Preparation and Photoluminescence of GdVO₄:Eu Nanophosphors for Flexible and Transparent Displays

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Europium ion doped metal orthovanadate (MVO₄:Eu, M = Y, Gd, La) has been widely used as commercial red-emitting phosphors in cathode ray tubes (CRTs), and fluorescent lamps, with photoluminescence quantum yields of up to 95%. Commercial micron-sized MVO₄: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.

MVO₄:Eu nanophosphors have been prepared by soft reactions, such as hydrothermal, solvothermal, sonochemical, microemulsion, and polymer-assisted methods. Despite there have been numerous studies of the synthesis of MVO₄:Eu nanophosphors, most attention has focused on the synthesis of powder-type MVO₄:Eu phosphors. Monodispersed 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 YVO₄:Eu nanophosphors in hexane have been prepared using surfactant-assisted hydrothermal reactions in a water-hexane bilayer system. In this system, most of the YVO₄: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 GdVO₄:Eu nanophosphors in toluene. The optimal conditions for the phosphors’ bright emission were also examined.

GdVO₄:Eu nanophosphors were prepared by solvothermal reactions from Gd-oleate, Eu-oleate, and tetraoctylammonium-VO₄ complexes in toluene in the presence of oleic acid and oleylamine. Gd-oleate and Eu-oleate were obtained by transferring aqueous Gd(NO₃)₃ and Eu(NO₃)₃ to the toluene phase by adding sodium olate in toluene. Tetraoctylammonium-VO₄ was obtained by transferring NH₄VO₃ in water with NH₄OH to toluene by introducing tetraoctylammonium bromide in toluene. Typical powder X-ray diffraction (XRD) patterns of GdVO₄:Eu phosphors prepared at 80 °C (Figure 1) indicated a structure matching that of tetragonal GdVO₄ (JCPDS 17-0260, a = 0.7212 nm, c = 0.6348 nm). The ionic radius of Eu³⁺ (0.0950 nm) is slightly larger than that of Gd³⁺ (0.0938 nm), Eu³⁺ ions are allowed to its facile occupation of Gd³⁺ sites in the host GdVO₄ structure. The broad XRD peak also indicates that the GdVO₄:Eu was present as nanoparticles. The XRD patterns confirm that the GdVO₄:Eu phosphor was synthesized without impurities. High-resolution transmission electron microscopy (HRTEM) images of the GdVO₄: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 GdVO₄ 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 GdVO₄:Eu phosphors prepared at 80 °C.
broad bands around 310 nm in the absorption spectra are attributed to a charge transfer transition between Eu$^{3+}$ and VO$_4^{3-}$ anions. The series of emission peaks between 550 and 750 nm in the photoemission spectra were assigned to the typical $^5D_0 \rightarrow ^7F_J$ ($J = 1, 2, 3, 4$) transitions of Eu$^{3+}$ ions in the GdVO$_4$:Eu structure. The strongest emission peak at 618 nm corresponds to the $^5D_0 \rightarrow ^7F_2$ transitions of Eu$^{3+}$.

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

Inorganic nanophosphors 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 monodispersed nanoparticle suspensions is important for their use in flexible and transparent displays. A highly transparent...
suspension was prepared by dispersing GdVO₄: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 PAS (series 800, Jujo) ink into the transparent suspension of GdVO₄:Eu phosphors, 0.1 g phosphor was added 100 mL ethanol to the clear solution. They were dispersed in 3 mL toluene in a 10 mL vial for 10 min. The water-toluene bilayered mixture was vigorously stirred for 1 h to transfer aqueous VO₄³⁻ to the toluene phase through coordination with tetraoctylammonium cations. The two toluene solutions containing Gd³⁺ and Eu³⁺complexes and VO₄³⁻ 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 prepare the GdVO₄: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 GdVO₄: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 GdVO₄: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 GdVO₄:Eu phosphor with stirring for 15 min. The GdVO₄:Eu ink was then coated onto commercial overhead transparency film to a thickness of 90 μm using an applicator.

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

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References