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Journal of Alloys and Compounds 408–412 (2006) 856–859

Journal of ALLOYS AND COMPOUNDS

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Luminescent properties of $YVO_4:Dy^{3+}$ phosphors prepared by spray pyrolysis

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Received 2 August 2004; received in revised form 26 November 2004; accepted 29 November 2004
Available online 6 June 2005

Abstract

Starting from nitrate aqueous solutions with citrate acid and polyethylene glycol (PEG) as additives, $YVO_4:Dy^{3+}$ phosphors were prepared by a two-step spray pyrolysis (SP). The obtained phosphors had spherical morphology. The luminescence properties of $YVO_4:Dy^{3+}$ phosphors were investigated by changing the concentration of Dy^{3+} and the annealing temperatures, respectively. The emission intensity of the phosphors increased with increasing the annealing temperature due to the increase of the crystallinity and particles size. The optimum concentration for the luminescence of Dy^{3+} was determined to be 2 mol% of Y^{3+} in YVO_4 host.

Keywords: Spray pyrolysis; Spherical; $YVO_4:Dy^{3+}$; Luminescence

1. Introduction

Recently, spray pyrolysis (SP) technique has been employed to prepare spherical phosphor materials [1–4]. In general, luminescent materials derived from this method have spherical shape, submicrometer size and smooth surface. $YVO_4:Dy^{3+}$ has been used as a potential white phosphor with high efficiency [5]. Normally, bulk YVO_4 based phosphors are prepared by solid-state reaction method [6,7], and YVO_4 nanophosphors are prepared by coprecipitation and hydrothermal methods [8,9]. However, the quantum yield of the nanophosphors is usually lower than bulk phosphors [6]. Therefore, microscale YVO_4 based phosphors are necessary for high luminescent performance. It is believed that spherical morphology is necessary for obtaining high brightness and high resolution due to the high packing densities and low scattering of light [10].

As far as we know, the preparation of $YVO_4:Dy^{3+}$ by spray pyrolysis has not been reported. Therefore, in this paper, using colloid solution instead of nitrate precursors as spray solution, we prepared $YVO_4:Dy^{3+}$ phosphor particles by a two-step spray pyrolysis method. The influences of annealing temperature and Dy^{3+} concentration on the luminescent properties of the resulted $YVO_4:Dy^{3+}$ phosphors were investigated.

2. Experimental

The starting materials for $YVO_4:Dy^{3+}$ phosphors were rare earth oxides Y_2O_3, Dy_2O_3 (all 99.99%, Shanghai Yuelong Non-Ferrous Metals Limited) and NH_4VO_3 (A.R.). The synthesis processes are as follows.

Stoichiometric amounts of Y_2O_3, Dy_2O_3 and NH_4VO_3 were dissolved in dilute nitrate acid under stirring and heating. Certain amount citric acid mono-hydrate (citric acid/metal ion = 3) and polyethylene glycol (PEG, molecular weight = 10,000) were added to the nitrate solution. The resulting mixture was stirred for additional 2 h. The solution was loaded to the spray pyrolysis apparatus (BüCHI Mini Spray Dryer B-191) to obtain SP precursor particles. Finally, the above obtained precursor particles were calcined at 300–1200 °C for 4 h in air, respectively.

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doi:10.1016/j.jallcom.2004.11.085

Phase development in the post-annealed powder samples were checked by X-ray diffraction (Rigaku, D/max-II B) using Cu Kα radiation (λ = 0.15405 nm). The morphology of the samples was inspected using scanning electron microscope (JEOL JXA-840). The excitation and emission spectra were taken on a Hitachi F-4500 spectrofluorimeter equipped with a 150 W xenon lamp as the excitation source. Luminescence lifetimes were measured with a SPEX 1934D phosphorimeter using a 7 W xenon lamp as the excitation source with the pulse width of 3 μs. All the measurements were performed at room temperature (RT).

