



Host-Sensitized Luminescence of Dy³⁺ in Nanocrystalline β -Ga₂O₃ Prepared by a Pechini-Type Sol-Gel Process

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Nanocrystalline undoped β -Ga₂O₃ and Dy³⁺-doped β -Ga₂O₃ were prepared through a Pechini-type sol-gel process. All the samples began to crystallize at 600°C, and the crystallinity increased with the increase of annealing temperatures until 1000°C. Field emission-scanning electron microscopy study revealed that the β -Ga₂O₃:Dy³⁺ sample is composed of aggregated particles with sizes ranging from 40 to 80 nm and spherical morphology. Undoped β -Ga₂O₃ sample shows a strong blue emission peaking at 438 nm. The Dy³⁺, mainly occupied the octahedral Ga³⁺ sites in β -Ga₂O₃, shows its characteristic emissions in the blue 460-505 nm (⁴F_{9/2}-⁶H_{15/2}) and yellow 570-600 nm (⁴F_{9/2}-⁶H_{13/2}) regions due to an efficient energy transfer from the β -Ga₂O₃ host lattices. The optimum concentration for the luminescence Dy³⁺ is determined to be 2 atom % of Ga³⁺ in Ga₂O₃ host. © 2004 The Electrochemical Society. [DOI: 10.1149/1.1847674] All rights reserved.

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Rare earth ions have been playing an important role in modern lighting and display fields due to the abundant emission colors based on their 4f-4f or 5d-4f transitions.¹ In order to be excited efficiently, phosphors activated with rare earth ions should have a strong and broad absorption band in the UV or VUV region depending on the practical application situation. For example, the tricolor fluorescent lamp phosphors have a strong and broad absorption band around 254 nm (UV) to meet the irradiation from the discharge of low-pressure mercury vapor.^{1,2}

The luminescence of trivalent dysprosium Dy³⁺ mainly consists of narrow lines in the blue (470-500 nm, ⁴F_{9/2}-⁶H_{15/2}) and yellow (⁴F_{9/2}-⁶H_{13/2}, 570-600 nm) wavelength region. The latter one belongs to the hypersensitive transition ($\Delta L = 2$, $\Delta J = 2$), which is strongly influenced by the environment.³ At a suitable yellow-to-blue intensity ratio, Dy³⁺ will emit white light. Thus luminescent materials doped with Dy³⁺ may be used as potential two-band phosphors.^{4,5} However, unlike the most frequently used Eu³⁺ and Tb³⁺ (in oxide hosts), which have allowed charge-transfer absorption band (CTB) or 4f⁸-4f⁷5d absorption band in the UV region, respectively, the excitation spectrum of Dy³⁺ consists of only narrow f-f transition lines from 300 to 500 nm (both the CTB and 4f⁹-4f⁸5d excitation band of Dy³⁺ are located below 200 nm⁶). As a result, the luminescence of Dy³⁺ cannot be excited with 254 nm UV light, and the excitation can occur only by the f-f transitions with low oscillator strength (10⁻⁶) due to their forbidden features by the parity selection rule.¹ This drawback of Dy³⁺ luminescence can be overcome by sensitization, such as host sensitization in YVO₄:Dy³⁺ and ion sensitization in Ca₂Gd₈(SiO₄)₆O₂:Pb²⁺, Dy³⁺.⁷

β -Ga₂O₃ is a wide bandgap semiconductor compound with an optical bandgap (E_g) of about 4.8 eV,⁸ which has long been known to show both conduction and luminescence properties with and without doping foreign impurities.⁹⁻¹³ Recently, much attention has been paid to the preparation of nanostructured β -Ga₂O₃ with different morphology, such as nanowires,¹⁴ nanoribbons,¹⁵ and nanobelts.¹⁶ β -Ga₂O₃ has also been used as a phosphor host material for application in thin-film electroluminescence (TFEL)¹⁷⁻¹⁹ and cathodoluminescence (CL) displays.²⁰ In this paper, we report host-sensitized luminescence of Dy³⁺ in nanocrystalline β -Ga₂O₃ prepared by a Pechini-type sol-gel process.

