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Photoluminescence properties and concentration quenching of Dy^{3+} doped YAG phosphors for domestic lighting

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$Y_3Al_5O_{12}$: xDy^{3+} (x = 0.02, 0.04, 0.06, 0.08, 0.1) phosphors were synthesized by sol-gel method. The strongest excitation peak at 352 nm was attributed to the $^6H_{15/2} \rightarrow {}^6P_{7/2}$ transition of Dy^{3+}. Under the excitation of 352 nm, the emission spectra showed three peaks at about 483 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$), 582 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) and 669 nm ($^4F_{9/2}{}^6 \rightarrow H_{11/2}$), respectively. The critical quenching concentration of Dy^{3+} in YAG : Dy^{3+} phosphors was about 6mol%, which was associated to the cross-relaxation processes. The CIE chromatic coordinate of YAG : $0.02Dy^{3+}$ phosphor was located at (0.385, 0.384) under 352 nm excitation, which was close to the National standard white light chromaticity (0.380, 0.380) for Energy Saving Lamp. Thus, white LED based on an UV LED chip and YAG : Dy phosphor has potential application for domestic lighting.

Key words: $Y_3Al_5O_{12}$: Dy^{3+}, domestic lighting, concentration quenching, luminescence properties.

Introduction

Recently, w-LED (white light-emitting diode) has attracted more and more attention owing to its characteristics of energy saving, high brightness, fast switching, mercury-free, solid-state lighting [1-3]. Commercial w-LEDs are usually fabricated by combining a blue LED chip and yellowish phosphors. So far, $Y_3Al_5O_{12}$: Ce^{3+} (YAG : Ce^{3+}) phosphors have been widely used in lighting field. However, YAG : Ce^{3+} phosphors have some drawbacks of low color-rendering index, poor color reproducibility, and high color temperature due to lack of red emission [4-6]. It is well known that rare earth (RE) ions have abundant energy level structures and superior luminescent properties and may realize different light emission with suitable dopant and its concentration [2]. In addition to the commercial YAG : Ce^{3+} phosphors, YAG:Tb^{3+} and YAG:Eu^{3+} phosphors have been reported to emit green and red light [7-10]. Gd, La, Lu, Sm, Eu co-doped YAG:Ce^{3+} phosphors have also been investigated [11-13]. So far, most of researchers focused on white LED, but few phosphors for domestic lighting were reported.

Recently, G. Seeta Rama Raju et al reported that $Gd_3Al_5O_{12}$: Dy^{3+} phosphors give white light emission due to the three characteristic emission bands of Dy^{3+} ions centered at 483 nm blue, 582 nm yellow and 669 nm red light [14-15]. L.P. Goss et al reported the thermographic application of co-precipitation YAG : Dy^{3+} phosphors as well as the effect of annealing temperature on phosphor structure and grain size[16-18]. In the present work, $Y_3Al_5O_{12}$: xDy^{3+} (x = 0.02, 0.04, 0.06, 0.08, 0.1) phosphors were synthesized by the sol-gel method and the influence of the dopant concentrations on the photoluminescence (PL) spectra was investigated. The dopant concentration was optimized for white light emission and the concentration quenching phenomenon was discussed.

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Experimental

The $Y_{3-x}Dy_xAl_5O_{12}$ (x = 0.02, 0.04, 0.06, 0.08, 0.1) phosphors were synthesized by the sol-gel method. $Y(NO_3)_3 \cdot q6H_2O$, $Al(NO_3)_3 \cdot q9H_2O$, $Dy(NO_3)_3$ and appropriate dosage of citric acid were dissolved in de-ionized water and mixed completely. The mole ratio of citric acid to the total metallic ions was 3 : 1. The PH value of the solution was modulated to 3. Then as-obtained solution turned into viscous sol by slow evaporation in water bath. Such sol was dried in oven at 110 °C for 24 h and preheated for 2 h at 400 °C. Finally, the YAG : Dy^{3+} phosphors were obtained after precursors were calcined at 1100 °C for 4 h.

