Host Sensitized White Luminescence from ZnGa2O4:Dy3+ Phosphor

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Dysprosium-doped zinc gallate phosphors with the nominal formulas ZnGa2(1-x)Dy2O4, were prepared by the high-temperature conventional solid-state reaction technique, the dopant concentration being varied in the range 0 ≤ x ≤ 0.025. ZnGa1.98O3:Dy0.02, and Ga2O3:Dy2O3 samples were also prepared for comparison for a dopant concentration of x = 0.02. Only the intrinsic self-activated emission of the ZnGa2O4 host is observed in the photoluminescence emission spectra of ZnGa2O4:Dy0.02, while both the host emission band and characteristic emission lines (F4G2 → H4H3) of Dy3+ are observed for ZnGa2(1-x)O3:Dy2x, and Ga2O3:Dy2O3 phosphors. The luminescent intensity differs in the phosphors due to the different energy-transfer rates from the respective hosts to the luminescent centers. Photoluminescent studies reveal the fact that Dy3+ ions replace Ga3+ ions in the host lattice at their octahedral sites. The source of white luminescence in the doped samples is the nonradiative resonant energy transfer via exchange interaction between the host and the activator. The CIE coordinates of the 2.5 atom % Dy3+-doped sample (0.32, 0.33) matches well with achromatic white (0.33, 0.33) on the chromaticity diagram.

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A major challenge in the area of flat panel display (FPD) technology is the identification of new multicolor or white-light-emitting phosphor materials for application in electroluminescent displays (ELDs), plasma display panels (PDPs), and field emission displays (FEDs). A suitable blend of currently available efficient blue, green, and red phosphors and light-emitting diodes (LEDs) gives a natural remedy to this issue.12 Co-doping in a single host lattice also gives desirable results3,4 with better luminous efficiency than the former. But a more feasible approach is via the combination of multicolor emissions from a single luminescence center. Rare-earth (RE) ions serve as excellent activators in modern lighting and display fields due to their characteristic emissions from 4f-4f or 5d-4f transitions. These emissions can be excited using the common fluorescent lamps that have a strong VUV to UV range and making it an ideal material for optoelectronic devices including FPDs, solar energy conversion devices, optical limiter for UV, and high-temperature stable gas sensors.13 Moreover, undoped ZnGa2O4 gives a strong blue luminescence attributed to a transition via a self-activated center under UV or low-voltage electron excitation.

Here, the effects of doping Dy3+ in ZnGa2O4 are investigated.

Experimental

Dysprosium-doped ZnGa2O4 powder phosphors were prepared by mixing the starting materials, namely ZnO (99.99%, Alfa Aesar), Ga2O3 (99.99%, Alfa Aesar), and Dy2O3 (99.99%, Indian Rare Earths, Ltd.), stoichiometrically in ethanol medium followed by calcination at 1350°C for 12 h. The doping concentration of Dy3+ was varied in the range of 0.25–2.5 atom %. For comparison, Zn1–xGa2O3:Dy1 (x = 0, 0.02, i.e., pure and 2 atom % doped sample where Dy3+ replaces Zn2+) and Ga1–xO3:Dy2x (x = 0.02, i.e., 2 atom % doped sample) phosphors were prepared. The crystal structure of the powder phosphors was analyzed using X-ray powder diffraction (XRD) method on a Rigaku diffractometer using Cu Kα radiation (1.5414 Å). The diffuse reflectance spectra (DRS) were recorded to analyze the bandgap using a Jasco V-570 spectrophotometer with an integrating sphere attachment. The reference used was BaSO4. The room-temperature photoluminescence emission (PL) and excitation (PLE) spectra were recorded using Spex Fluoromax-3 Spectrofluorimeter equipped with a 150 W xenon lamp as the excitation source.

Results and Discussion

The XRD patterns of ZnGa2(1−x)O3:Dy2x, matched well with the standard reflections of host ZnGa2O4 for all dopant concentrations. No peaks of the used raw materials or other allotropes forms are detected. The absence of any secondary phase indicates that the samples have crystallized in the spinel structure similar to that of the host and that the dopant ions have been successfully dissolved into the host lattice. Figure 1 shows the XRD patterns of ZnGa1.98O3:Dy0.02, ZnGa1.96O3:Dy0.02, and Ga2O3:Dy2O3. Each of them closely resembles the respective host reflections. JCPDS data of the normal spinel ZnGa2O4 (card no. 38-1240) and monoclinic Ga2O3 (card no. 87-1901) is given for reference.