Experimental

Nanocrystalline undoped β -Ga₂O₃ and Dy³⁺-doped β -Ga₂O₃ samples were prepared through a Pechini-type sol-gel process by using β -Ga₂O₃ [content \geq 99.99%, impurities: Σ (Cu, Pb, Zn) \leq 1.0 ppm; Σ (Al, In, Ca) \leq 0.7 ppm; Σ (Fe, Sn, Ni) \leq 2.5 ppm; Σ (Si, Hg, Mg) \leq 1.5 ppm, Shanghai Shiyi Chemicals Reagent Co., Limited] and Dy₂O₃ (content \geq 99.9%, Shanghai Yuelong Nonferrous Metals Co., Limited) as the starting materials. The doping concentration of Dy³⁺ is 1.0-3.5 atom % of Ga³⁺ in β -Ga₂O₃. The stoichiometric amounts of the starting materials β -Ga₂O₃ and Dy₂O₃ were dissolved in diluted hydrochloric acid (HCl) under stirring and heating. Then citric acid and polyethylene glycol (PEG, molecular weight = 10,000) were dissolved in the above solution ($C_{\text{PEG}} = 0.01$ M, citric acid/metal ion = 2:1 in per mole). The resultant mixture was stirred at 75°C for 8 h. After concentrating the solution by slow evaporation, a slightly yellow transparent sol was obtained. Such sol was dried in an oven at 110°C overnight, leading to the formation of a yellow gel. The gel was preheated at 500°C for 4 h in air. After an intermediate grinding, the powder was sintered at various temperatures from 600 to 1000°C in air.

Phase development in the postannealed powder samples was checked by X-ray diffraction (XRD) on a Rigaku, D/max-IIB 2500 diffractometer using Cu K α radiation (0.15405 nm). The morphology of the samples was inspected using field emission scanning electron microscope (FE-SEM, XL30, Philips). The excitation and emission spectra were taken on a F-4500 spectrofluorimeter equipped with a 150 W xenon lamp as the excitation source. Luminescence decay curves were obtained from a Lecroy Wave Runner 6100 digital oscilloscope (1 GHz) using 254 nm laser (pulse width = 4 ns) as the excitation source (Continuum Sunlite, OPO). All the measurements were performed at room temperature.

Results and Discussion

The results of XRD indicate that the sample remained amorphous after a 500°C heat-treatment, began to crystallize at 600°C, and the crystallinity increased with raising the annealing temperature to 1000°C. Representative XRD patterns of the undoped (a) and Dy³⁺-doped (b) samples annealed at 1000°C as well as that for the standard β -Ga₂O₃ (c, JCPDS card no. 11-370) are shown in Fig. 1. As seen clearly in Fig. 1, all the diffraction peaks of the undoped and Dy³⁺-doped samples can be assigned exactly to the standard data of β -Ga₂O₃. No second phase was detected, indicating that the Dy³⁺ ions have been successfully dissolved in the β -Ga₂O₃ host lattices by substitution for the Ga³⁺. β -Ga₂O₃ belongs to monoclinic crystal system with a space group of $C2/m$, and there are four

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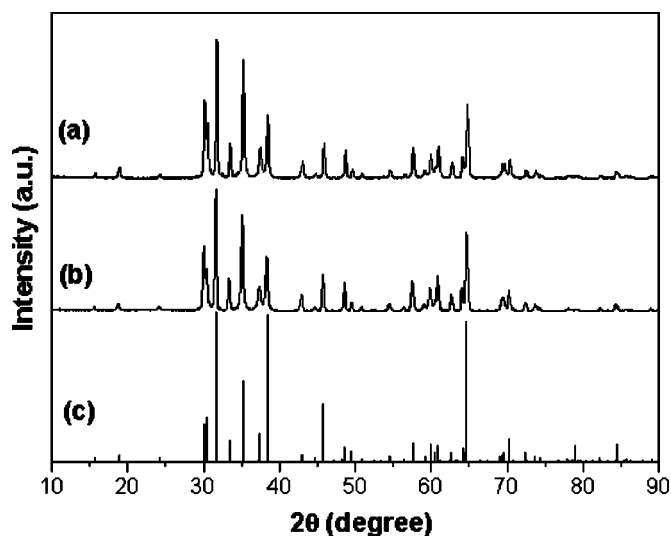


