

## Preparation and Photoluminescence of GdVO<sub>4</sub>:Eu Nanophosphors for Flexible and Transparent Displays

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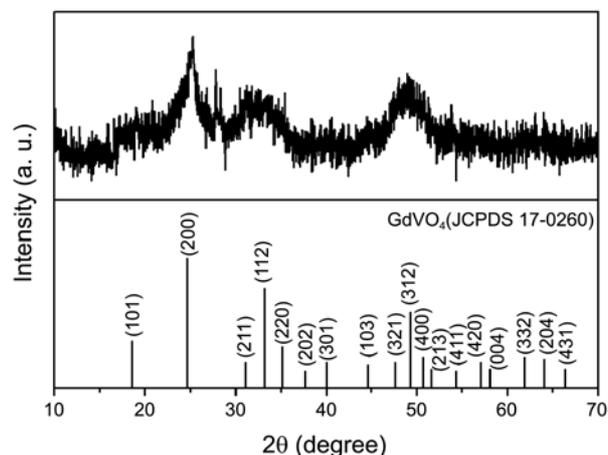
Europium ion doped metal orthovanadate (MVO<sub>4</sub>:Eu, M = Y, Gd, La) has been widely used as commercial red-emitting phosphors in cathode ray tubes (CRTs), and fluorescent lamps,<sup>1,2</sup> with photoluminescence quantum yields of up to 95%.<sup>3,4</sup> Commercial micron-sized MVO<sub>4</sub>:Eu phosphors are generally prepared by high-temperature solid-state reactions. However, these micron-sized phosphors cannot be used in flexible and transparent displays due to their high scattering. Because nano-sized materials do not show any scattering in the visible region, inorganic nanophosphors have received much attention for their applicability in flexible and transparent display devices.<sup>5-7</sup>

MVO<sub>4</sub>:Eu nanophosphors have been prepared by soft reactions, such as hydrothermal, solvothermal, sonochemical, microemulsion, and polymer-assisted methods.<sup>8-14</sup> Despite there have been numerous studies of the synthesis of MVO<sub>4</sub>:Eu nanophosphors, most attention has focused on the synthesis of powder-type MVO<sub>4</sub>:Eu phosphors. Mono-dispersed nanophosphors prepared by soft reactions can easily agglomerate in organic solvents. Transparent suspensions of nanophosphors without an agglomeration in organic solvents are needed for these phosphors to be used in flexible and transparent displays. However, there are few reports of preparing transparent suspensions of nanophosphors. Transparent suspensions of small amounts of YVO<sub>4</sub>:Eu nanophosphors in hexane have been prepared using surfactant-assisted hydrothermal reactions in a water-hexane bilayer system.<sup>15</sup> In this system, most of the YVO<sub>4</sub>:Eu nanophosphors aggregated in the water phase that is not adequate for the flexible and transparent displays. New methods for the large-scale synthesis of nanophosphors are required that can prepare phosphors in single organic solvent phase. This work reports the first simple method of preparing transparent suspensions of GdVO<sub>4</sub>:Eu nanophosphors in toluene. The optimal conditions for the phosphors' bright emission were also examined.

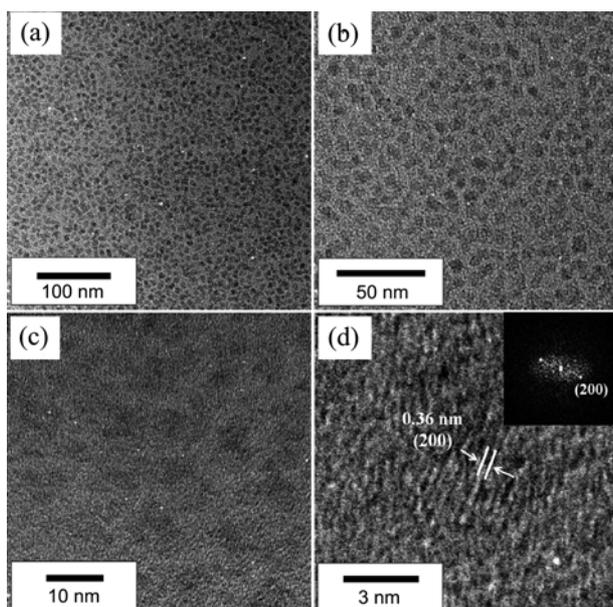
GdVO<sub>4</sub>:Eu nanophosphors were prepared by solvothermal reactions from Gd-oleate, Eu-oleate, and tetraoctylammonium-VO<sub>4</sub> complexes in toluene in the presence of oleic acid and oleylamine. Gd-oleate and Eu-oleate were obtained by transferring aqueous Gd(NO<sub>3</sub>)<sub>3</sub> and Eu(NO<sub>3</sub>)<sub>3</sub> to the toluene phase by adding sodium oleate in toluene. Tetraoctylammonium-VO<sub>4</sub> was obtained by transferring NH<sub>4</sub>VO<sub>3</sub> in

