HIGH-TEMPERATURE CADMIUM-FREE NANOPHOSPHORS FOR DAYLIGHT-QUALITY WHITE LEDs

REU Student: Nathaniel C. Cook
Graduate Student Mentor: Brian A. Akins
Faculty Mentor: Dr. Marek Osiński

FINDINGS

Fig. 1. PL spectra of ZnSe:Mn/ZnS NC’s bright 497 nm emission excited by 453 nm light. Followed by PL excitation spectrum of ZnSe:Mn/ZnS NC’s taken at 497 nm, showing peak excitations at 453 nm & 483 nm.
Photoluminescence (PL) and quantum efficiency (QE) were measured using a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer, using Spectrosil® quartz cuvettes. ZnSe:Mn/ZnS NCs have two emission peaks: a shorter wavelength emission peak at 497 nm, which is excited by 453 nm light and has a shoulder at 525 nm (Fig. 1), and the longer wavelength peak at 587 nm that was excited by 418 nm light (Fig. 2).

Fig. 2. PL spectra of ZnSe:Mn/ZnS NC’s bright 587 nm emission excited by 418 nm light. Followed by PL excitation spectrum of ZnSe:Mn/ZnS NC’s taken at 587 nm, showing peak excitations at 418 nm.
QE measurements of ZnSe:Mn/ZnS NCs were performed using the Fluorolog-3 integrating sphere attachment and a liquid sample holder. QE measurements at the 497 nm emission with 453 nm excitation resulted in a quantum yield of 91.26\% (Fig. 3). At 587 nm emission with 418 nm excitation, QE was 39\% (Fig. 4).

![ QE measurement of ZnSe:Mn/ZnS NCs at 497 nm using Horiba Jobin Yvon Fluorolog 3 system with integrating sphere attachment.](image3)

![ QE measurement of ZnSe:Mn/ZnS NCs at 587 nm using Horiba Jobin Yvon Fluorolog 3 system with integrating sphere attachment.](image4)
The high temperature emission from ZnSe:Mn/ZnS NCs was observed in contrast to CdSe/ZnS NCs (Fig. 5), whose emission drops sharply with increasing temperature, and practically disappears above 60 °C. High PL efficiency at elevated temperatures makes the ZnSe:Mn/ZnS NCs particularly attractive for applications as nanophosphors in high-power white LEDs. Abnormal thermal behavior comes from competing thermal factors, such as thermal release of trapped charges and phonon-electron interaction [1].

![Graph showing temperature dependence of PL from ZnSe:Mn/ZnS NCs (blue) compared to CdSe/ZnS NCs (black).]

Fig. 5. Temperature dependence of PL from ZnSe:Mn/ZnS NCs (blue) compared to CdSe/ZnS NCs (black).

TEM images of the ZnSe:Mn/ZnS NCs sample were completed on the JEOL 2010 high-resolution transmission electron microscope located in the labs of the Earth and Planetary Science Department at UNM. This device uses the following systems to perform extremely important forms of characterization: Gatan Orius digital camera system, Digital Micrograph system, and Oxford – Inca energy dispersive x-ray spectroscopy system. Unfortunately, at the time these images were recorded the Oxford – Inca energy dispersive x-ray spectroscopy system was under repair. TEM images are produced from the interaction between the electron beam and the sample. The portion of the image that is bright, is where the electron beam is just passing thru and not interacting with any material, but the dark areas are where the beam encounters material that absorbs some of the electrons. These images were used to determine the size and the shape of this NC material. The first image at 80k magnification (Fig.6) shows that these nanocrystals
are evenly dispersed. Depending on the orientation, some individual crystals may appear to have different sizes and shapes, but most of these NCs are identical in size and shape.

Fig. 6. TEM image of ZnSe:Mn/ZnS NCs at 80k magnification. Scale bar 50 nm.

The next image in Fig. 7 gives a closer look at the individual crystals in this sample. At higher magnification, it is possible to view fringes, which are the planes of atoms for the individual crystals. The image in Fig. 7 is a good representation of this phenomenon. In this image at 1000k magnification, fringes of single nanocrystals can be seen. These fringes can be measured using fast Fourier transform (FFT) to determine the crystal structure for this sample.

Fig. 7. TEM image of ZnSe:Mn/ZnS NCs at 1000k magnification scale bar 2 nm.
The image in Fig. 8 at 300k magnification also shows some fringing on individual crystals. A few larger particles are also visible in this image. These larger particles are not consistent with the other particles in this image, because they may have a different orientation. These larger particles are more likely multiple particles being either completely or partially on top of each other. This can result in fringes that are cross hatched, depending on the orientation of the individual crystals.

