Synthesis and luminescence properties of YlnGe$_2$O$_7$ phosphors activated by dysprosium ions

Pin-Lun Dai$^a$, Bin-Siang Tsai$^b$, Yeou-Yih Tsai$^c$, Hao-Long Chen$^d$, Te-Hua Fang$^d$, Kun-Hou Liao$^e$, Yee-Shin Chang$^{a,*}$

$^a$ Department of Electronic Engineering, National Formosa University, Huwei, Yunlin 632, Taiwan
$^b$ Fab III Thin Film Department, ProMOS Technologies Inc., Taichung 428, Taiwan
$^c$ Department of Electronic Engineering, Kao Yuan University, Lujhu, Kaohsiung 821, Taiwan
$^d$ Institute of Mechanical and Electromechanical Engineering, National Formosa University, Huwei, Yunlin 632, Taiwan
$^e$ Department of Military Meteorology Engineering, Air Force Institute of Technology, Kaohsiung 820, Taiwan

**Abstract**

The Dy$^{3+}$-doped YlnGe$_2$O$_7$ phosphor was synthesized by solid-state reaction and calcined at 1300 °C for 10 h in air. The structure and optical properties of YlnGe$_2$O$_7$:Dy$^{3+}$ phosphors have been investigated. XRD results indicated that all of the diffraction peaks can be attributed to the monoclinic YlnGe$_2$O$_7$ phase when the Dy$^{3+}$ ion concentration is increased up to 40 mol%. In the photoluminescence studies, under ultraviolet (349 nm) excitation, the emission spectrum exhibited a weak group of peaks for the 4F$_{9/2}$ transition at 543 nm, and two groups of strong peaks at 484 nm and 574 nm due to the 4I$_{13/2}$ + 4K$_{17/2}$ + 4F$_{7/2}$ → 4H$_{15/2}$ transition of Dy$^{3+}$ ions, respectively. The optimum concentration for the Dy$^{3+}$ luminescence is about 10 mol%, indicating that the concentration quenching effect is active when the Dy$^{3+}$ ion concentration is larger than 10 mol%. The CIE color coordinate of emission is at x = 0.3031 and y = 0.3251, which is located in the near-white light emission region.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Luminescent materials (phosphors) have many everyday applications, such as in fluorescent lighting, computer screens, televisions, and so on [1]. In 1997 the first white-light-emitting-diodes (WLEDs) became commercially available, and in recent years, inorganic phosphors have been extensively investigated for applications in various types of flat panel display (FPD), such as plasma display panels (PDPs), thin film electroluminescence devices (TFEL), field emission displays (FEDs), and vacuum fluorescent displays (VFDs) [2–8]. Nichia Chemical and Osram control many of the patents on phosphors, leading outside manufacturers to invest in three main emissions in various types of flat panel display (FPD), such as plasma display panels (PDPs), thin film electroluminescence devices (TFEL), field emission displays (FEDs), and vacuum fluorescent displays (VFDs) [2–8].

In this investigation, YlnGe$_2$O$_7$ was selected as the host material, with a thortveitite [13] structure and symmetry described by the space group C2/m (No. 12). This material crystallizes in the monoclinic system, and each In$^{3+}$ and Y$^{3+}$ cation occupy the same octahedral site, forming a hexagonal arrangement on the ab planes. In their turn, the hexagonal arrangement of InO$_6$/YO$_6$ octahedral layers are held together by sheets of isolated Ge$_2$O$_7$ diorthogroups built up from two tetrahedra sharing a common vertex [14].

The rare earth Dy$^{3+}$ ion has two dominant emission bands in the blue region for the 6H$_{15/2}$ → 4H$_{11/2}$ transition and the yellow region for the 6H$_{15/2}$ → 4H$_{11/2}$ transition. The yellow emission of Dy$^{3+}$ is especially hypersensitive to the local environment, while its blue emission is not. Therefore, by suitably adjusting the yellow-to-blue intensity ratio value, it is possible to obtain a phosphor with near-white light emission [15,16]. To date, the optical properties of the rare earth Dy$^{3+}$ ion doped yttrium indium germanate have not been reported. Consequently, in this investigation YlnGe$_2$O$_7$ phosphors were synthesized by solid-state reaction, calcined at 1300 °C for 10 h in air, and doped with different Dy$^{3+}$ ion concentrations. The phases, morphologies, and optical properties of the YlnGe$_2$:Dy$^{3+}$ thus produced phosphors were then investigated.