water with NH<sub>4</sub>OH to toluene by introducing tetraoctylammonium bromide in toluene. Typical powder X-ray diffraction (XRD) patterns of GdVO<sub>4</sub>:Eu phosphors prepared at 80 °C (Figure 1) indicated a structure matching that of tetragonal GdVO<sub>4</sub> (JCPDS 17-0260, *a* = 0.7212 nm, *c* = 0.6348 nm). The ionic radius of Eu<sup>3+</sup> (0.0950 nm) is slightly larger than that of Gd<sup>3+</sup> (0.0938 nm), Eu<sup>3+</sup> ions are allowed to its facile occupation of Gd<sup>3+</sup> sites in the host GdVO<sub>4</sub> structure.<sup>16</sup> The broad XRD peak also indicates that the GdVO<sub>4</sub>:Eu was present as nanoparticles. The XRD patterns confirm that the GdVO<sub>4</sub>:Eu phosphor was synthesized without impurities. High-resolution transmission electron microscopy (HRTEM) images of the GdVO<sub>4</sub>:Eu phosphor prepared at 80 °C (Figure 2) show square-like sheet morphologies with an average width of 6.5 nm. The fringe pattern of an individual phosphor in the HRTEM image shows a spacing of 0.36 nm, corresponding to the (200) plane of the GdVO<sub>4</sub> crystal (Figure 2(d)), indicating that the growth of the square sheet crystals occurred along the [100] direction.

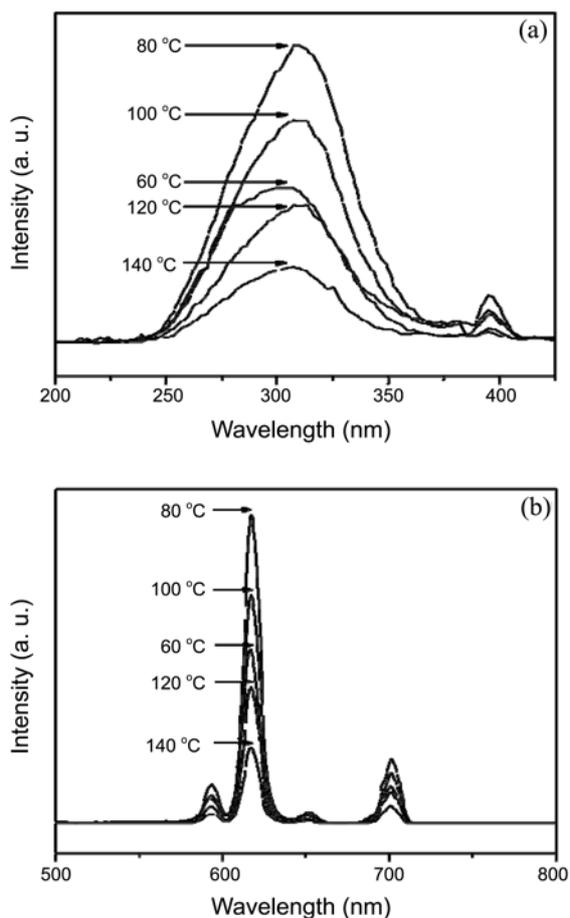
Synthesis temperatures ranged from 60 °C to 140 °C were tested to obtain the brightest phosphors. Absorption at 310 nm and the strongest emission at 618 nm increased with increasing temperature up to 80 °C, before decreasing with further increases of temperature (Figure 3). Therefore, synthesis at 80 °C was best for the brightest phosphors. The