3. Results and discussion

3.1. Phase and morphology control

The spray pyrolysis method includes two steps. The first step is to prepare the precursor particles by spray drying process. Subsequently, the obtained precursor particles were calcined in air to produce the phosphor samples. All samples were sintered between 300 and 1200 °C with an interval of 100 °C and checked by XRD. The results of XRD indicated that the sample began to crystallize at 400 °C, and the crystallinity increased with raising the annealing temperature until 1200 °C. The representative XRD patterns for the sample (YVO_4:0.02Dy^{3+}) annealed at 500, 700 and 1000 °C together with the standard data for YVO_4 (JCPDS card 17-341) are present in Fig. 1. It can be seen that all the peaks in the diffraction patterns can be indexed to the tetragonal YVO_4 (space group $I4_1/amd$), and no other crystalline phase can be detected. In general, the crystallite size can be estimated from the Scherrer equation, $D = 0.941\lambda/\beta\cos\theta$, where D is the average grain size, λ the X-ray wavelength (0.15405 nm), and θ and β are the diffraction angle and full-width at half-maximum (FWHM, in radian) of an observed peak, respectively [11]. The strongest peak (2 0 0) at $2\theta = 25.0°$ was used to calculate the average crystallite size (D) of YVO_4:Dy^{3+} sample annealed at 500 °C (15 nm), 700 °C (24 nm), 1000 °C (40 nm) and 1200 °C (40 nm), respectively (the values in the parentheses refer to the estimated crystallite sizes). Clearly, the crystallite size increases with raising the annealing temperature from 500 to 1000 °C, and no difference was observed for the crystallite size between 1000 and 1200 °C.

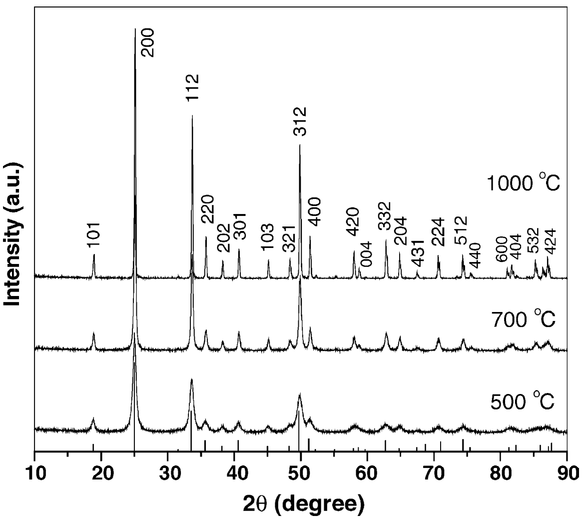

Fig. 1. XRD patterns of YVO_4:0.02Dy^{3+} derived from SP method annealed at 500, 700 and 1000 °C as well as the JCPDS card 17-341 for YVO_4 as a reference.

Fig. 2 shows the SEM micrographs of YVO_4:0.02Dy^{3+} phosphors calcined at 500 °C (a), 700 °C (b), 1000 °C (c) and 1200 °C (d). It can be seen that all the samples have solid spherical morphology and submicrometer size. Moreover, the phosphor particles with smooth surface were observed when the annealing temperature was not higher than 1000 °C. Annealing at 1200 °C resulted in the particles with rough surface. Furthermore, it can be observed that the average particle size increased slightly with increase of the annealing temperature (1.5 μm for 500 and 700 °C, 2 μm for 1000 and 1200 °C).