The phase composition of the obtained phosphors was examined by the powder X-ray diffraction (XRD) analysis using Rigoku X-RAY DIFFRACTOMETER (D/MAX 2000/PC) operated at 40 kV and 20θ mA in the 2 range of 10-90°. The transmission electron microscope (TEM) images of the phosphors were measured using a FEI tecnai G2F30 TEM. Excitation, emission spectra and decay curves have been obtained using Edinburgh Instruments (FLS920) Fluorescence Spectrometer.

Results and Discussions

XRD of YAG:Dy^{3+} phosphors

The XRD patterns of YAG:xDy^{3+} phosphors for x= (0.02, 0.04, 0.06, 0.08 and 0.1) were given in Fig. 1. The diffraction peaks of all samples were in agreement with the standard card of pure YAG (JCPDS No. 33-0040). No extra peaks related to the starting materials were observed. The results indicated that single phase YAG : Dy^{3+} phosphors were obtained. From the Bragg's equation (1) and (2), the cell parameters for cubic structure can be calculated,

$$2d \sin\theta = \lambda \quad (1)$$

$$1/d_{hkl}^2 = (h^2+k^2+1^2)/a^2 \quad (2)$$

Where d was interplanar distance, was the diffraction angle which was determined from the XRD results, λ was the wavelength of CuKα radiation (1.54 Å), and h, k, l were Miller indices. The inset was the calculated cell parameters of YAG : Dy^{3+} phosphors. It showed that cell parameters were almost constant with increase of Dy^{3+} concentration, this is because that the radius of Dy^{3+} (0.908) was close to that of Y^{3+} (0.893) in YAG host and the dopant concentration was too low to cause the marked change of cell parameters.

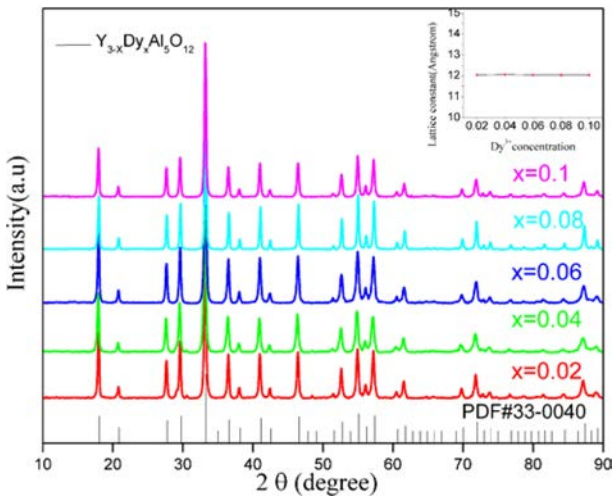

Fig. 1. XRD patterns of YAG:xDy^{3+} (x = 0.02-0.1) phosphors (Inset graph is the lattice constants of YAG:Dy^{3+} phosphors with different doping concentrations).

TEM of the YAG : 0.06Dy^{3+} phosphor

TEM and HRTEM micrographs of YAG:0.06Dy^{3+} phosphor were presented in Fig. 2. It showed that the phosphors were spherical-like particles with the diameter ranged of 61-72 nm and there were slight aggregation of particles. From Fig. 2(b), we can find that the spherical-like particles have clear lattice fringes. The spacing of the lattice fringe was about 3.002 Å and it matched well the interplanar distance of the (400) planes of cubic YAG. It indicated the good crystalline of YAG : 0.06Dy^{3+} phosphor.

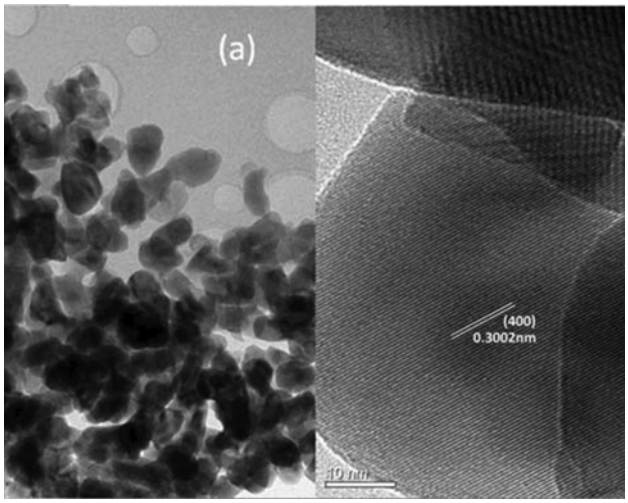

Fig. 2. TEM (a) and HRTEM (b) images of YAG : 0.06Dy^{3+} phosphor.