**Figure 1.** Powder X-ray diffraction patterns of GdVO<sub>4</sub>:Eu phosphors prepared at 80 °C.

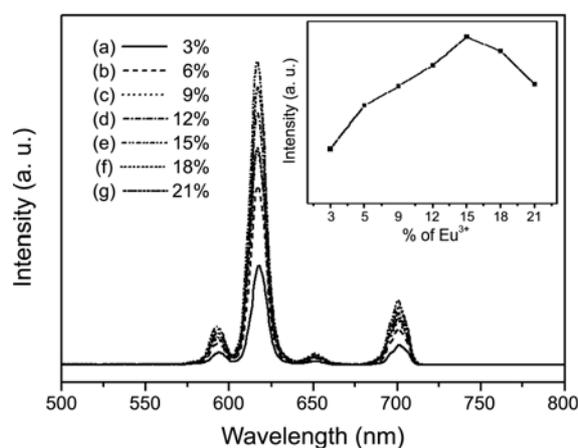


**Figure 2.** HRTEM images at various magnifications of  $\text{GdVO}_4:\text{Eu}$  phosphors prepared at  $80^\circ\text{C}$ . Inset in (d) shows FFT patterns of an individual  $\text{GdVO}_4:\text{Eu}$  phosphor.



**Figure 3.** (a) Excitation ( $\lambda_{\text{em}} = 618 \text{ nm}$ ) and (b) emission spectra ( $\lambda_{\text{ex}} = 310 \text{ nm}$ ) of  $\text{GdVO}_4:\text{Eu}$  phosphors prepared at  $60\text{--}140^\circ\text{C}$ .

broad bands around  $310 \text{ nm}$  in the absorption spectra are attributed to a charge transfer transition between  $\text{Eu}^{3+}$  and

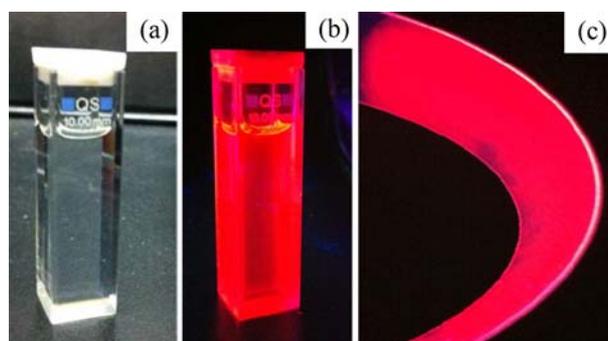


**Figure 4.** Emission spectra ( $\lambda_{\text{ex}} = 310 \text{ nm}$ ) of  $\text{Gd}_{1-x}\text{VO}_4:x\text{Eu}$  phosphors prepared with different values of  $x$ ; (a) 0.03, (b) 0.06, (c) 0.09, (d) 0.12, (e) 0.15, (f) 0.18, and (g) 0.21. Inset shows the relative intensity of the  $618 \text{ nm}$  emission as a function of  $x$ .

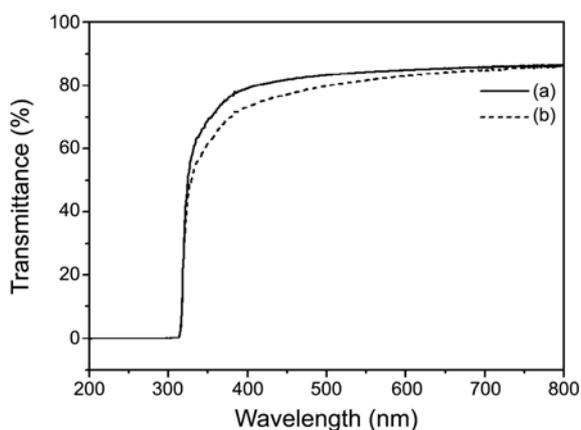
$\text{VO}_4^{3-}$  anions. The series of emission peaks between  $550$  and  $750 \text{ nm}$  in the photoemission spectra were assigned to the typical  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$  ( $J = 1, 2, 3, 4$ ) transitions of  $\text{Eu}^{3+}$  ions in the  $\text{GdVO}_4:\text{Eu}$  structure.<sup>17</sup> The strongest emission peak at  $618 \text{ nm}$  corresponds to the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transitions of  $\text{Eu}^{3+}$ .

The photoluminescence intensity depends strongly on the concentration of activators in the inorganic phosphors. Various  $\text{Gd}_{1-x}\text{VO}_4:x\text{Eu}$  phosphors ( $x = 0.03, 0.06, 0.09, 0.12, 0.15, 0.18,$  and  $0.21$ ) were prepared at  $80^\circ\text{C}$  to examine the effects of europium concentration on the photoluminescence intensity (Figure 4). The emission intensity increased with increasing  $\text{Eu}$  concentration up to  $15 \text{ mol } \%$  and decreased with further increases of  $\text{Eu}$  concentration, which is a typical concentration quenching behavior in inorganic phosphors. Therefore, the brightest emission was obtained from  $\text{Gd}_{0.85}\text{VO}_4:0.15\text{Eu}$  prepared at  $80^\circ\text{C}$ .