3.2. Luminescence properties

Fig. 3 shows the excitation (a) and emission (b) spectra of the SP-derived YVO_4:0.02Dy^{3+} phosphor sample fired at 1200 °C, respectively. The excitation spectrum (Fig. 3a) consists of a broad band ranging from 200 to 350 nm with a maximum 308 nm and a shoulder at 265 nm and some sharp lines in the longer wavelength region. The former is due to the absorption of VO_4^{3-} group and the latter to the f–f transitions within Dy^{3+} $4f^9$ configuration [12]. The absorption of VO_4^{3-} is ascribed to a charge transfer from the oxygen ligands (O^{2-}) to the central vanadium atom (V^{5+}). In crystalline YVO_4 the original T_d symmetry of VO_4^{3-} (free ion) is reduced to D_{2d} by the crystal field, which causes a splitting of the degenerate energy levels of VO_4^{3-} ion [13]. From the viewpoint of molecular orbital theory, the two bands (265, 308 nm) correspond to electric or magnetic dipole allowed transitions from the $^1A_2(^1T_1)$ ground state to $^1E(^1T_2)$ and $^1A_1(^1E)$ excited states of VO_4^{3-} ion, respectively [12]. In the emission spectrum (Fig. 3b), the characteristic transition lines from the lowest excited $^4F_{9/2}$ level of Dy^{3+} to $^6H_{15/2}$ and $^6H_{13/2}$ are observed, dominated by the Dy^{3+} $^4F_{9/2}$–$^6H_{13/2}$ hypersensitive transition ($\Delta J = 2$). This is because the Dy^{3+} is located at a low symmetry local site (D_{2d}, without inversion center) in the YVO_4 host lattices [11].

The presence of the VO_4^{3-} absorption in the excitation spectrum of Dy^{3+} indicates that an energy transfer occurs from VO_4^{3-} to Dy^{3+} in YVO_4:Dy^{3+}, and the energy transfer is very efficient because no emission of VO_4^{3-} is observed and only the emission of Dy^{3+} is observed upon excitation at the VO_4^{3-}. The energy transfer from VO_4^{3-} to Dy^{3+} is dominated by exchange interaction at room temperature like $VO_4^{3-} \rightarrow Eu^{3+}$ energy transfer in YVO_4 [14].

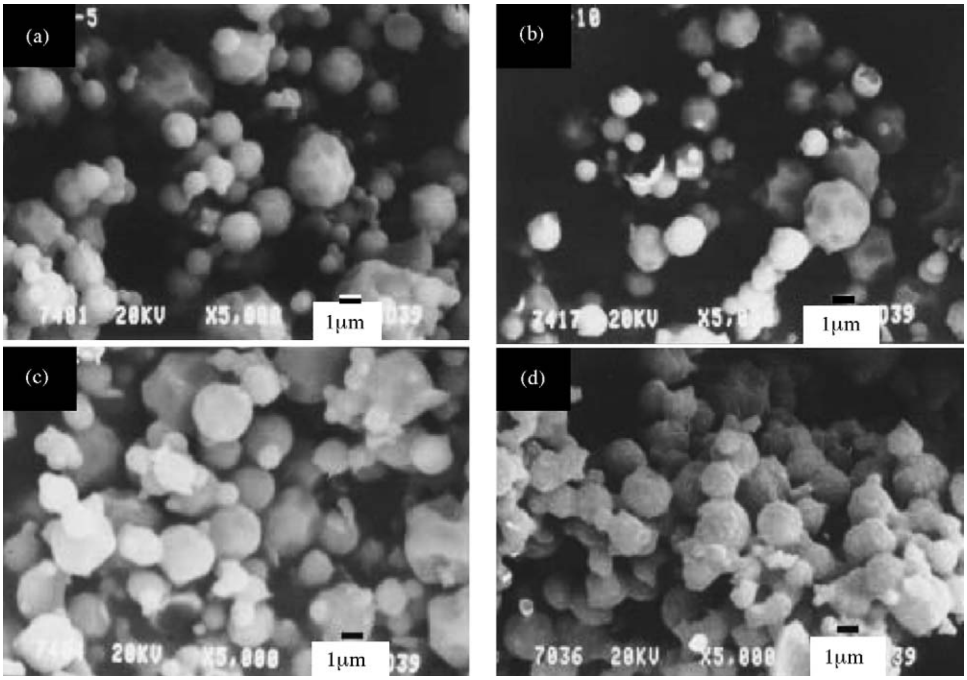

Fig. 2. SEM micrographs of SP-derived YVO_4:$0.02Dy^{3+}$ phosphor particles annealed at: 500 °C (a), 700 °C (b), 1000 °C (c) and 1200 °C (d), respectively.

