.

Furthermore, the optical properties of semiconductors nanoparticles can be modified by doping the material with metal and, sometimes, non-metal ions. This often leads to the creation of new emission properties due to the dopant and alteration of the optical properties of the host semiconductor. Doped semiconductors with dimension on the micron or larger scale constitute a large portion of commercial phosphor materials. Doped semiconductor nanoparticles present an attractive system for studying effects of doping in spatially confined materials. The most extensively studied doped nanoparticle system is Mn^{2+}-doped ZnS, denoted as ZnS:Mn; however, recently other doped II-VI semiconductor systems have been reported[9-14].

One of the most important doped semiconductors is ZnS:Ag, and its bulk form, micro or large sized powders, has been used as a commercial blue phosphor for many years[15, 16]. There have been few studies on the chemical synthesis and optical properties of ZnS:Ag nanoparticles[17]. To our best knowledge, there have been no studies reported on ZnSe:Ag nanoparticles to date. Comparison between ZnS:Ag and ZnSe:Ag nanoparticles will help to gain insight into how the optical properties of the Ag(I) ion are affected by the nature of the host semiconductor and how Ag(I) doping could potentially affect the optical properties of the host semiconductor nanoparticle.

In this paper we report the first synthesis and characterization of local structure and emission properties of ZnSe:Ag nanoparticles using spectroscopic and XAFS techniques. The synthesis was achieved by thermally decomposing $Zn_{10}Se_4$ and Ag_5 molecular clusters in the presence of a coordinating solvent. XAFS analysis of the ZnSe:Ag nanoparticle suggests that the Ag(I) dopant prefers the octahedral site in the lattice. The observed emission spectrum can be attributed to ZnSe band-edge emission and Ag(I) donor-acceptor emission.

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2. Experiment

2.1 Synthesis of $Zn_{10}Se_4$ cluster

A Zn_4 cluster was prepared following a method of Dance *et al*[18]. Briefly 21 g of $Zn(NO_3)_2 * 6H_2O$ was dissolved in 60 mL of methanol, and added to a 120 mL methanol solution of thiophenol (20.5 mL) and triethlyamine (28.1 mL). Next 8.4 g of lithium nitrate was dissolved in methanol and added to the $Zn(NO_3)_2$-thiophenol-triethelyamine solution. A white precipitate formed immediately. The precipitate was collected and washed with cold methanol.

The $Zn_{10}Se_4$ cluster was prepared by dissolving 3.86608 g of the Zn_4 cluster, and 0.3483 g of Se in 25 mL of N,N-dimethylformamide (DMF). The solution was stirred constantly for several minutes and then filtered to remove any unreacted Se. Cold ether was used to precipitate the $Li_4[Zn_{10}Se_4(SPh)_{16}]$ cluster, which was then collected by filtration.

2.2 Synthesis of Ag_5 cluster

The silver cluster was also prepared by following a method developed by Dance[19]. Approximately 5.1 mL of thiophenol and 3.4 mL of triethylamine were mixed with 60 mL of acetonitrile, while 1.7423 g of silver nitrate was dissolved separately in acetonitrile, and 3.4608 g lithium nitrate was dissolved in methanol. The silver nitrate solution was added slowly to the thiophenol-triethlyamine solution. After all the silver nitrate solution was added the lithium nitrate solution was added to the thiophenol-triethlyamine-silver nitrate reaction mixture solution immediately forming a precipitate. The reaction vessel was placed in a freezer over night then the $Li_2Ag_5(SPh)_7$ crystals were collected by vacuum filtration.

2.3 Synthesis of Ag(I) doped ZnSe Nanoparticles

The nanoparticles were synthesized following the method of Cumberland *et al* [18, 20] for ZnSe nanoparticle synthesis with some modification for introducing the Ag(I) dopant. Approximately 0.6 g of the $Li_4[Zn_{10}Se_4(SPh)_{16}]$ cluster and 0.1280g of the $Li_2Ag_5(SPh)_7$ were added to 80 mL of hot HDA, which had been previously dried and degassed under vacuum at 120 °C for two hours. Once the clusters had dissolved, the temperature was raised slowly to 280 °C. Particle growth was monitored by UV-VIS and luminescence spectroscopy, and the temperature was modulated between 200 °C and 280 °C to control the rate of particle growth. After three hours the temperature was lowered to 180 °C, where the particles were annealed at overnight.

To extract the particles from solution, the reaction solution was cooled to 80 °C and then poured into 100 mL of methanol, immediately forming a precipitate. The mixture was centrifuged, and the methanol was discarded. The remaining powder was dissolved in toluene to form a pale yellow solution.