Figure 1. The XRD patterns for undoped (a) and 1.5 atom % Dy^{3+} -doped (b) $\beta\text{-Ga}_2\text{O}_3$ annealed at 1000°C as well as that for the standard $\beta\text{-Ga}_2\text{O}_3$ [(c) JCPDS Card no. 11-370].

Ga_2O_3 formulas in unit cell ($Z = 4$). The calculated lattice constants $a = 1.213$ nm, $b = 0.304$ nm, $c = 0.580$ nm, $\beta = 103.6^\circ$ for $\beta\text{-Ga}_2\text{O}_3:\text{Dy}^{3+}$ sample are in good agreement with the reported values ($a = 1.223$ nm, $b = 0.304$ nm, $c = 0.580$ nm, $\beta = 103.7^\circ$) of $\beta\text{-Ga}_2\text{O}_3$. No obvious change is observed for the lattice constants due to the low doping concentration (1.5 atom % of Ga^{3+}) of Dy^{3+} in $\beta\text{-Ga}_2\text{O}_3$.

In general, the nanocrystallite size can be estimated from the Scherrer equation, $D = 0.941\lambda/\beta \cos \theta$, where D is the average grain size, λ is the X-ray wavelength (0.15405 nm), θ and β are the diffraction angle and full-width at half-maximum (fwhm) of an observed peak, respectively.²¹ The strongest peak (200) at $2\theta = 31.62^\circ$ was used to calculate the average crystallite size (D) of $\beta\text{-Ga}_2\text{O}_3:\text{Dy}^{3+}$ sample annealed at 1000°C , which yields a value about 38 nm. Figure 2 shows the FE-SEM micrograph of $\beta\text{-Ga}_2\text{O}_3:\text{Dy}^{3+}$ sample annealed at 1000°C . It is seen clearly that the $\beta\text{-Ga}_2\text{O}_3:\text{Dy}^{3+}$ sample is composed of aggregated particles with sizes ranging from 40–80 nm and spherical morphology. The average grain sizes estimated from the Scherrer equation are smaller than those determined from the FE-SEM micrograph. This is not

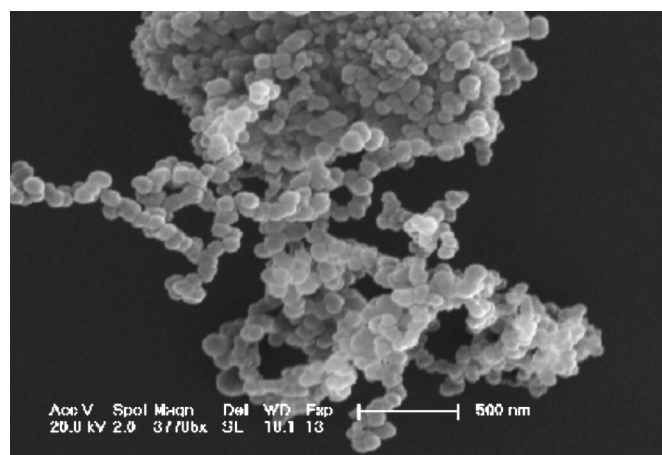


Figure 2. FE-SEM micrograph for 1.5 atom % Dy^{3+} -doped $\beta\text{-Ga}_2\text{O}_3$ annealed at 1000°C .