The decay behavior for the luminescence of Dy^{3+} in YVO_4 depends strongly on the excitation situations. Fig. 4 shows the typical decay curves of Dy^{3+} ${}^4F_{9/2}$–${}^6H_{13/2}$ emission (574 nm) upon excitation into the Eu^{3+} f–f transition at 369 nm and the vanadate group at 310 nm in 1000 °C annealed YVO_4:$0.02Dy^{3+}$ phosphor sample. For excitation into the f–f transition, the obtained decay curve can be well fitted by a singly exponential function as $I = I_0 \exp(-t/\tau)$ (where I_0 is the initial intensity at $t = 0$ and τ is the $1/e$ lifetime of the rare earth ion), and the lifetime of Dy^{3+} (${}^4F_{9/2}$–${}^6H_{13/2}$) is determined to be 82 μs. However, excitation into the $VO_4{}^{3-}$ yields a decay curve consisting of an initial rise until $t = 0.87$ ms and a subsequent decay which cannot be fitted by simple single or second-order exponential function. This complicated decay behavior of Dy^{3+} can be ascribed to the energy transfer from $VO_4{}^{3-}$ to Dy^{3+} in the YVO_4:Dy^{3+} phosphor upon exciting into the vanadate group [13,14].

Generally, the luminescence properties of phosphors depend on the activator concentration and crystallinity. Dependence of the emission intensity of Dy^{3+} upon the doping concentration (x) in crystalline $Y_{1-x}Dy_xVO_4$ (700 °C annealed) is shown in Fig. 5. It is found that the emission intensity of Dy^{3+} first increases with increasing its concentration (x), reaching a maximum at $x = 2$ mol%, then decreases

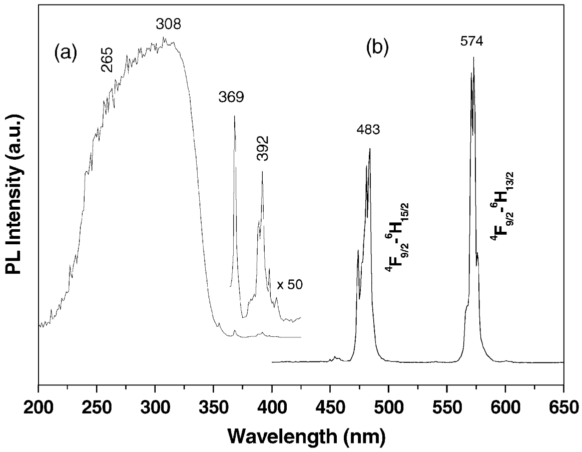

Fig. 3. Excitation (a) and emission (b) spectra of YVO_4:$0.02Dy^{3+}$ phosphor annealed at 1200 °C.

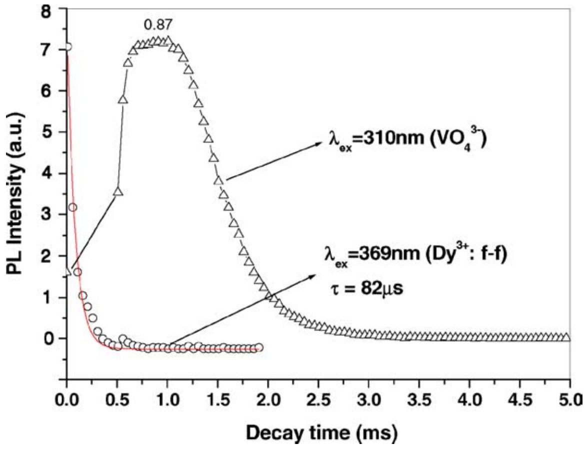

Fig. 4. Decay curves of Dy^{3+} (${}^4F_{9/2}$–${}^6H_{13/2}$) in YVO_4:$0.02Dy^{3+}$ annealed at 1000 °C with different excitation wavelengths.