Photoluminescence properties

The excitation and emission spectra of YAG : 0.06Dy^{3+} phosphor were shown in Fig. 3. The excitation spectrum monitored at 582 nm were composed of broad bands from 250 to 300 nm and several sharp lines which correspond to f-f transition excitation of Dy^{3+}, located at 325 nm ($^6H_{15/2} \rightarrow {}^6P_{3/2}$), 352 nm ($^6H_{15/2} \rightarrow {}^6P_{7/2}$), 366 nm ($^6H_{15/2} \rightarrow {}^6p_{5/2}$), 385 nm($^6H_{15/2} \rightarrow {}^4I_{13/2}$), respectively [19]. The former broad band was assigned to the host absorption band related to the energy transfer between the central oxygen ligands of Y^{3+} to Dy^{3+} [20].

The emission spectrum of YAG:Dy^{3+} under excitation of 352 nm, showed a blue band at 483 nm ($^4F_{9/2} \rightarrow {}^6H_{15/2}$), a yellow band at 582 nm ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) and a small red region at 669 nm ($^4F_{9/2} \rightarrow {}^6H_{11/2}$) of Dy^{3+}. It was obvious that the intensity of yellow band was higher than blue band, in agreement with the results in literatures [15] and [21]. The emission spectra under 352 nm excitation for the YAG : xDy^{3+} phosphors with

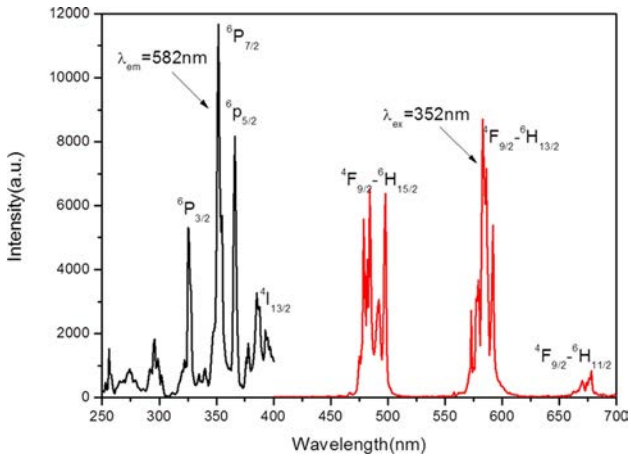

Fig. 3. PL excitation and emission spectra of YAG : 0.06 Dy^{3+} phosphor.

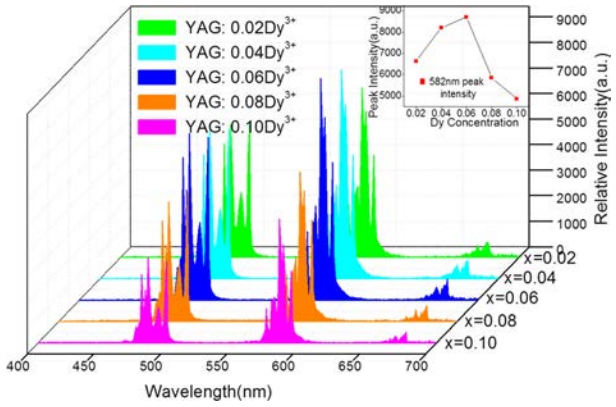

Fig. 4. PL spectra of (λ_{ex} = 352 nm) of YAG:xDy^{3+} (x = 0.02-0.10), Inset graph is 582 nm peak intensity as the function of Dy^{3+} doping concentration.