2.4 X-ray Absorption Fines Structure of Ag(I) doped ZnSe

XAFS data were taken at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam line 10-2 using a Si 333 monochromator. Nickel foil was placed in the x-ray beam to attenuate all but the third harmonic of the x-ray beam diffracted from the monchromator. The samples used for XAFS were prepared by adsorbing a toluene solution of the Ag(I) doped ZnSe nanoparticles onto filter paper. Fluorescence data were taken at the Ag K-edge at 20 K. The data were reduced by fitting the pre and post edge backgrounds to a line with a constant baseline and a spline function, respectively. The XAFS were then Fourier Transformed and fitted in real space using RSFIT with standards generated by FEFF7[21-23]. A 3.5 $Å^{-1}$ to 10.5 $Å^{-1}$ Fourier Transform range was used for the analysis of the data, and the data were fitted over a 1.55 Å to 3.55 Å R range.

3. Results

Figure 1 shows the UV-VIS spectrum of the ZnSe:Ag nanoparticles, and figure 2 shows a representative emission spectrum with 390 nm excitation. The absorption spectrum lacks a sharp exciton feature expected for ZnSe nanoparticles, indicating possibly a broad size distribution. The emission spectrum contains three peaks, centered at ~432 nm, ~517 nm, and ~484 nm, respectively. The 432 nm peak can be attributed to ZnSe band edge emission, though it is significantly red shifted from what has been reported[24], possibly due to larger particle sizes in the present study. The 517 nm emission peak can be assigned to donor-accepter emission from the vacancies and trap states in the ZnSe lattice to the Ag(I) dopant [17]. The 484 nm emission could also be attributed to the donor-accepter emission from the vacancies and trap states in the ZnSe lattice to the dopant.
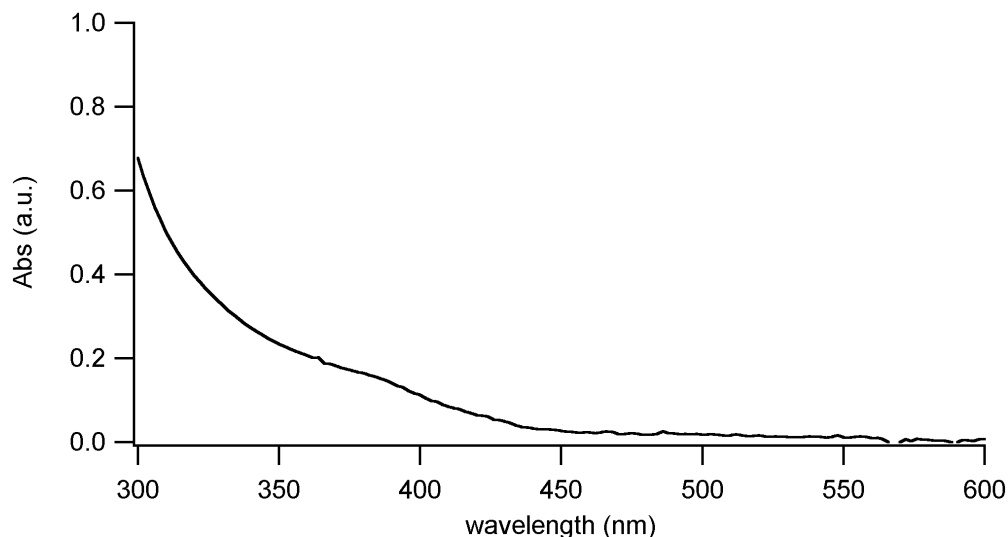
Figure 1: Electronic absorption spectrum of the ZnSe:Ag nanoparticles
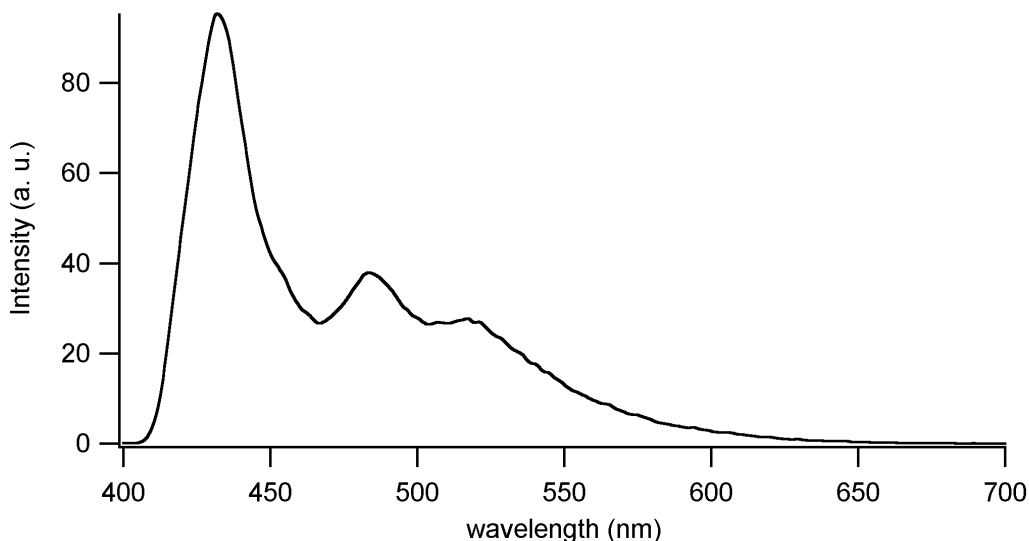
Figure 2: Luminescence spectrum of Ag(I) doped ZnSe nanoparticles. The excitation wavelength was 390 nm.