2. Experimental procedure

2.1. Powder preparation

The Dy$^{3+}$-doped YlnGe$_2$O$_7$ phosphors formulated (Y$_{1-x}$Dy$_x$)ln Ge$_2$O$_7$, with x equal to 0.1, 0.5, 1.0, 2.0, 3.0 and 4.0, were...
synthesized by solid-sate reaction. The starting materials were Y2O3, In2O3, GeO2, Dy2O3 (purity ≥ 99.99%) from Alfa Aesar Company. After mechanical mixing by planetary ball milling for 30 min at a speed of 150 rpm with zirconia balls in a polyethylene jar, the mixtures were calcined at 1300 °C for 10 h in a programmable furnace.

Fig. 1. The X-ray diffraction patterns of YInGe2O7 doped with different Dy3+ ion concentrations calcined at 1300 °C for 10 h in air.

Fig. 2. The SEM micrographs of YInGe2O7 doped with (a) 1, (b) 10, (c) 30 and (d) 40 mol% Dy3+ ions powders calcined at 1300 °C for 10 h in air.
2.2. Characterizations

The phase identification was performed by X-ray powder diffraction (XRD). The XRD patterns were recorded with a Rigaku D/Max-33 X-ray diffractometer, using Cu Kα (1.5406 Å) radiation with a source power of 30 kV and a current of 20 mA. The surface morphology of the powders was examined using high-resolution scanning electron microscopy (HR-SEM, S4200, Hitachi). Optical absorption spectra were measured from 200 to 500 nm at room temperature using a Hitachi U-3010 UV-Vis spectrophotometer. Both excitation and luminescence spectra of these phosphors were analyzed with a Hitachi F-4500 fluorescence spectrophotometer using a 150 W Xe-lamp as the excitation source at room temperature.

3. Results and discussion

3.1. Structure

The X-ray powder diffraction patterns of (Y_{1-x}Dy_x)InGe_2O_7 powders with x = 0.0–0.4 calcined at 1300 °C for 10 h in air are shown in Fig. 1. As can be seen, all of the diffraction peaks were...
attributed to be the monoclinic YInGe2O7 crystal structure, and no impurity peaks were found. In addition, the trivalent dysprosium ions (0.91 Å) [17] substitute the trivalent yttrium ions (0.9 Å) [17] in the (Y1-xDyxCInGe2O7 system, and this may be attributed to the similar ionic radius and the same valence of the Dy3+ and Y3+ ions. Therefore, there are no charge compensation issues for the Dy3+ ions substituting the Y3+ ions in YInGe2O7 lattice, and they can easily form solid solutions [4].

3.2. Microstructures

Microstructure control is a key issue in materials engineering, because almost all properties depend on internal microstructures. With increased control and knowledge of preparation conditions, the desired properties of the final products can be significantly enhanced. Fig. 2 shows the SEM micrograph of YInGe2O7 powders doped with 1, 10, 30 and 40 mol% Dy3+ ions calcined at 1300 °C for 10 h in air. The results show that the crystallized particles aggregated and were irregular. The powder micrographs are very similar as the Dy3+ ion concentration increases, which indicate that this has no influence on the surface morphology of the powders.