The DRS of the 2.5 atom % Dy3+-doped sample is shown in Fig. 2. The bandgap of the sample was determined to be 4.45 eV from the (k/s) vs hv curves (inset of Fig. 2) obtained from diffuse reflectance measurements. The values of all the doped samples fall in the range 4.48 ± 0.05 eV for ZnGa2(1−x)O3:Dy2x, which is close to the reported value of 4.55 eV for pure ZnGa2O4.18

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Figure 3 shows the PL emission spectra of pure ZnGa\textsubscript{2}O\textsubscript{4} and 2.5 atom % Dy\textsuperscript{3+}-doped samples for an excitation wavelength of 270 nm. The undoped sample shows a strong broad blue luminescence with a peak at 439 nm resulting from the self-activated transition of regular O\textsubscript{h}Ga–O groups.\textsuperscript{19} The emission spectrum of the Dy\textsuperscript{3+}-doped sample exhibits both the emission band of the host extending from UV to blue and the characteristic fluorescence transitions 4F\textsubscript{9/2} $\rightarrow$ 6H\textsubscript{15/2}, 4F\textsubscript{9/2} $\rightarrow$ 6H\textsubscript{13/2}, 4F\textsubscript{9/2} $\rightarrow$ 6H\textsubscript{11/2}, and 4F\textsubscript{9/2} $\rightarrow$ 6H\textsubscript{9/2}, respectively. These emissions correspond to the spectral transitions 4F\textsubscript{9/2} $\rightarrow$ 6H\textsubscript{15/2}, the dominant one being 4F\textsubscript{9/2} $\rightarrow$ 6H\textsubscript{15/2}. The Stark levels of the multiplet manifolds could be well resolved as the crystal field had sufficient strength to lift off the degeneracy of the free-ion states of Dy\textsuperscript{3+} in the lattice.

The integral intensity of the blue emission 4F\textsubscript{9/2} $\rightarrow$ 6H\textsubscript{15/2} is stronger than that of the yellow emission 4F\textsubscript{9/2} $\rightarrow$ 6H\textsubscript{13/2}. This spectral property of Dy\textsuperscript{3+} provides some information on the site occupation of Dy\textsuperscript{3+} in the host lattice. It is well known that the 4F\textsubscript{9/2} $\rightarrow$ 4I\textsubscript{13/2} yellow emission of Dy\textsuperscript{3+} is a hypersensitive transition that is strongly influenced by the crystal-field environment.\textsuperscript{9,20,21} When Dy\textsuperscript{3+} is located at a low-symmetry local site without an inversion symmetry, the yellow emission dominates the PL spectrum. The blue emission 4F\textsubscript{9/2} $\rightarrow$ 4I\textsubscript{13/2} is stronger than the yellow one when Dy\textsuperscript{3+} is located at a high-symmetry local site with inversion symmetry. In the host lattice, Zn\textsuperscript{2+} ions occupy tetrahedral sites (Td point symmetry without inversion center) coordinated by four oxygen atoms and Ga\textsuperscript{3+} ions occupy octahedral sites (Oh point symmetry with inversion-center) coordinated by six oxygen atoms. Because the blue emission dominates in the spectrum of all the samples, one can be sure that Dy\textsuperscript{3+} replaces Ga\textsuperscript{3+} more in the spinel-structured host. Moreover, the ionic radii of Dy\textsuperscript{3+} is 0.0912 nm for six coordination than that for four coordination. Though the ionic radii of Zn\textsuperscript{2+} is 0.074 nm for six coordination, Dy\textsuperscript{3+} ions rarely substitutes at its tetrahedral site due to charge imbalance.

The PLE spectrum (Fig. 4) of the Dy\textsuperscript{3+}-doped sample consists of a strong excitation band extending from 255 to 320 nm with peak maximum at 266 nm and a convolution of several weak lines (at

![Figure 1. XRD patterns of JCPDS data of (a) ZnGa\textsubscript{2}O\textsubscript{4}, (b) ZnGa\textsubscript{1.96}O\textsubscript{4}:Dy\textsubscript{0.04}, and (c) Zn\textsubscript{0.98}Ga\textsubscript{2}O\textsubscript{4}:Dy\textsubscript{0.02} and JCPDS data of (d) Ga\textsubscript{2}O\textsubscript{3}, and (e) Ga\textsubscript{1.96}O\textsubscript{4}:Dy\textsubscript{0.04}.](image)

![Figure 2. Diffuse reflectance spectra of ZnGa\textsubscript{1.95}O\textsubscript{4}:Dy\textsubscript{0.05} powder. (Inset) Plot of [(k/s)hv\textsuperscript{2}] vs energy.](image)