The first peak at ~1.95 Å and the second peak at ~2.75 Å in the FT-XAFS traces of Ag K-edge for the ZnSe:Ag nanoparticles (Figure 4) could correspond to the first Ag-Se and Ag-Zn coordination shells for Ag(I) occupying the octahedral site of the ZnSe lattice, but they could also be that of bulk Ag_2Se. Fitting the data to either model produces unsatisfactory results. Another possibility is that there is a mixture of the two environments; however, there is not enough k-space data to explore this possibility. A further complication is that Ag(I) could also substitute for Zn in the ZnSe lattice, but fitting the data to that model is problematic as well.
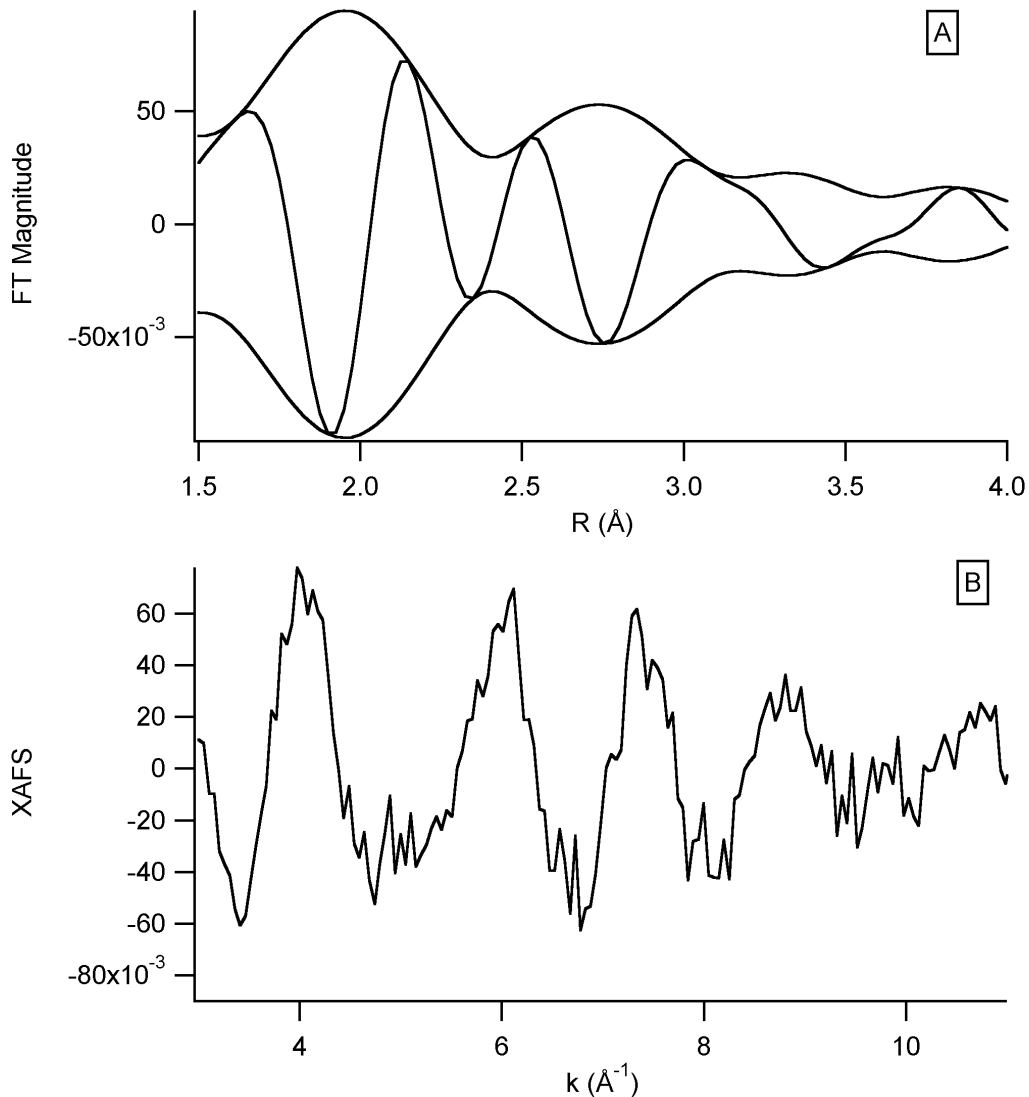