3.3. Absorption and excitation spectrum

Fig. 3a shows the UV–Visible absorption spectrum of YInGe2O7 doped with 10 mol% Dy3+ ion, as measured at room temperature. According to the work of Chang et al. [4], for pure YInGe2O7, the major absorption spectrum of the phosphors can be classed into two bands. The first absorption band between 200 and 280 nm corresponds to the charge transfer between the In3+ and O2− ions of the InO6 anionic group in the host lattice [18–19]. Meanwhile, the absorption band between 280 and 450 nm is caused by the oxygen deficient center of the GeO4 anion [20–21]. For YInGe2O7:10 mol% Dy3+, the compounds exhibited an absorption peak...
between 220 and 300 nm due to the charge transfer state (CTS) of the Dy\(^{3+}\)-O\(^2-\) ions [16,22]. Furthermore, there is a series of sharp absorption bands present between 320 and 480 nm, centered at 324, 338, 349, 366, 386, 427, 453 and 474 nm for each absorption peak labeled from 5 to 12 in the absorption spectrum, respectively, which correspond to the typical f-f transition of Dy\(^{3+}\) ions. The strongest peak is located at 349 nm, which can be assigned to the \( ^{4}I_{13/2} \rightarrow ^{6}H_{15/2} + ^{6}P_{7/2} \) transition [23]. The excitation spectrum (\( \lambda_{em} = 574 \) nm) for YInGe\(_2\)O\(_7\) doped with 10 mol% Dy\(^{3+}\) ions calcined at 1300 °C for 10 h in air is shown in Fig. 3b, and it contains two parts: (1) the broad band between 200 and 275 nm is the charge transfer state (CTS) bands due to the dysprosium–oxygen interactions [16,22]; and (2) the sharp peaks in the range from 292 to 490 nm are associated with the typical intra-4f transitions of the Dy\(^{3+}\) ions that appear at 298, 324, 338, 349, 366, 386, 427, 453 and 474 nm (labeled 4–12 in the excitation spectrum), which were attributed to (\( ^{4}H_{15/2} \rightarrow ^{4}I_{15/2} + ^{4}I_{13/2} \), (\( ^{4}H_{15/2} \rightarrow ^{4}K_{13/2} + ^{4}H_{11/2} \)), (\( ^{4}H_{15/2} \rightarrow ^{4}G_{11/2} + ^{4}F_{7/2} \)), (\( ^{4}H_{15/2} \rightarrow ^{4}G_{9/2} + ^{4}F_{7/2} \)), (\( ^{4}H_{15/2} \rightarrow ^{4}G_{7/2} + ^{4}F_{5/2} \)), (\( ^{4}H_{15/2} \rightarrow ^{4}F_{5/2} + ^{4}F_{3/2} \)), (\( ^{4}H_{15/2} \rightarrow ^{4}F_{9/2} + ^{4}F_{7/2} \)), (\( ^{4}H_{15/2} \rightarrow ^{4}F_{7/2} + ^{4}F_{5/2} \)), (\( ^{4}H_{15/2} \rightarrow ^{4}F_{5/2} + ^{4}F_{3/2} \)), and (\( ^{4}H_{15/2} \rightarrow ^{4}F_{3/2} \)) [23–24]. The strongest excitation peak is located at 349 nm, which is good accordance with the results of the absorption analysis.

3.4. Emission spectrum

Because 349 nm is the strongest absorption peak for excitation, 349 nm was chosen to be the excitation wavelength to observe the emission behavior for YInGe\(_2\)O\(_7\)-Dy\(^{3+}\) phosphors. Fig. 4a shows the emission spectrum (\( \lambda_{ex} = 349 \) nm) of YInGe\(_2\)O\(_7\) doped with different concentrations of Dy\(^{3+}\) ions calcined at 1300 °C for 10 h in air. In YInGe\(_2\)O\(_7\)/Dy\(^{3+}\), different concentrations of Dy\(^{3+}\) ions did not change the shape of the curves, but did change the intensities of the emission spectra. In Fig. 4a, the emission spectrum exhibited a weak group of emission peak at 453 nm corresponding to the \( ^{4}M_{21/2} \rightarrow ^{6}H_{13/2} + ^{4}K_{17/2} \) and \( ^{4}F_{7/2} \rightarrow ^{6}H_{13/2} \) transitions, and two groups of strong peak at 484 nm and 574 nm due to the \( ^{4}F_{9/2} \rightarrow ^{6}H_{15/2} \) and \( ^{4}F_{9/2} \rightarrow ^{6}H_{13/2} \) transitions of the Dy\(^{3+}\) ions, respectively. These groups of peak are dominated by the \( ^{4}F_{9/2} \rightarrow ^{6}H_{13/2} \) hypersensitive transition (\( \Delta J = 2 \)) of Dy\(^{3+}\) ions, which is strongly influenced by the