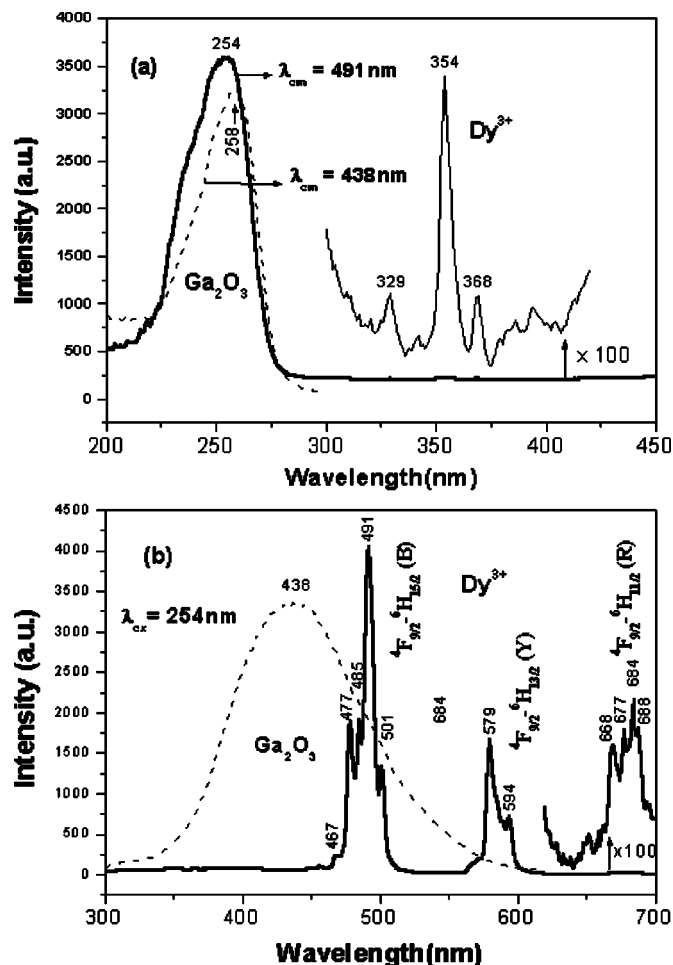


Figure 3. Excitation (a) and emission (b) spectra of 1.5 atom % Dy^{3+} -doped $\beta\text{-Ga}_2\text{O}_3$ (black solid line) and undoped $\beta\text{-Ga}_2\text{O}_3$ (dash line) annealed at 1000°C .

surprising because smaller nanograins contribute more to the broadening of the diffraction peaks as reported previously.²¹

Under 254 nm UV excitation, the nanocrystalline $\beta\text{-Ga}_2\text{O}_3:\text{Dy}^{3+}$ sample shows a strong blue luminescence. Figure 3b shows emission spectrum of $\beta\text{-Ga}_2\text{O}_3:\text{Dy}^{3+}$, which is dominated by two main groups of lines in the blue region 460–505 nm (B) and yellow region 570–600 nm (Y) accompanied by a group of weak lines in the red region from 650 to 700 nm (R, seen 100 times magnification). These emissions correspond to the transitions from $^4\text{F}_{9/2}$ to $^6\text{H}_{15/2}$, $^6\text{H}_{13/2}$, and $^6\text{H}_{11/2}$ of Dy^{3+} , respectively.³⁻⁵ The crystal splitting components of Dy^{3+} emission can be observed, but not totally resolved due to the weak experimental resolution. Note that the integrated intensity of the blue emission ($^4\text{F}_{9/2}-^6\text{H}_{15/2}$) is stronger than that of the yellow emission ($^4\text{F}_{9/2}-^6\text{H}_{13/2}$) for Dy^{3+} in the nanocrystalline $\beta\text{-Ga}_2\text{O}_3$. This spectral property of Dy^{3+} provides some information on the site occupation of Dy^{3+} in $\beta\text{-Ga}_2\text{O}_3$ host lattices. It is well known that like the $^5\text{D}_0-^7\text{F}_2$ red emission of Eu^{3+} , the $^4\text{F}_{9/2}-^6\text{H}_{13/2}$ yellow emission of Dy^{3+} belongs to hypersensitive transitions with $\Delta J = 2$, which is strongly influenced by the outside surroundings.^{3,4} When Dy^{3+} is located at a low symmetry local site (without inversion symmetry center), this emission is often dominated in the emission spectrum; on the other hand, when Dy^{3+} at a high symmetry local site (with inversion symmetry center), its $^4\text{F}_{9/2}-^6\text{H}_{15/2}$ blue emission will be stronger than the yellow one ($^4\text{F}_{9/2}-^6\text{H}_{13/2}$) and dominated in the emission spectrum.^{1,3,4} The latter case occurs for Dy^{3+} in $\beta\text{-Ga}_2\text{O}_3$ and can be explained accord-