![Figure 3. PL emission spectra of (a) pure ZnGa\textsubscript{2}O\textsubscript{4} host and (b) 2.5 atom % Dy\textsuperscript{3+}-doped sample, $\lambda_{ex} = 270$ nm.](image)

![Figure 4. PLE spectra of (a) pure ZnGa\textsubscript{2}O\textsubscript{4} host ($\lambda_{em} = 439$ nm) and (b) 2.5 atom % Dy\textsuperscript{3+}-doped sample ($\lambda_{em} = 499$ nm).](image)
365, 399, 420, 425, and 442 nm) in the longer wavelength region. The weak lines positioned between 320 and 445 nm are due to the f-f transitions of Dy$^{3+}$ within its 4f$^9$ ground-state configuration.21 The origin of the strong band can be correlated taking into consideration the excitation of the host. The excitation spectrum of pure ZnGa$_2$O$_4$ is also composed of a strong band ranging from 220 to 320 nm with a maximum at 271 nm whose spectral profile almost matches that of the doped sample. This indicates that the two strong excitation bands have the same origin, i.e., from the host lattice. The emission spectrum of undoped ZnGa$_2$O$_4$ contains a broad band ranging from 325 to 530 nm with peak maxima at 439 nm (blue emission) which is also present in the emission spectrum of the doped sample, but with reduced intensity. These results suggest that an energy transfer has occurred from the host lattice to the Dy$^{3+}$ luminescence center. Here, this emission is not very efficient because a broad band of the host still persists with reduced intensity in the doped sample.

A luminescent material comprising of a sensitizer (S) and an activator (A) can exhibit either a radiative or a nonradiative energy transfer. Radiative transfer of energy is not very efficient in the case of intrashell transitions due to the low magnitude of the oscillator strength for absorption.21 The transfer rate of the nonradiative resonance transfer mechanism depends both on the spectral overlap of the S emission band and the A absorption band and on the interference between the initial and final states of the transfer between the S and the A. This interaction can be either an exchange interaction or an electric multipolar interaction; the transfer rate in either case depends on the distance R between the S and the A. The distance dependence is exponential for exchange interaction and $R^{-6}$ dependence ($n = 6$ for dipole-dipole interactions and 8 for dipole-quadrupole interactions) for electric multipolar interactions. Thus, spectral overlap and distance R significantly affects energy-transfer rate.21

In the present case, there is only a small spectral overlap between ZnGa$_2$O$_4$ emission band (Ga being the sensitizer) and the 4f$^9$ intra-configurational absorption lines of Dy$^{3+}$ (being the activator); the latter are forbidden by parity selection rule. Moreover, the strong absorption band of the activator lies outside the zinc gallate emission band. This makes the energy transfer by electric multipolar interactions less probable. Thus, the dominant energy-transfer mechanism in Dy$^{3+}$-activated ZnGa$_2$O$_4$ is most likely due to exchange interactions. This is more favored the smaller the value of R. For this, Dy$^{3+}$ ions must replace Ga$^{3+}$ at its octahedral site so that the energy of the strong emission band (peak at 439 nm) resulting from the transition of regular $O_6$ Ga–O groups can be efficiently and effectively transferred to the luminescent center Dy$^{3+}$ by nonradiative resonance mechanism mediated by exchange interactions.

A comparison was made between the PL emission spectra of host ZnGa$_2$O$_4$ along with the emission spectra of Zn$_{1-x}$Ga$_x$O$_4$;Dy$_{2x}$, ZnGa$_{2(1-x)}$O$_2$;Dy$_{2x}$, and Ga$_{21(1-x)}$O$_7$;Dy$_{2x}$ prepared under similar synthetic conditions for a doping concentration of 2 atom % (Fig. 5). The emission spectra of Zn$_{0.98}$Ga$_{0.02}$O$_4$;Dy$_{0.02}$ exhibits the UV-to-blue-emission band of the host itself, whereas that of ZnGa$_{0.98}$O$_2$;Dy$_{0.04}$ includes both the emission band of ZnGa$_2$O$_4$ and the characteristic fluorescence transitions $^4F_{9/2}$-$^6H_j$ of the dopant. The blue emission of the Zn$_{0.98}$Ga$_{0.02}$O$_4$;Dy$_{0.02}$ sample is more intense than the host. But the ZnGa$_{0.98}$O$_2$;Dy$_{0.04}$ compound gives weaker ZnGa$_2$O$_4$ emission and strong dysprosium emissions. In the former case, because Dy$^{3+}$ is thought to substitute for Zn$^{2+}$ at its tetrahedral site, the energy transfer via exchange interactions is greatly reduced due to larger S-A distance (R) suppressing Dy$^{3+}$ emissions. In the latter case, Dy$^{3+}$ emission gets enhanced as R is greatly reduced. The PL emission intensity of Ga$_{0.98}$O$_2$;Dy$_{0.04}$ is much stronger than ZnGa$_{2(1-x)}$O$_2$;Dy$_{2x}$, indicating that host sensitization is more effective in the former.