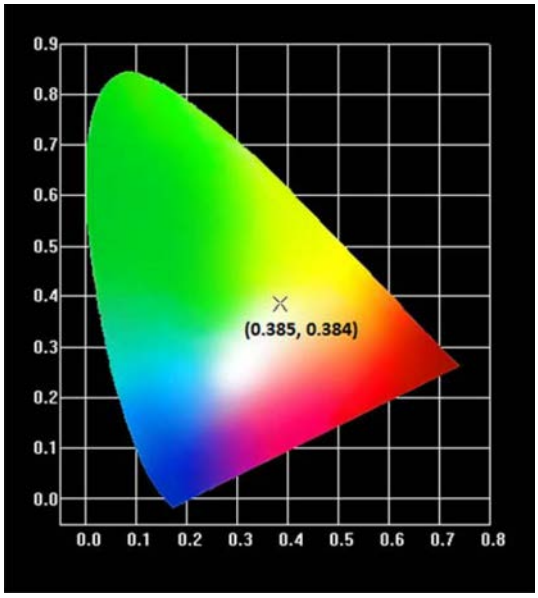

Fig. 5. CIE chromatic coordinates diagram of YAG : 0.02Dy^{3+} phosphor.

different Dy^{3+} concentration (x = 0.02, 0.04, 0.06, 0.08, 0.1) were demonstrated in Fig. 4. The emission intensity of the YAG: xDy^{3+} phosphors increased with increasing Dy^{3+} content up to 0.06 and then decreased with higher dopant concentrations, declined to a minimum at 0.1. The inset graph in Fig. 4 showed 582 nm peak intensity as the function of Dy^{3+} doping concentration. It implied

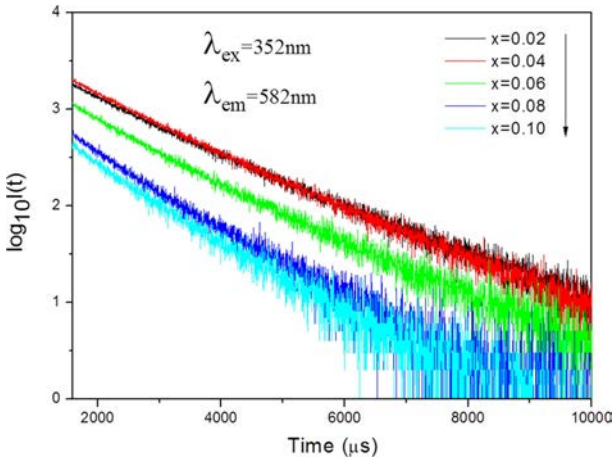

Fig. 6. Decay curve of the YAG : xDy^{3+} (x = 0.02-0.10) phosphors.

the concentration quenching took place and the optimum doping concentration was x = 0.06.

We have measured the CIE chromatic coordinates diagram of all samples under 352 nm excitation. We found that the CIE of YAG:0.02Dy^{3+} phosphor was (0.385, 0.384), which was very close to the National standard white light chromaticity (0.380, 0.380) for Energy Saving Lamp, as shown in Fig. 5. Compared with the commercial w-LED phosphor YAG:Ce^{3+}, its color temperature was lower (3907K). It was known that high color temperature lighting stimulates human eyes. Thus, YAG:Dy^{3+} phosphor had a potential application in domestic lighting to replace the energy saving lamp.

PL lifetime

The decay curves of the $^4F_{9/2}$ level of all YAG : xDy^{3+} phosphors are well fitted by bi-exponential, as shown in Fig. 6. The bi-exponential decay equation was:

$$I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) \quad (3)$$

Where I is the luminescence intensity; A_1 and A_2 are the fitting parameters; t is the time; τ_1 and τ_2 are the luminescence lifetimes. With the increase of Dy^{3+} concentration, the decay curves were gradually close to non-exponential. This may be associated to the energy transfer process between the Dy^{3+} ions provided extra

Table 1. Dates of the decay curves of Dy^{3+} emission of YAG:0.06Dy^{3+} phosphors, based on the fitted bi-exponential decay equation, λ_{ex} = 352 nm, λ_{em} = 582 nm.