outside environment [15,23]. In all of the emission peaks, the \( ^{4}F_{9/2} \rightarrow ^{6}H_{15/2} \) transition is the magnetic dipole transition, and it hardly varies with the crystal field strength around the dysprosium ion. Additionally, the strongest \( ^{4}F_{9/2} \rightarrow ^{6}H_{13/2} \) transition belongs to the forced electric dipole transition, which is occurs only with a low symmetry lattice with no inversion center. The emission ratios of the \( ^{4}F_{9/2} \rightarrow ^{6}H_{15/2} \) transition and \( ^{4}F_{9/2} \rightarrow ^{6}H_{13/2} \) transition can be used as a measurement of the site symmetry in which the dysprosium is situated. When the Dy\(^{3+}\) ion is located at low-symmetry local sites with no inversion center, the \( ^{4}F_{9/2} \rightarrow ^{6}H_{13/2} \) emission transition is often prominent in its emission spectra [15]. From the results in Fig. 4a, the intensities of \( ^{4}F_{9/2} \rightarrow ^{6}H_{13/2} \) transition are higher than that of \( ^{4}F_{9/2} \rightarrow ^{6}H_{15/2} \) transition which indicates that the Dy\(^{3+}\) ion is located at low-symmetry local sites with no inversion center in YInGe\(_2\)O\(_7\)-Dy\(^{3+}\) phosphors. Fig. 4b shows the relationships between the intensity of the emission peak (\( ^{4}F_{9/2} \rightarrow ^{6}H_{13/2} \)) and concentration of Dy\(^{3+}\) ions. It can be observed that the emission intensities increase with increasing Dy\(^{3+}\) ion concentrations, reaching the maximum value at 10 mol%, and then decreasing with increased Dy\(^{3+}\) ion concentrations. This is because of the concentration quenching effect in rare earth-doped systems due to the Dy\(^{3+}\)–Dy\(^{3+}\) mutual interactions [15–16,22].

3.5. Decay curve and decay time

Fig. 5 shows the decay curve and decay time of YInGe\(_2\)O\(_7\) doped with different Dy\(^{3+}\) ion concentrations under an excitation of 349 nm with signals detected at 574 nm. Different concentrations of Dy\(^{3+}\) ion doping did not obviously change the decay behavior, and all of the decay curves were attributed to a single exponential behavior, indicating that there is only a single decay mechanism [25]. The concentration quenching effect occurred when Dy\(^{3+}\) concentrations were above 10 mol%, and the decay time obviously decreased with increasing Dy\(^{3+}\) concentration (1 mol%: 0.535 ms, 5 mol%: 0.506 ms, 10 mol%: 0.428 ms, 20 mol%: 0.417 ms, 30 mol%: 0.381 ms, 40 mol%: 0.374 ms). This was caused by the effect of energy exchange between the Dy\(^{3+}\) ions as the distance between them decreased with increasing Dy\(^{3+}\) ion concentrations, enhanc-
ing the energy depletion rate and causing the decay time to decrease.

Fig. 6 shows the CIE chromaticity diagram for YInGe$_2$O$_7$:10 mol% Dy$^{3+}$ phosphors. The color coordinates of the emission were $x = 0.3031$ and $y = 0.3251$, which is located in the near-white light region.

4. Conclusions

A novel near-white light emitting phosphor, Dy$^{3+}$-doped YInGe$_2$O$_7$, was synthesized and its luminescence properties were investigated. The XRD patterns show that all of the peaks can be attributed to the monoclinic YInGe$_2$O$_7$ crystal structure when the Dy$^{3+}$ ion concentration is increased up to 40 mol%, and indicating that Y$^{3+}$ ions are well substituted by Dy$^{3+}$ ions to form stable solid solutions. The crystallinity decreased markedly as the Dy$^{3+}$ concentration increased, due to the lattice distortion when the Dy$^{3+}$ ions entered the YInGe$_2$O$_7$ crystal. Under ultraviolet (349 nm) excitation, a weak group of emission peaks were observed for the $^4M_{21/2} ightarrow ^6H_{13/2} + ^4K_{17/2} + ^4F_{7/2}$ transition at 453 nm, and two groups of strong emission peaks were seen at 484 nm and 574 nm, corresponding to the $^4F_{9/2} ightarrow ^6H_{15/2}$ and $^4F_{9/2} ightarrow ^6H_{13/2}$ transitions of Dy$^{3+}$ ions, respectively. The concentration quenching effect occurs when Dy$^{3+}$ ions rose above 10 mol% with a CIE color coordinate of $x = 0.3031$ and $y = 0.3251$, which is located in the near-white light region. The decay curve results indicate that the decay mechanism of the $^4F_{9/2} ightarrow ^6H_{13/2}$ transition is a single decay component between Dy$^{3+}$ ions only.

Acknowledgements

The authors would like to thank the National Science Council of the Republic of China for financially supporting this research under Contract No. (NSC96-2622-E-150-034-CC3).

References


Fig. 6. The CIE chromaticity diagram for YInGe$_2$O$_7$:Dy$^{3+}$ phosphors.