ing to the crystal structure of β -Ga₂O₃. The monoclinic β -Ga₂O₃ contains two kinds of Ga³⁺ ions within equal quantity, one in tetrahedral site (T_d point symmetry, without inversion center) coordinated by four oxygen atoms, the other in octahedral site (O_h point symmetry, with an inversion center) coordinated by six oxygen atoms.²² The spectral property of Dy³⁺ indicates that the Dy³⁺ ions mainly occupy the octahedral Ga³⁺ sites in β -Ga₂O₃ host lattices. In fact, the octahedral Ga³⁺ sites would be more suitable for Dy³⁺ than the tetrahedral Ga³⁺ sites. Considering the ionic radii, $r(\text{Dy}^{3+}) = 0.0912$ nm for six coordination, $r(\text{Ga}^{3+}) = 0.062$ nm for six coordination and 0.047 nm for four coordination respectively,²³ it is easier for Dy³⁺ to replace the octahedral Ga³⁺ than the tetrahedral Ga³⁺ in β -Ga₂O₃ host lattices. Few compounds contain four-oxygen coordinated Dy³⁺ in nature.

The excitation spectrum of Dy³⁺ in nanocrystalline β -Ga₂O₃ is exhibited in Fig. 3a, which consists of a strong excitation band from 200 to 275 nm with a maximum at 254 nm and some weak lines (329, 354, 368 nm, only seen clearly by 100 times magnification) in the longer wavelength region. Clearly, the latter is due to the f-f transitions (329 nm: ⁶H_{15/2}-⁶P_{3/2}; 354 nm: ⁶H_{15/2}-⁶P_{7/2}; 368 nm: ⁶H_{15/2}-⁶P_{5/2}) of Dy³⁺ within its 4f⁹ configuration. In order to identify the origin of the former (strong excitation band at 254 nm), the excitation and emission spectra of undoped nanocrystalline β -Ga₂O₃ were measured and shown as dashed lines in Fig. 3a, b, respectively. The excitation spectrum of undoped nanocrystalline β -Ga₂O₃ is also composed of a strong band ranging from 200 to 275 nm with a maximum at 258 nm, whose profile is very similar to the strong UV excitation band of the β -Ga₂O₃:Dy³⁺. This indicates that the two strong excitation bands have the same origin, *i.e.*, both from the β -Ga₂O₃ host lattices. On the other hand, the emission spectrum of undoped nanocrystalline β -Ga₂O₃ contains a broad band ranging from 350 to 600 nm with a maximum at 438 nm (blue emission), which is absent in the emission spectrum of β -Ga₂O₃:Dy³⁺ under excitation into the UV band at 254 nm. These results suggest that an energy transfer has occurred from β -Ga₂O₃ host lattices to the doped Dy³⁺ in β -Ga₂O₃. Moreover, such energy transfer is very efficient (close to 100%) because no emission from β -Ga₂O₃ host lattices is detected in β -Ga₂O₃:Dy³⁺, *i.e.*, an efficient host-sensitized luminescence of Dy³⁺ occurs in the nanocrystalline β -Ga₂O₃, just like YVO₄:Dy³⁺ reported previously.³

