

Photoluminescent properties of di(8-hydroxyquinolato) zinc impregnated in nanoporous glass

Dayuan Xiong (熊大元)¹, Yuyan Liu (刘煜炎)¹, and Suihua Yuan (袁绥华)²

¹Key Laboratory of Optical and Magnetic Resonance Spectroscopy, Department of Physics, East China Normal University, Shanghai 200062

²Department of Physics, South-West China Normal University, Chongqing 400715

Received May 26, 2003

Photoluminescent properties of a metal-organic complex, di(8-hydroxyquinolato) zinc, impregnated in nanoporous glass were investigated. In comparison with those in the normal organic fluorescent material, the emission band of the impregnated organic phosphor became wider. Blueshift (14 nm) was observed due to $\pi^* \rightarrow n$ emission transition. The excitation band of the embedded organic phosphor had a larger blueshift and was divided into several sub-bands. The intensity in the short wavelength end of the embedded organic fluorescent material became much stronger.

OCIS codes: 160.4890, 160.6030, 300.6280.

The investigations of materials that are confined in nano-scaled pores have drawn attention recently due to the unusual properties of such materials. The properties of materials such as the melting temperature, the superconducting transition and the magnetic ordering transition have been found changeable when confined to nano-metered pores^[1–3]. Nearly all of the researches focused on the inorganic materials. A very few reports are found for the study of organic materials confined to nano-metered pores^[4], especially on their luminescent properties.

This letter reported the luminescent properties of di(8-hydroxyquinolato) zinc embedded in nanoporous glass. The objective of this research includes two sides: 1) The study of luminescent properties of nano-metered particle of di(8-hydroxyquinolato) zinc since only a few investigations were reported on the properties of nano-metered particle of organic compounds. 2) The composite glass may be developed into an electroluminescent glass or film since zinc 8-hydroxyquinoline compound that is a strong-emitting electroluminescent material.

The nanoporous glass was prepared in our laboratory by etching sodium borosilicate glass. In a proper heat treatment, the sodium borosilicate glass resulted in two-phase separation: silica rich insoluble phase and alkali boric soluble phase. The soluble phase was leached out with an acid such as HCl at 85–90 °C temperature in several days, then a nanoporous glass was obtained in which a nearly pure silica skeleton and a lot of interconnected nano-metered pores remained.

Di(8-hydroxyquinolato) zinc was prepared with a reaction of zinc acetate solution and 8-hydroxyquinoline-ethanol mixed solution. The PH value of the reaction mixture was adjusted to 8.0 by adding 0.25 mol/dm³ sodium hydroxide aqueous solution and a yellow-green precipitate was formed. The precipitate was filtered out, washed with ethanol, and dried at 65 °C for a few hours. The yield di(8-hydroxyquinolato) zinc was dissolved into hydrochloric acid to form a transparent solution. The nanoporous glass was immersed into such a solution for full impregnation. The impregnated glass and the above solution are dried in an oven at 60 °C temperature for

several days to obtain a yellow-green color transparent glass and a yellow-green powder. The composite material samples were well polished for measurement. Success of the impregnation process was based on the uniform topology of the porous structure and the homogenous distribution of the pores in the silica glass. The photoluminescence excitation and emission spectra of samples were measured in an FP-6500 spectrafluorometer (JASCO) equipped with a Xe lamp as the light source. The power of the Xe lamp was 150 W. The scanning electronic microscopic (SEM) images of the nanoporous glass were taken on a Philip XL30-FEG scanning electron microscope. All measurements were performed at room temperature.

The SEM images of the nanoporous glass (Fig. 1) showed that a silica skeleton interwoven with a lot of interconnected nano-metered pores with diameters of about 20–30 nm remained. Based on the SEM image, the particle size of the impregnated di(8-hydroxyquinolato) zinc would be smaller than 30 nm.