In order to obtain images like these that show the fringing, it is necessary to use higher magnification and to be slightly out of focus. Depending on the type of material that is being imaged fringes can become visible around 250k to 300k magnification. The image in Fig. 9 is another bright field image, but at a magnification of 100k. This image shows a smaller group of the nanocrystals to provide another good representation of the size and shape of this material. From this image, it is easier to see that the nanocrystals range from about 10 to 20 nm in size and appear in this orientation to be rod shaped.
The next type of characterization that will be shown also has to do with the size of ZnSe:Mn/ZnS quantum dots. Dynamic light scattering (DLS) is another tool that is used in characterizing nanomaterials. As the laser light hits the small particles in solution, light is scattered and that scatter is collected by the detector and analyzed. The data is then returned in the form of intervals of time and relative particle size that was detected. That data can then be plotted in a histogram for graphical representation of the analysis. This process requires that the particles in the sample to be less than 250 nm in size. It is also important that the sample is not too concentrated, because this can overload the detector as more of the light will be scattered. Once the sample was properly prepared, it was placed in a special DLS cuvette that was unaffected by the toluene solution that the sample is suspended in. The graph below, which resulted from the collected data, confirms that the sample contains nanoparticles that are approximately 15 nm in diameter (Fig. 10).
The final characterization method used on this material was X-ray Diffraction (XRD). This is a process that uses different types of x-rays depending on the type of anode that is selected. The anode is typically a copper anode with a wavelength of 1.54Å. However, depending on the type of sample this can be changed to a number of different types of anodes to improve the collection of the diffraction pattern. The x-rays from the anode interact with the sample as it passes thru a series of 2θ angles, which, with a randomly orientated powder sample, will result in all possible diffractions from the lattice. The peaks in the pattern at the given angles can be compared to known material, therefore providing a relatively quick confirmation of the phases of materials that are present in a given sample. The ZnSe:Mn/ZnS nanocrystals were analyzed and the following data was recorded in the graph below (Fig. 11). This XRD pattern of ZnSe:Mn/ZnS
NCs shows the phase match to Zn$_{0.95}$Mn$_{0.05}$Se, which confirms the material that was expected to be present in the sample.

The polymerization of the ZnSe:Mn/ZnS NCs in poly methyl methacrylate (PMMA) first required the material to be dried in the oven at 110 °C, after the sample was synthesized and dispersed in toluene. A 7 mL vial was weighed and then 1 mL of the ZnSe:Mn/ZnS NCs were added, and the vial was placed in the oven to dry. Once the sample was completely dried, the vial was weighed again and compared to the first weight to determine the weight of the nanocrystals that were dispersed in the polymer. Then the vial was transferred into the glove box for the NCs to be dispersed into the distilled monomer solution. The monomer was distilled in the glove box by passing methyl methacrylate (MMA) dropwise thru the inhibitor removal tube (Hydroquinone (HQ) and Monomethyl Ether Hydroquinone (MEHQ) Removal Column) and into a beaker. 0.0025g of initiator was added to the dried sample and then a 10mL syringe was used to add 5 mL of distilled monomer into the vial. The vial was capped and removed from glove box and placed in sonication until the sample was fully dispersed in the monomer. Once the sample was fully dispersed in the monomer the vial was placed in the oven at 60 °C. The sample was
checked regularly and sonicated in order to prevent bubbles from forming. After the sample remained in the oven for 24 hrs, the sample had not completely polymerized, so the temperature was increased to 70 °C. The sample was checked regularly, and after 24 hrs at 70 °C the sample was completely polymerized.

Once the sample was polymerized, it was cut and polished to enable front face PL measurements to compare to previous PL measurements of the sample in solution. These measurements were also done using a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer. This comparison was to provide information on whether or not polymer encapsulation enhanced PL for this sample. The polymerized sample was analyzed on the PL setup using a solid sample holder and using the same excitation and emission slit widths as it was done for the sample in solution (Fig. 12).

![PL spectra of ZnSe:Mn/ZnS NCs encapsulated in PMMA at 453 nm excitation.](image)

Under these same settings, the sample in PMMA did not provide as strong of a signal as the sample in solution. Although the peak locations are very much the same with only a small variation, the peak intensity has dropped from approximately 700,000 counts per second (CPS) to below 100,000 CPS. The graph in Fig. 13 shows that with the 418 nm excitation the results were also not ideal in comparison.
Fig. 13. PL spectra of ZnSe:Mn/ZnS NCs encapsulated in PMMA at 418 nm excitation.

This graph obtained under the same settings as for the sample in solution shows a greater shift in the peaks location and intensity. The original peaks locations were 496 nm and 587 nm. The original peak intensity for the 496 nm peak was approximately 100,000 CPS, while the 587 nm peak was at 550,000 CPS. However, in the PMMA the first peak is a broader peak with a maximum at 459 nm and intensity at 150,000 CPS. The second peak being at 593 nm is still close to the original 587 nm mark, but the intensity dropped to 275,000 CPS. With the results that have been obtained during this project, other polymers that may be able to enhance PL of ZnSe:Mn/ZnS NCs will be investigated.

As this project continues, the next polymer that will be investigated will be PVT (polyvinyltoluene), while other types are being researched. Although the PMMA did not prove to be a beneficial choice, the sample itself turned out to be a great success. With quantum efficiencies as high as 91% and multiple peaks with a single excitation, ZnSe:Mn/ZnS NCs may in the near
future provide us with a single material that can produce day-light quality LEDs. Work will be continued on this project to improve the efficiency of these materials.

References: