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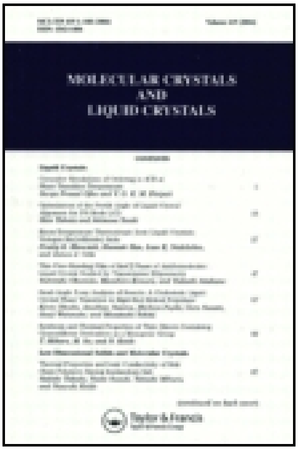

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Composites from Luminescent Nanosized ZnS and Optical Polymer

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Version of record first published: 31 Aug 2012.

To cite this article: K. Matras, M. Bredol, A. Szatkowski, O. Sakhno, J. Stumpe & D. Bogdal (2008): Composites from Luminescent Nanosized ZnS and Optical Polymer, Molecular Crystals and Liquid Crystals, 485:1, 776-779

To link to this article: http://dx.doi.org/10.1080/15421400801918062

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Mol. Cryst. Liq. Cryst., Vol. 485, pp. 28/[776]–31/[779], 2008
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801918062

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Composites from Luminescent Nanosized ZnS and Optical Polymer

K. Matras[1,2], M. Bredol[2], A. Szatkowski[2], O. Sakhno[3], J. Stumpe[3], and D. Bogdal[1]
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In this work, transparent luminescent nanocomposites were obtained using manganese – doped ZnS nanoparticles with crystallite sizes of about 10 nm, dispersed in the monomer isobornyl acrylate (IBOA). Suited nanocrystals of Mn^{2+}-doped ZnS have been prepared by arrested precipitation in the presence of capping agents like cysteamine, combined with hydrophobization. Transparent ZnS:Mn/PIBOA nanocomposites were subsequently prepared via in situ polymerization. Nanocomposites were produced by adding different percentages of nanoparticles up to 30% by weight. The structural properties of the ZnS:Mn nanoparticles were studied in detail using X-ray diffractometer (XRD), Fourier transform IR spectrometer (FT-IR), spectroscopy (UV-VIS) and dynamic light scattering (DLS). The X-ray diffraction pattern exhibited peaks corresponding to the cubic phase of ZnS. The emission spectrum (at 320 nm excitation) of the composites showed the same broad band as bulk ZnS:Mn, centered at 590 nm.

Keywords: nanocomposites; photoluminescence; polymer matrix; ZnS:Mn nanoparticles

INTRODUCTION

During the last decade, research into nanocomposites has become quite popular in various fields of chemistry. Recently, fabrication of inorganic nanoparticles in solid polymer matrices has attracted much attention, because the combination of inorganic nanoparticles and a polymer provides a simple route to stable and processable composite materials, integrating the promising properties of both components [1].

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In this context, doped ZnS nanocrystals (NC's) are promising materials for applications in luminescent systems. Semiconductor nanoparticles from the II/VI-family have been applied to many different technological areas, including biological labelling and diagnostics, light-emitting diodes, electroluminescent devices, photovoltaic devices, lasers and single electron transistors [2–7]. The size of these nanoparticles can be smaller than 15 nm, thus offering the possibility of fully transparent light emitters. Very small nanoparticles do not scatter light significantly, and thus it is possible to make transparent nanocomposites with improved electrical or mechanical properties. However, sometimes nanoparticles can form agglomerates inside the matrix, resulting in turbid composites, and thus dedicated techniques need to be developed that allow for the integration of particles with a high external surface area into polymers.

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EXPERIMENTAL

Preparation of ZnS:Mn Nanocrystal Powders

The ZnS:Mn nanoparticles were synthesized in aqueous solution, using $Zn(Ac)_2$, $Mn(Ac)_2$ and Na_2S as starting materials. Capping agent used was cysteaminium chloride combined with a hydrophobic agent. $Zn(Ac)_2$ and $Mn(Ac)_2$ aqueous solution were mixed together with stabilizers. In a second solution, Na_2S was dissolved in deionized water. This solution was added dropwise under stirring to the $Zn(Ac)_2$ solution. The nanoparticles were isolated from solution by precipitation, centrifugation and drying.

Synthesis of ZnS:Mn/PIBOA Nanocomposite

Transparent nanocomposites with ZnS:Mn were synthesied via in situ polymerization. First, nanoparticles of ZnS:Mn prepared as described above were dispersed directly into the monomer (isobornyl acrylate), and polymerized after the addition of photoinitiator Igracure 369. Polymerization was carried out using UV radiation for 30 min. Nanocomposites were produced by adding different percentages of nanoparticles from 5% up to 30% by weight.

RESULTS AND DISCUSSION

We report on nano-ZnS:Mn synthesis using a system of capping agents like cysteaminium chloride combined with a hydrophobic modifier.