Sample	x	Fitting parameter		Decay time (μs)		
		A_1 (%)	A_2 (%)	τ_1	τ_2	τ_{av}
	0.02	2783.662 (16.68)	4262.192 (83.32)	464.012	1513.884	1338.775
	0.04	3505.604 (16.54)	5103.077 (83.46)	413.835	1434.357	1265.549
	0.06	2484.752 (19.94)	2946.516 (80.06)	381.683	1291.915	1110.370
	0.08	2837.307 (27.23)	2056.767 (72.77)	288.123	1062.256	851.469
	0.1	3284.775 (34.59)	1660.797 (65.41)	272.904	1020.790	762.113

decay channel to change the decay curves [21].

The average decay lifetimes (τ) of YAG:xDy^{3+} phosphors were calculated by the Equation (4) [22]:

$$\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \quad (4)$$

The results were shown in Table 1, which were 1339, 1265, 1110, 851 and 762 μs with the increasing of the Dy^{3+} ions concentration, respectively. It showed that the strong concentration quenching took place, which was due to the non-radiative energy transfer between Dy^{3+} ions. It was also known that the cross-relaxation was characteristic in several host lattices containing Dy^{3+} ions. Furthermore, relatively large phonon energy of YAG (865 cm^{-1}) implied that the cross-relaxation channels weren't very rigorously resonant, because energy mismatches can readily be compensated by a single phonon. Thus, the concentration quenching was mainly attributed to cross-relaxation by means of direct transfer between two Dy^{3+} ions. The possible cross-relaxation channels in YAG:xDy^{3+} phosphors were shown in Fig. 7[23].

Based on the Van Uitert theory, the emission intensity (I) and activator concentration (x) satisfied the equation (5) [24-26]:

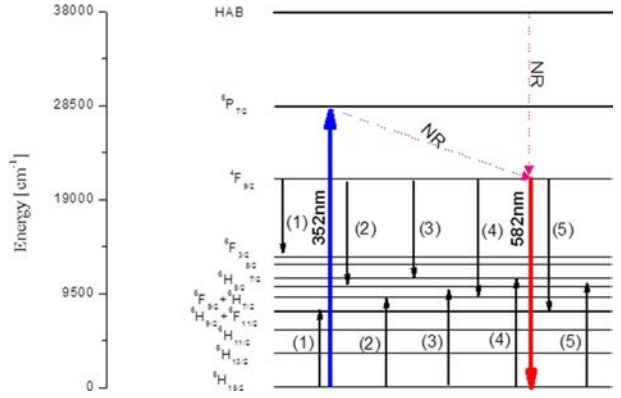

Fig. 7. Possible cross-relaxation channels of $^4F_{9/2}$ level in YAG : Dy^{3+} [23].

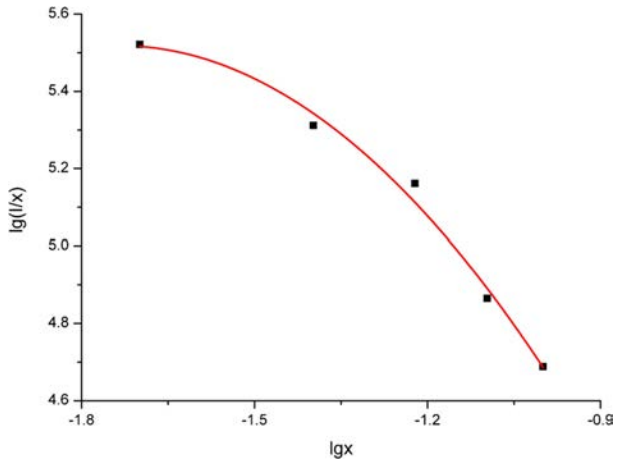

Fig. 8. The polynomial trendline fitting between the lg(I/x) and lgx.

$$1g(I/X) = A - \frac{Q}{3}1gx \quad (5)$$

Here A is constant. Q is 3, 6, 8 and 10 for the nearest-neighbor ions, dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions, respectively [24, 26]. The concentration dependence curves (log (I/x) ~ logx) for $^4F_{9/2} \rightarrow {}^6H_{13/2}$ of Dy^{3+} was shown in Fig. 8. By the slope of the linear part, the value of Q can be calculated as 6.431, which was close to 6. It revealed that the interactions between Dy^{3+} ions were ascribed to the dipole-dipole interactions.