The photoluminescence from β -Ga₂O₃ host lattices has been reported both in polycrystalline powder^{9,10} and single-crystal forms.^{11,12} Briefly, the blue emission can be attributed to the recombination of an electron on a donor formed by oxygen vacancies with a hole on an acceptor consisting of either gallium vacancies or gallium-oxygen vacancy pairs.¹² These vacancies would be produced by the impurities in the starting material (it should be kept in mind that undoped Ga₂O₃ contains impurities in the ppm range, as stated in the Experimental section). A simple model illustrating the blue emission process in β -Ga₂O₃ and the energy transfer to Dy³⁺ is shown in Fig. 4. Under the excitation of 254 nm irradiation (band-gap excitation), an electron (●) is excited from the valence band (VB) to the conduction band (CB). The electron (●) moves freely around the CB, finally relaxes to the donor band (oxygen vacancies). The recombination of the electron in the donor band with the acceptor (gallium vacancies or gallium-oxygen vacancy pairs) yields a blue emission with a maximum wavelength at 438 nm (Fig. 4, left). When Dy³⁺ is present in β -Ga₂O₃ host lattices, the excitation energy can be nonradiatively transferred to Dy³⁺, resulting in its characteristic emission, as shown in Fig. 4 (right). The blue emission of β -Ga₂O₃ host lattices has been quenched when a low concentration of Dy³⁺ (1.5 atom % of Ga³⁺) was introduced, indicating that an energy migration has occurred in β -Ga₂O₃ host lattices. This can be further proved by the kinetics study for the luminescence of β -Ga₂O₃ and β -Ga₂O₃:Dy³⁺.

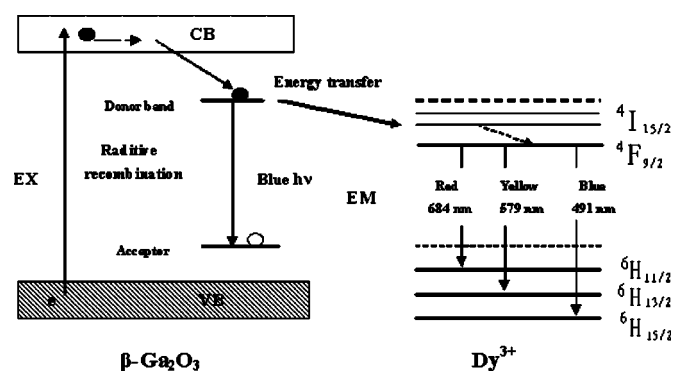


Figure 4. A simple model illustrating the blue emission process in β -Ga₂O₃ and the energy transfer to Dy³⁺.

The luminescence decay curves for undoped β -Ga₂O₃ and β -Ga₂O₃:Dy³⁺ are shown in Fig. 5a-c, respectively. For undoped β -Ga₂O₃, the decay curve (Fig. 5a) is complicated, *i.e.*, the luminescence first shows a rise from $t = 0$ to $t = 14$ ns followed a decay from $t = 14$ ns to $t = 21$ ns, again a rise from $t = 21$ ns to $t = 28$ ns, then decays exponentially. This kind of decay behavior indicates that there exists an energy migration process after excitation in undoped β -Ga₂O₃. The main decay is very fast: the time from the maximum intensity I_m ($t = 28$ ns) to its 1/e intensity $I_{1/e}$ (I_m/e , e is the irrational number 2.71828...) is 32 ns. The energy migration can occur either by diffusion of free holes or diffusion of self-trapped holes, and can also be observed in β -Ga₂O₃:Dy³⁺ sample. The luminescence (491 nm) decay curves of Dy³⁺ in β -Ga₂O₃ contain short component (Fig. 5b) and long component (Fig. 5c). The decay behavior of the short component (Fig. 5b) is similar to that of β -Ga₂O₃ host lattices in Fig. 5a. Note that the β -Ga₂O₃ host lattices also show emission at 491 nm with moderate intensity (Fig. 3b). So this short decay component must be due to the β -Ga₂O₃ host lattices. However, for β -Ga₂O₃:Dy³⁺ in Fig. 5b, the time from the maximum intensity I_m ($t = 28$ ns) to its 1/e intensity $I_{1/e}$ is 19 ns, a value shorter than that (32 ns) of undoped β -Ga₂O₃. This is because the excitation energy has transferred to an additional emission center (Dy³⁺) in β -Ga₂O₃:Dy³⁺. The long component (Fig. 5c) can be fitted by a second exponential function as $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where τ_1 and τ_2 are the fast and slow components of the luminescent lifetimes, A_1 and A_2 are the fitting parameters, respectively. The fitting results in Fig. 5c are $A_1 = 0.0064$, $\tau_1 = 0.613$ ms, $A_2 = 0.0039$, $\tau_2 = 5.62$ ms. It is assumed that the fast component τ_1 (0.613 ms) is mainly from the Dy³⁺ itself, and the slow component τ_2 (5.62 ms) is from an unknown emission center which coincides with the emission of Dy³⁺ in β -Ga₂O₃ host lattices. At this stage this emission center cannot be identified clearly.