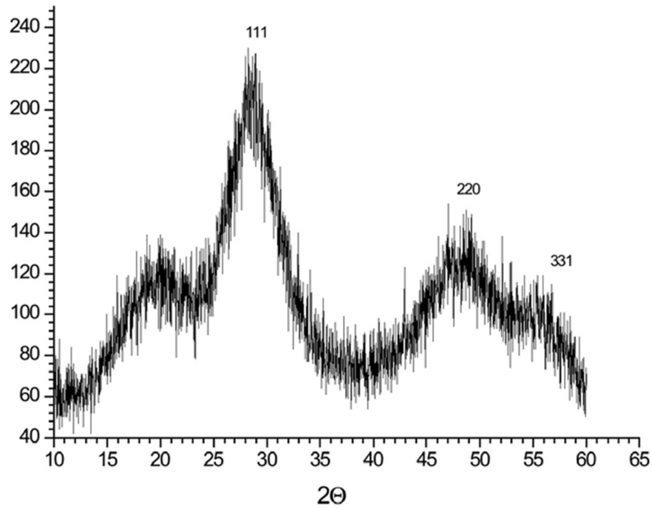

FIGURE 1 X-ray powder pattern of manganese-doped ZnS nanoparticles as obtained by precipitation. Crystallite size is estimated to be 2 nm from Debye-Scherrer's formula.

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The synthesis took place in aqueous solution. The nanocrystals were characterized by strong luminescence and very good dispersability in various organic media, especiality in hydrophobic monomers. The structural properties of the ZnS:Mn nanoparticles were studied in detail using a X-ray diffractometer (XRD), a Fourier transform IR spectrometer (FT-IR), UV-VIS-spectroscopy and dynamic light scattering (DLS). Figure 1 shows the XRD pattern of the ZnS:Mn particles which is characteristic of the zinc-blende modification of ZnS (sphalerite). The average crystallite size of the particles as calculated from Debye-Scherrer's equation is around 2 nm. DLS measurement revealed a hydrodynamic radius of about 10 nm after dispersion in IBOA monomer. Accordingly, the resulting polymers were completely transparent.

Figure 2 shows the photoluminescence emission (PL) of the ZnS:Mn/PIBOA nanocomposites with various concentrations of nanoparticles in polymer matrix. In the PL spectra of ZnS:Mn/PIBOA nanocomposites, blue and orange emissions exist at about 480 nm and 590 nm, respectively. The Mn^{2+}-based orange emission has been assigned to the $^4T_1$–$^6A_1$ transition of the Mn ion, whereas the emission at 480 nm is assigned to the polymer.

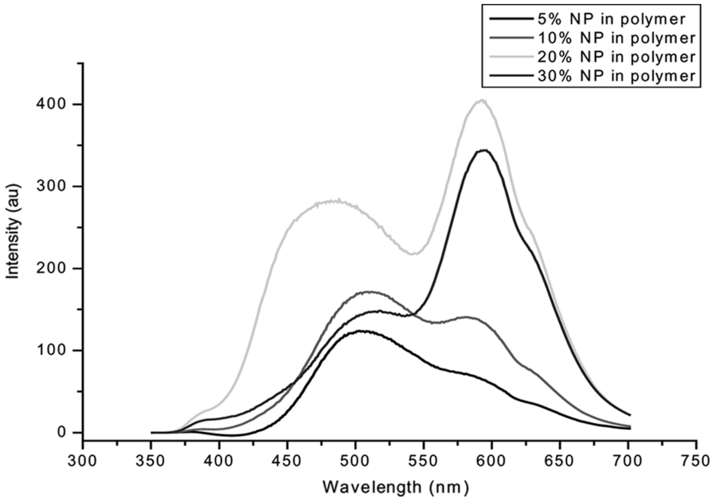

FIGURE 2 Emission spectrum of the ZnS:Mn/PIBOA nanocomposites with various concentrations of nanoparticles in polymer matrix (5, 10. 20, 30% by weight), (320 nm excitation).

CONCLUSION

Summarizing, an efficient method for the preparation of transparent ZnS:Mn/PIBOA nanocomposites with nanoparticles (about 10 nm) and of varying concentrations upt to 30 wt% was developed. All materials have excellent optical properties such as strong UV absorption and bright visible luminescence.

REFERENCES

[1] Pyun, J. & Matyjaszewski, K. (2001). *Chem. Mater.*, *13*, 3436.
[2] Hu, J., Yang, L., Manna, L., Wang, L., & Alivisatos, A. (2001). *Science*, *292*, 2060.
[3] Pustelny, T. & Pustelny, B. (2002). *O-ER*, *10*, 193.
[4] Koutsogeorgis, D. C., Mastio, E. A., Cranton, W. M., & Thomas, C. B. (2001). *Thin Solid Films*, *383*, 31.
[5] Manzoor, K., Vadera, S. R., Kumar, N., & Kutty, T. R. N. (2005). *Appl. Phys. Lett.*, *84*, 284.
[6] Adachi, D., Hasui, S., Toyama, T., & Okamoto, H. (2000). *Appl. Phys. Lett.*, *77*, 1301.
[7] Hwang, J., Oh, M. O., Kim, I., Lee, J. K., & Ha, Ch. S. (2005). *Curr. Appl. Phys.*, *5*, 31.

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