Inorganic nanoposphors can reduce scattering light losses due to their small particle size. Despite nanoparticles being obtained from soft reactions, they are easily agglomerated to form larger aggregates. Therefore, the preparation of mono-dispersed nanoparticle suspensions is important for their use in flexible and transparent displays. A highly transparent



**Figure 5.** Transparent suspension of  $\text{GdVO}_4:\text{Eu}$  phosphors in toluene (a) in daylight and (b) under  $254 \text{ nm}$  UV irradiation. (c) Transparent flexible film coated with the  $\text{GdVO}_4:\text{Eu}$  phosphors under UV irradiation.



**Figure 6.** UV-vis transmittance spectra of (a) the original overhead transparency film and (b) when coated with the  $\text{GdVO}_4:\text{Eu}$  phosphors.

suspension was prepared by dispersing  $\text{GdVO}_4:\text{Eu}$  nanophosphors in toluene (Figure 5(a)). The use of oleic acid and oleylamine capping agents allowed the suspension to remain stable without sedimentation or agglomeration. The nanophosphors' ionic crystals interacted with the polar heading groups of the oleic acid and oleylamine, gaining a hydrophobic coating due to the long-chained alkyl groups of the oleic acid and oleylamine. Therefore, suspended nanophosphors were stabilized by interactions between their hydrophobic outer parts and the nonpolar toluene solvent. Irradiating the suspension under a 254 nm hand-held UV lamp resulted in a very bright red emission (Figure 5). To demonstrate the suspension's applicability in flexible and transparent electronic displays, it was applied to a flexible transparent film and irradiated with UV light (Figure 5(c)).

The film's UV-vis transmittance was recorded to examine its optical transparency (Figure 6). The coated film retained 96.0% of the uncoated film's transmittance at 500 nm, indicating excellent transparency in all the visible wavelengths with minimal scattering. Therefore, the prepared suspension of  $\text{GdVO}_4:\text{Eu}$  nanophosphor appeared adequate for use in flexible and transparent thin film displays.

In conclusion,  $\text{GdVO}_4:\text{Eu}$  nanophosphors were prepared by solvothermal reactions of Gd-oleate, Eu-oleate, and tetraoctylammonium- $\text{VO}_4$  complexes in toluene in the presence of oleic acid and oleylamine. They formed square-like sheets with an average width of 6.5 nm. Their hydrophobic surfaces allowed them to form stable suspensions without aggregation. When suspended in toluene, the nanophosphors were transparent and did not scatter visible light, allowing them to be used in the next generation of flexible and transparent displays.

### Experimental Section

$\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aldrich),  $\text{NH}_4\text{VO}_3$  (Aldrich),  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aldrich),  $\text{NH}_4\text{OH}$  (28%, Aldrich), tetraoctylammonium bromide (TOABr, Aldrich), sodium oleate (TCI), oleic acid (Aldrich) and oleylamine (TCI) were used as received. In a

typical synthesis of  $\text{Gd}_{0.90}\text{VO}_4:0.10\text{Eu}$  phosphor, 0.060 M  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and 0.0067 M  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were prepared in 30 mL water. To which 1.83 g sodium oleate, 5.0 mL oleic acid, and 40 mL toluene were added. The water-toluene bilayered mixture was vigorously stirred for 1 h to allow aqueous  $\text{Gd}^{3+}$  and  $\text{Eu}^{3+}$  to transfer to the toluene phase through coordination with oleate anions at room temperature. 0.067 M  $\text{NH}_4\text{VO}_3$  was dissolved in 30 mL water and adjusted to pH 10.5 by the dropwise addition of  $\text{NH}_4\text{OH}$  solution. 3.28 g TOABr in 40 mL toluene was then added and vigorously stirred for 1 h to transfer aqueous  $\text{VO}_4^{3-}$  to the toluene phase through coordination with tetraoctylammonium cations. The two toluene solutions containing  $\text{Gd}^{3+}$  and  $\text{Eu}^{3+}$  complexes and  $\text{VO}_4^{3-}$  complexes were mixed and 5.0 mL oleylamine was added under stirring. The mixture was then transferred to a 100 mL Teflon-lined autoclave.