By varying the content of Dy³⁺ ion in Ga₂O₃ samples, we determined the compositions with the highest emission intensity. Figure 6 shows the dependence of the emission intensity of Dy³⁺ (⁴F_{9/2}-⁶H_{15/2}) on its doping concentration (x) in Ga_{2(1-x)}Dy_{2x}O₃ samples. It can be found from Fig. 6 that the emission intensity of Dy³⁺ increases with the increase of their concentrations (x) first, reaching a maximum value at $x = 2$ mol %, and then decreases with increasing its content (x) due to the concentration quenching. Thus the optimum concentrations for Dy³⁺ is 2 mol % of Ga³⁺ in the Ga₂O₃ host. The concentration quenching of Dy³⁺ luminescence is mainly caused by cross relaxation, *i.e.*, energy transfer from one Dy³⁺ to another by transition that are matched in energy.³ These transitions are mainly Dy³⁺(⁴F_{9/2}) + Dy³⁺(⁶H_{15/2}) → Dy³⁺(⁶F_{3/2}) + Dy³⁺(⁶F_{11/2}). Because the luminescence quenching is caused by the energy transfer within the same rare

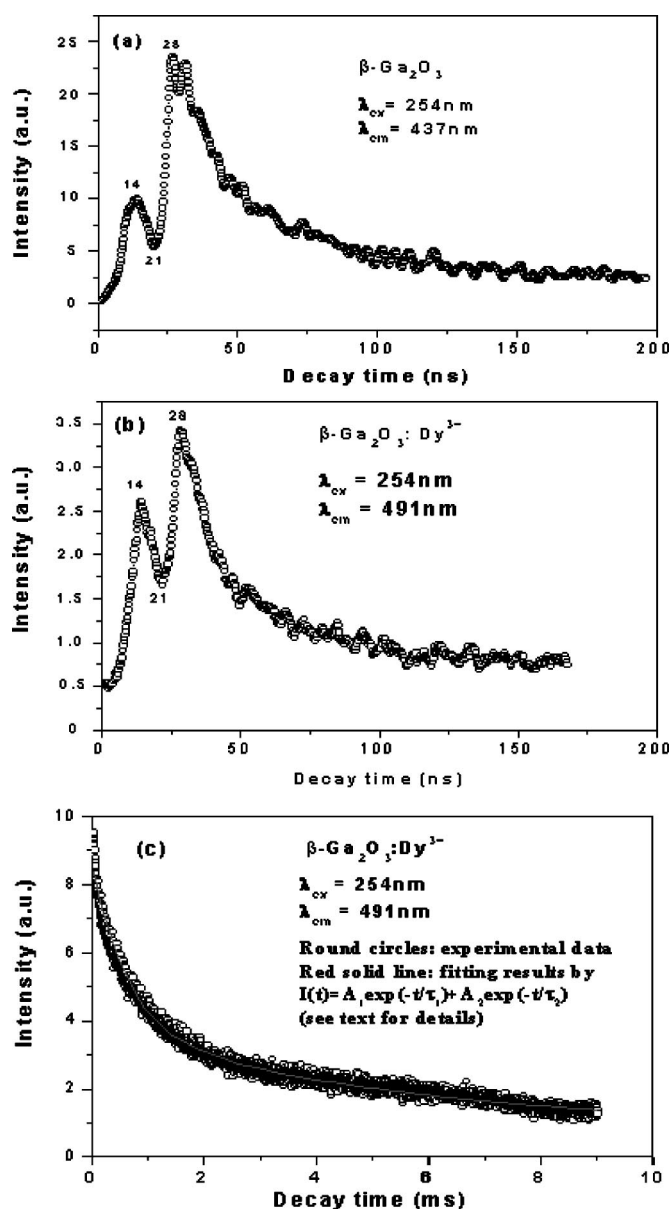


Figure 5. The luminescence decay curves for undoped β -Ga₂O₃ (a) and 1.5 atom % Dy³⁺-doped β -Ga₂O₃ (b,c) annealed at 1000°C.

earth ions, the critical distance (R_C) can be estimated in terms of the equation, $R_C = 2(3V/4\pi NX_C)^{1/3}$ (where V is the volume of the unit cell, X_C is the critical concentration, and N is the number of available crystallographic sites occupied by the activator ions in the unit cell).