The emission spectra of di(8-hydroxyquinolato) zinc impregnated in the nanoporous glass (hereafter called the embedded organic phosphor) and the original phosphor powder were showed in Fig. 2. The excitation wavelengths were adjusted at 334 and 360 nm in measurement,

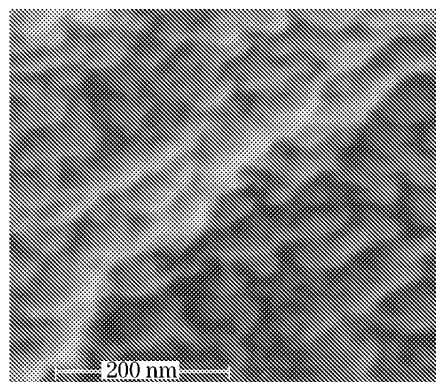


Fig. 1. Typical SEM image of the nanosized porous glass with the calibration of 200 nm.

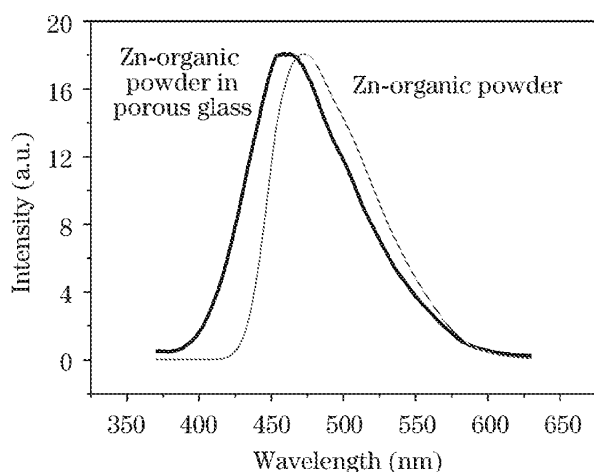


Fig. 2. Emission spectrum of the embedded di(8-hydroxyquinolato) zinc ($\lambda_{\text{ex}}=334$ nm) together with that of the normal organic phosphor powder ($\lambda_{\text{ex}}=360$ nm).

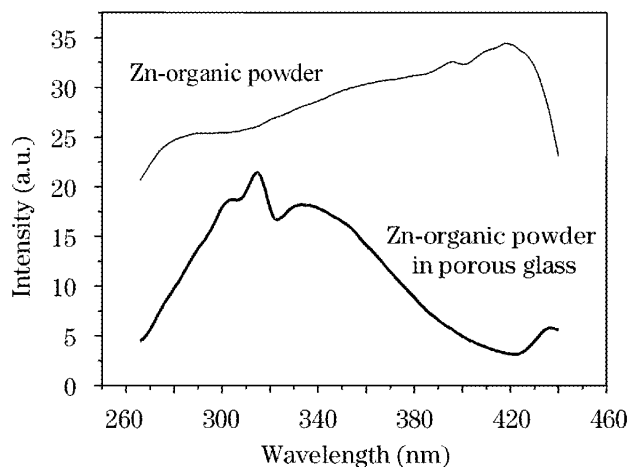


Fig. 3. Excitation spectrum of the embedded di(8-hydroxyquinolato) zinc ($\lambda_{\text{em}}=461$ nm) together with that of the normal organic phosphor ($\lambda_{\text{em}}=473$ nm).

respectively. The intensities of the emission spectrum of the embedded organic phosphor and the original phosphor powder were normalized to the same scale. The emission band of the embedded organic phosphor and the powder organic fluorescent material are similar to that of di(8-hydroxyquinolato) zinc, which is ascribed to the $\pi^* \rightarrow n$ transition. The emission band of the embedded organic phosphor becomes wider by 8 nm and shifts blue end (from 472.5 to 458.5 nm) in comparison with that of the original phosphor powder. These broaden and blueshift phenomena have been observed for the nano-metered inorganic fluorescent material^[5,6]. Since di(8-hydroxyquinolato) zinc was confined into the nano-metered scale pores in the porous glass, nano-metered particle of this inorganic compound should be expected. Based on our experimental results and the explanation of nano-metered inorganic fluorescent material^[5,7], the wider emission band and its blue shift of the embedded organic phosphor powder would be also ascribed to size effects.