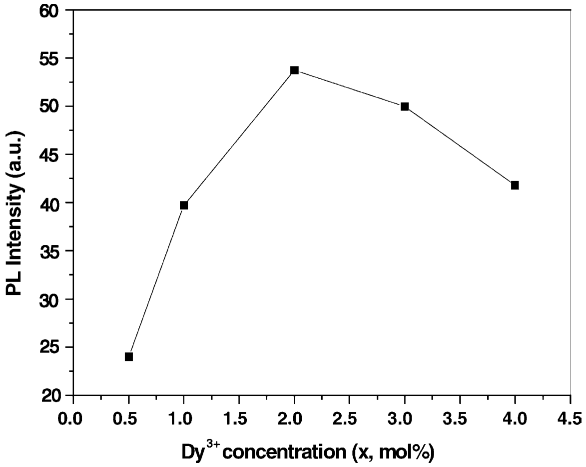

Fig. 5. Emission intensity of Dy^{3+} as a function of its doping concentration (x) in $Y_{1-x}Dy_xVO_4$ phosphors annealed at 700 °C.

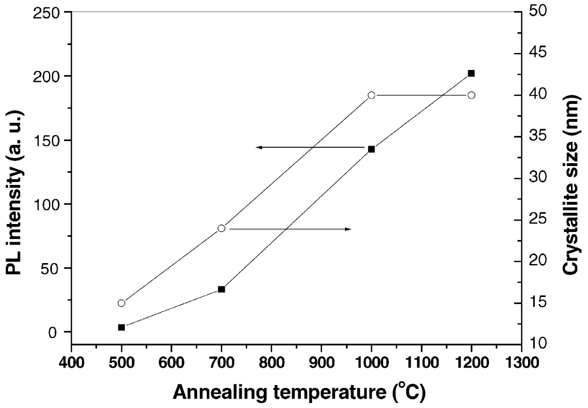

Fig. 6. Emission intensity and crystallite size of YVO_4:0.02Dy^{3+} as a function of the annealing temperature.

with the doping concentrations. This indicates the concentration quenching effects for the luminescence of Dy^{3+} in YVO_4 host. Thus, the optimum concentration for Dy^{3+} is determined to be 2 mol% of Y^{3+} in YVO_4 host.

Fig. 6 shows the variation of the emission intensity and crystallite size of YVO_4:0.02Dy^{3+} samples as a function of annealing temperatures. It can be observed that the emission intensity increases with the increase of annealing temperature. This is a common phenomenon due to the improvement of crystallinity and crystalline size with raising the annealing temperature [12].

4. Conclusions

The YVO_4:Dy^{3+} phosphors were successfully prepared by spray pyrolysis method with the citric acid and PEG as additives in precursor solutions. The obtained phosphors have spherical morphology and submicrometer size. The YVO_4:Dy^{3+} phosphors show the characteristic emission lines of Dy^{3+}, dominated by the hypersensitive $^4F_{9/2}$–$^6H_{13/2}$ yellow emission due to an efficient energy transfer from the vanadate group to Dy^{3+}. The decay behavior for the Dy^{3+} $^4F_{9/2}$–$^6H_{13/2}$ emission depends strongly on the excitation situations, and the optimum concentration of Dy^{3+} is determined to be 2 mol% of Y^{3+} in the YVO_4 host lattices. The emission intensity of YVO_4:Dy^{3+} increases with the increase of annealing temperature.

Acknowledgements

This project is financially supported by the foundation of “Bairen Jihua” of Chinese Academy of Sciences, the MOST of China (No. 2003CB314707) and the National Natural Science Foundation of China (20270148 and 50225205).

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