To preparation the  $\text{GdVO}_4:\text{Eu}$  phosphor, solvothermal reactions were conducted at 60–140 °C for 16 h. The solution was then centrifuged at 4000 rpm for 10 min, giving a clear solution after the precipitate was removed. The  $\text{GdVO}_4:\text{Eu}$  phosphors were obtained as a precipitate by adding 100 mL ethanol to the clear solution. They were redispersed in toluene. Precipitation and redispersion were repeated several times to purify the phosphors. The precipitate was then centrifuged, washed several times with ethanol, and dried at 60 °C for 12 h. To prepare a transparent suspension of the  $\text{GdVO}_4:\text{Eu}$  phosphors, 0.1 g phosphor was dispersed in 3 mL toluene in a 10 mL vial for 10 min. The flexible transparent film was prepared by dispersing 1.0 g PAS (series 800, Jujo) ink into the transparent suspension of  $\text{GdVO}_4:\text{Eu}$  phosphor with stirring for 15 min. The  $\text{GdVO}_4:\text{Eu}$  ink was then coated onto commercial overhead transparency film to a thickness of 90  $\mu\text{m}$  using an applicator.

The structure of the phosphor was analyzed by powder X-ray diffraction (XRD, PANalytical, X'pert-pro MPD) using  $\text{Cu K}\alpha$  radiation. Their morphologies were observed by transmission electron microscopy (TEM, JEOL JEM-3010). Their excitation and emission spectra were measured using a spectrum analyzer (DARSA, PSI). UV excitation was with a hand-held 12 W UV lamp (Uvitec,  $\lambda_{\text{max}} = 254 \text{ nm}$ ). The transmittance of the coated film was measured using a UV-vis spectrometer (Perkin Elmer Lambda 25).

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### References

- Ozawa, L.; Itoh, M. *Chem. Rev.* **2003**, *103*, 3835.
- Jüstel, T.; Nikol, H.; Ronda, C. *Angew. Chem. Int. Ed.* **1998**, *37*, 3084.
- Mahalley, B. N.; Dhoble, S. J.; Pode, R. B.; Alexander, G. *Appl. Phys. A* **2000**, *70*, 39.
- Anitha, M.; Ramakrishnan P.; Chatterjee, A.; Alexander, G.; Singh, H. *Appl. Phys. A* **2002**, *74*, 153.
- Yan, B.; Wu, J. H. *Mater. Lett.* **2009**, *63*, 946.

6. Taniguchi, T.; Watanabe, T.; Katsumata, K. I.; Okada, K.; Matsushita, N. *J. Phys. Chem. C* **2010**, *114*, 3763.
  7. Song, W. S.; Choi, H. N.; Kim, Y. S.; Yang, H. *J. Mater. Chem.* **2010**, *20*, 6929.
  8. Nguyen, H. D.; Mho, S. I.; Yeo, I. H. *J. Lumin.* **2009**, *129*, 1754.
  9. Jin, D.; Yang, H.; Ding, G.; Yu, X.; Wang, L.; Zheng, Y. *Inorg. Mater.* **2008**, *44*, 1121.
  10. Cho, Y. S.; Huh, Y. D. *Bull. Kor. Chem. Soc.* **2010**, *31*, 2368.
  11. Chung, J. W.; Yang, H. K.; Moon, B. K.; Choi, B. C.; Jeong, J. H.; Bae, J. S.; Kim, K. H. *Curr. Appl. Phys.* **2009**, *9*, S222.
  12. Zhu, L.; Li, J.; Li, Q.; Liu, X.; Meng, J.; Cao, X. *Nanotech.* **2007**, *18*, 055604.
  13. Sun, L.; Zhang, Y.; Zhang, J.; Yan, C.; Liao, C.; Lu, Y. *Solid State Commun.* **2002**, *124*, 35.
  14. Wang, J.; Xu, Y.; Hojamberdiev, M.; Wang, M.; Zhu, G. *Mater. Chem. Phys.* **2010**, *119*, 169.
  15. Cho, Y. S.; Huh, Y. D. *Bull. Kor. Chem. Soc.* **2011**, *32*, 335.
  16. Weast, R. C. *Handbook of Chemistry and Physics*, 70th ed.; 1989; F-187.
  17. Kano, T. *Phosphor Handbook*; Shionoya, S., Yen, W. M., Eds.; CRC Press: New York, 1998; Ch. 3, Section 3.
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