The excitation spectra of the embedded organic fluorescent material and the organic phosphor powder monitored at their maximum emission wavelength were displayed in Fig. 3. The monitor wavelengths were 461 and 473 nm, respectively. The excitation band was originated from the $\pi \rightarrow \pi^*$ transition of di(8-hydroxyquinolato) zinc based on the Ref. [8]. The spectrum of the organic powder phosphor is the same as that of di(8-hydroxyquinolato) zinc. However, the spectrum of the embedded organic phosphor is a large difference from that of the original phosphor powder. Blueshift (from 418 to 314 nm) was observed due to the $\pi \rightarrow \pi^*$ transition. The excitation band of the organic fluorescent powder material is strong and continuous ranged from 270.5 nm to 440 nm, while that of the embedded organic fluorescent material is split into four sub-bands. The sub-band centered around 324 nm becomes quite narrow. The intensities distribution of the $\pi \rightarrow \pi^*$ transition of the embedded phosphor is also quite different from that of the powder. In the short wavelength end, the intensity of the embedded organic fluorescent material is stronger. Additionally, owing to the dissolution of di(8-hydroxyquinolato) zinc in diluted hydrochloric acid, species like ZnCl_2 and 8-hydroxyquinoline would come into being, which would contribute to the form of sub-bands in the excitation spectra of the embedded organic fluorescent material.

According to the quantum size effects of nano-metered particles, the energy level of nanoparticle compound would become scattered and higher up. The excitation band splitting into several sub-bands of the embedded organic phosphor would be result from the quantum size effects. While the interactions among semiconductor atoms or inorganic ions are strong covalent bonds or ionic bonds, interaction among organic fluorescent material molecules is weak Van der Waals force. The quantum size effects in the embedded organic compound can be considered as the molecular orbital overlap changed with the grain size. The increase of orbital overlap would lead to the increase of the bonding or anti-bonding energy gap. The energy gap between the π bond orbital and the π^* bond orbital of the embedded organic phosphor is wider than that of the bulk organic fluorescent material. The molecular orbital overlap becomes larger in the embedded organic phosphor powder. The wider energy gap between the π and π^* bond orbital of the embedded organic phosphor would also account for the shorter excitation wavelength in emission spectral measurement (Fig. 2). In addition, the roles that the internal tension and interface effects of the nanopores played in the embedded phosphor may be an object to be investigated further.

In conclusion, the luminescent properties of di(8-hydroxyquinolato) zinc have been modified when it is embedded into a nanoporous glass. The emission spectrum of the embedded organic phosphor becomes broader and shifts to the shorter wavelength end. In comparison with those of the organic phosphor powder, the excitation band of the embedded organic fluorescent material has a larger blueshift and is divided into several sub-bands. The luminescence in the shorter wavelength end of the embedded organic phosphor is enhanced.

This work was supported by the National Natural Science Foundation of China under Grant No. 10174020 and 60087002. The authors thank Dr. Xiaoqing Zeng for his insight and suggestions. D. Xiong's e-mail address is dy3xiong@163.com.

References

1. E. Molz, A. P. Y. Wong, M. H. W. Chan, and J. R. Beamish, *Phys. Rev. B* **48**, 5741 (1993).
2. E. V. Charnaya, C. Tien, K. J. Lin, and C. S. Wur, *Phys. Rev. B* **58**, 467 (1998).
3. I. V. Golosocsky, I. Mirebeau, G. André, D. A. Kuryukov, and S. B. Vakhruhev, *Phys. Rev. Lett.* **86**, 5783 (2001).
4. J. X. Meng, T. K. Li, W. K. Wong, and K. W. Cheah, *Appl. Phys. Lett.* **77**, 2795 (2000).
5. Y. Tao, G. Zhao, X. Shao, X. Ju, W. Zhang, and S. Xia, *Mater. Lett.* **28**, 137 (1996).
6. Q. Li, L. Gao, and D. S. Yan, *Nanostructured Material* **8**, 825 (1997).
7. P. D. Milewski, S. K. Streiffer, A. I. Kingon, I. K. Shmagin, R. M. Kolbas, and S. Krishnankutty, *J. Soc. Information Display* **6**, 143 (1998).
8. W. Streck, E. Zych, and D. Hreniak, *J. Alloys. Comp.* **344**, 332 (2002).