Conclusions

YAG:xDy^{3+} (x = 0.02, 0.04, 0.06, 0.08, 0.1) phosphors were synthesized by Sol-gel method. The emission spectra under the excitation of 352 nm showed three peaks at about 483 nm, 582 nm and 669 nm, respectively. The doping concentration was optimized as 6 mol% and the concentration quenching phenomenon was attributed to cross-relaxation processes. When x = 0.02, the CIE chromatic coordinate of YAG:xDy^{3+} phosphors was (0.385, 0.384), which was close to the National standard white light chromaticity (0.380, 0.380) for Energy Saving Lamp. It indicated YAG:0.02Dy^{3+} phosphor is suitable to fabricate white LED for domestic lighting.

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References

1. P.-C. Lin, C.-H. Huang and W.-R. Liu, J. Ceram. Process. Res. 15 [3] (2014) 185-188.
2. Z. Y. Mao, Y. C. Zhu, Y. Zeng and L. Gan, J. Lumin. 143 (2013) 587-591.
3. Y. P. Jin, J. H. Lee and G. Seeta Rama Raju, Ceram. Int. 40 [4] (2014) 5693-5698.
4. P. Dai, X. Zhang, X. Li, G. Wang and C.Zhao, J. Lumin. 131 [4] (2011) 653-656.
5. F. Tao and C. R. Hu, Ceram. Int. 39 [4] (2013) 4089-4098.
6. L. Zhang, Z. Lu and J. Z. Zhu, J. Rare Earth, 30 [4] (2012) 289-296.
7. G. F. Li, Q. X. Cao, Z. M. Li and Y. X. Huang, J. Alloy. Compd. 485 [1-2] (2009) 561-564.
8. X. Li, H. Liu and J. Y.Wang, J. Phys. Chem. Solids. 66 [1] (2005) 201-205.
9. L. Zhang , H. P. Xia and Y. Qiu, J. Rare Earth. 28 (2010) 236-240.
10. X. Li, Q. Li, J. Y. Wang and S. L.Yang, Mater. Sci. Eng. B. 131 [1] (2006)32-35.
11. L. Kong, S. C.Gan, G. Y. Hong and J. L. Zhang, J. Rare Earth. 25 (2007) 692-696.
12. H. Y. Sun, X. Y. Zang and Z. H. Bai, J. Rare Earth. 31 [3] (2013) 231-234.
13. K. Y. Hyun, M. N. Hyeon and H. J. Jung, Solid State Sci. 27 (2014) 43-46.

14. G. Seeta Rama Raju, H. C. Jung and J. Y. Park, J. Alloy. Compd. 481 (2009) 730-734.
15. Y. Zhou, J. Lin, M. Yu and S. Wang, J. Alloy. Compd. 375 (2004) 93-97.
16. J. Y. Chong, Y. L. Zhang and K. W. Brent, J. Alloy. Compd. 581 (2013) 484-487.
17. G. Seeta Rama Raju, H. C. Jung and J. Y. Park, J. Optoelectron. Adv.Mater., 12 (2010) 1273-1278.
18. L.P. Goss, Rev. Sci. Instrum. 60 [12] (1989) 3702-3706.
19. B. N. Tian, B. J. Chen and Y.Tian, J. Phys. Chem. Solids. 73 [11] (2012) 1314-1319.
20. G. Seeta Rama Raju, H. C. Jung and J. Y. Park, J. Korean Phys. Soc. 54 [4] (2009) 1470-1474.
21. M. Klimczaka, M. Malinowski and J. Sarnecki, J. Lumin. 129 [12] (2009) 1869-1873.
22. S. D. Meetei and S. D.Singh, J. Alloy. Compd. 587 (2014) 143-147.
23. C. Y. Shen, Y. Yang and S. Z.Jin, Optik. 121 [16] (2010)1487-1491.
24. L G. Van Uitert, J. Electrochem. Soc. 114 [10] (1967) 1048-1053.
25. X.M. Zhang, F.G. Meng and W.L. Li, J. Alloy. Compd. 578 (2013) 72-76.
26. B. Han, J. Zhang and Z. M. Wang, J. Lumin. 149 (2014) 150-154.