Figure 4: A) The Fourier Transform of the Ag K-edge XAFS of Ag(I) doped ZnSe nanoparticles, where the solid line is the data and the dotted line is the fit, and B) the XAFS of the K -edge of Ag(I) doped ZnSe nanoparticles.

4. Discussion

The electronic absorption and emission as well as XAFS data suggest that doping of ZnSe with Ag(I) was achieved in the present synthesis. Thus the two emission peaks observed at 432 nm, and 517 nm can be attributed to ZnSe band-edge and Ag(I) donor-acceptor emission. The ZnSe band-edge emission is significantly red shifted from that observed in ZnSe and ZnSe:Mn nanoparticles[24]. This could be the result of the formation of larger particles in this present synthesis, which would decrease the confinement of

electrons, causing redder emission. The 517 nm emission can be attributed to Ag(I) donor-acceptor emission, where ZnSe trap states or vacancies in the lattice act as a electron donor and the Ag(I) ion acts as the acceptor. The 484 nm emission band could have similar origins. The distortion on the lattice caused by the introduction of the large Ag(I) in conjunction with large surface to volume ratio could result in the formation of new trap states. These new states could act as donor sites for which Ag(I) could act as acceptor. One way to determine the origins of these emission bands is time resolved luminescence studies, which are currently in progress.

Ag Environment	Space Group	Lattice Constant (Å)	Ag-Se Distance (Å)	Ag-Se Coordination	Ag-Metal Distance (Å)	Ag-Metal Coordination
Ag_2Se (Bulk)	Im3m	4.99	2.16	2	2.50	6
Ag_2Se In $NiSe_2$	(Fm3m)	6.12	(2.65)	(4)	(3.06)	(6)
Ag in ZnSe octahedral site	F-43m	5.66	2.45	4	2.83	6
Ag in ZnSe Zn site	F-43m	5.66	2.45	4	4.00	12

Table 1. Theoretical structural parameters for Ag(I) in different environments. The space group for N iSe_2 is Pa3 and the lattice constant is 6.034 Å. The distance and coordination number for Ag_2Se in $NiSe_2$ were calculated based on Fm3m environment using the lattice constant measured in reference.

There is ambiguity in the XAFS data concerning the local environment of Ag(I) in the nanoparticle. Bulk Ag_2Se has the cuprite structure with Ag coordinated to two Se atoms with Se atoms arranged in a BCC lattice (Table 1). When small quantities of Ag_2Se are incorporated into $NiSe_2$ the Ag_2Se unit cell expands, and an FCC lattice structure is stabilized[25]. An allotrope of Cu_2S has an FCC lattice, and posses the anti-fluorite structure; therefore it is like that Ag_2Se can also posses this structure when incorporated into a FCC host lattice. The octahedral site in the ZnSe lattice and the cation site in an anti-fluorite lattice are virtually the same, so it reasonable to assume that Ag(I) dopant occupies that site. The second peak in the FT-XAFS trace is in the general region of where a Ag-metal coordination peak should be for Ag(I) occupation of the octahedral site. What makes this interpretation problematic is that the Ag-metal coordination shell of bulk Ag_2Se could also produce a peak in the general region. A fit to a model of pure Ag_2Se or Ag occupation of the octahedral site in ZnSe does not produce reasonable results. Because of the limits introduced by the noise in the data and the short k range, a fit of the data to a mixture of Ag_2Se and Ag occupation of the octahedral site in ZnSe proved difficult. To further complicate matters Ag(I) can also occupy the Zn(II) site in the lattice by forming a defect complex with Se vacancies. It is likely that the Ag(I) dopant occupies more than one site in the lattice, but the data lacks the resolution to determine which environments are present.

5. Conclusion

ZnSe:Ag nanoparticles we re prepared from molecular cluster precursors. The 432 nm emission band can be attributed to ZnSe band-edge emission, while the 517 nm and 484 nm emission bands can be attributed to donor-accepter emission, where the ZnSe trap states act as donors and the Ag(I) ion acts an acceptor. The Ag(I) dopant is likely to have occupied a variety of environments in the ZnSe lattice.

ACKNOWLEDGEMENTS

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