Figure 6 compares the PL emission spectra of the ZnGa$_{2(1-x)}$O$_2$;Dy$_{2x}$ samples with different doping concentrations, all spectra recorded at an excitation wavelength of 270 nm. In the low-dopant-concentration range ($x = 0.0025$ to 0.01), intensive blue-emission band of the host and weaker luminescent transitions of Dy$^{3+}$ activator are observed. The emission maximum occurs for the 1 atom % doped sample, and hereafter it weakens and red-shifts gradually due to larger Zn/Ga ratio.22,23 In the dopant-concentration range ($x = 0.0125$–0.025), the characteristic luminescent transitions of Dy$^{3+}$ activator predominates over the host emission and the intensity ratio $I_{499}$/$I_{399}$, $I_{499}$ and $I_{399}$ correspond to the maxima of $^4F_{9/2}$-$^6H_{15/2}$ and $^4F_{9/2}$-$^6H_{13/2}$ fluorescent transitions of Dy$^{3+}$ such that a luminescent emission that appears white to the human eye is observed. The variation of the host and the activator emissions with doping concentration is shown in the inset of Fig. 6. It is quite evident that the host emission intensity falls below the activator emission intensity for all dopant concentrations above 1 atom %, indicative of host-sensitized luminescence.

For some suitable blue-to-yellow intensity ratio $I_{499}$/$I_{589}$, Dy$^{3+}$ emits white light. The intensity ratio $I_{499}$/$I_{589}$ plotted in Fig. 6 reveals that when the ratio falls in between 1 and 1.5, the samples exhibit white luminescence, and this has been observed in the case of all Dy$^{3+}$-doped samples for dopant concentration above
samples lie in between that of the ZnGa2O4 host 1.5 for low dopant concentrations yellow intensity ratio blue PL intensity at 441 nm CIE chromaticity diagram of the ZnGa2 host 1 atom %. This observation also supports the fact that Dy3+ substitutes the element with the same valency2 in the host. The inset shows that the intensity ratio I441/I589 (I441 corresponds to the host blue PL intensity at 441 nm) falls below 1 for all samples above x = 0.01, i.e., the whiteness is due to the simultaneous blue and yellow emissions of Dy3+ itself. Both the intensity ratios lie above 1.5 for low dopant concentrations (x = 0.0025–0.01) and these samples are found to exhibit bluish luminescence. The blue-to-yellow intensity ratio I441/I589 of Ga1.96O3:Dy0.04 which also gave white luminescence, was found to be 1.05.

The PL emissions of the samples were gauged employing the CIE coordinates (Fig. 8). The CIE coordinates of the Dy3+-doped samples lie in between that of the ZnGa2O4 host (x = 0.13, y = 0.16) and that for achromatic white (x = 0.33, y = 0.33). The 2.5 atom % Dy3+-doped sample shows the best white emission; its CIE coordinates were calculated to be x = 0.32 and y = 0.33 and it lies just to the left of achromatic white in the chromaticity diagram. The Ga1.96O3:Dy0.04 sample prepared for comparison also gave a white emission and has a higher intensity than the Dy3+-doped ZnGa2O4 sample, but the CIE coordinates were calculated to be x = 0.27, y = 0.27. That is, the white emission of Ga1.96O3:Dy0.04 phosphor is much inferior to that of ZnGa1.96O3:Dy0.05 phosphor.

Conclusion

ZnGa2(1-x)Ox: Dy2 phosphors were prepared by conventional solid-state reaction technique. The doped samples exhibit the normal spinel-phase development as the host. PL studies reveal the fact that Dy3+ ions replace Ga3+ ions in the host lattice at their octahedral sites. The source of the white emission in the doped samples is the nonradiative resonant energy transfer via exchange interaction between the host and the activator. The poor spectral overlap accounts for the reduced PL emission intensity of the doped samples. The best white emission is obtained for the sample with a dopant concentration of 2.5 atom % whose CIE coordinates are found to be (x, y) = (0.32, 0.33). The present investigation highlights the possibility of Dy3+-doped ZnGa2O4 as an active layer in alternating current thin film electroluminescent (ACTFEL) devices.

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References