²⁴ The values of V and N for the crystalline Ga₂O₃ ($Z = 4$, $N = Z \times 2$, $V = abc \sin \beta$) are 0.208 nm³ and 8, respectively. Considering the above optimum concentration as the critical concentration X_C , we obtain $R_C(\text{Dy}^{3+}) = 1.35$ nm in the nanocrystalline Ga₂O₃ host.

Conclusion

Undoped β -Ga₂O₃ and Dy³⁺-doped β -Ga₂O₃ nanocrystalline powders were successfully prepared by a Pechini-type sol-gel process. There exists an efficient energy transfer from the β -Ga₂O₃ host lattices to Dy³⁺ in β -Ga₂O₃:Dy³⁺. The excitation energy first migrates in the host lattices and then is captured by the Dy³⁺, resulting in its characteristic emissions. The emission properties of

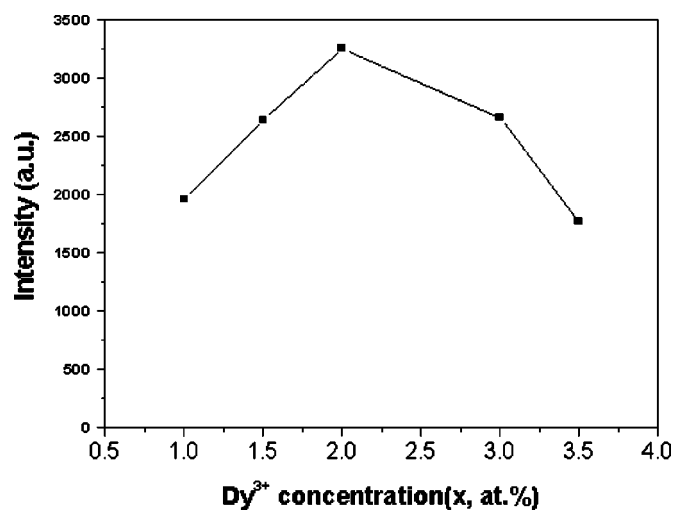


Figure 6. The emission intensity of Dy³⁺ (⁴F_{9/2}-⁶H_{15/2}) as a function of its doping concentration (x) in Ga_{2(1-x)}Dy_{2x}O₃ samples annealed at 1000°C.

Dy³⁺ indicate that the doped Dy³⁺ ions mainly occupy the octahedral coordinated Ga³⁺ sites that possess an inversion symmetry center in β -Ga₂O₃ host lattices. The optimum concentration for the luminescence Dy³⁺ is determined to be 2 atom % of Ga³⁺ in Ga₂O₃ host. The nanocrystalline β -Ga₂O₃:Dy³⁺ is a good photoluminescent material suitable for 254 nm UV excitation.

Acknowledgments

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