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Luminescent properties of nanoparticles $YP_XV_{1-X}O4$:Dy phosphors

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Abstract

Phosphors of nanoparticles $YP_XV_{1-X}O_4:Dy^{3+}$ ($0 \leqslant X \leqslant 1$) have been prepared by a citrate sol–gel method. X-ray diffraction, transmission electron microscope (TEM), scanning electron microscope (SEM) and photoluminescence excitation and emission spectra were utilized to characterize the phosphors. The results of XRD showed that a solid solution formed in $YP_XV_{1-X}O_4:Dy^{3+}$ phosphor series from $X = 0$ to $X = 1$ with zircon structure. TEM and SEM studies revealed that the obtained $YP_XV_{1-X}O_4:Dy^{3+}$ nanocrystals appeared to be spherical with some agglomeration and their sizes ranged from 30 to 80 nm. Upon short ultraviolet excitation, the optical properties of all the powder presented that the characteristic transitions of Dy^{3+} due to $^4F_{9/2}$–$^6H_{15/2}$ (blue) and $^4F_{9/2}$–$^6H_{13/2}$ (yellow) were detected. Besides this, in the system of $YP_XV_{1-X}O_4:Dy^{3+}$, the yellow-to-blue intensity ratio (Y/B) depended on the value of P/V greatly, with the increasing of X value and the decreased Y/B value. The phosphor found to yield white light when the value of X in the range of $X = 0.775$–0.85, the optimum concentration for Dy^{3+} is 1 mol% of Y in the host, and the emission intensity increased with the annealing temperature.

Keywords: Luminescence; Phosphor; White emission; $YP_XV_{1-X}O_4:Dy^{3+}$

1. Introduction

Rare-earth activated phosphors have attracted great interest because of their marked improvements in lumen output, color rendering index, energy efficiency and greater radiation stability [1–5]. The rare-earth ions are characterized by a partially filled 4f shell that is shielded by $5s^2$ and $5p^6$ electrons. Accordingly, the host has only a weak influence on the RE^{3+} energy levels, and the radiative emissions resemble those of the free ion in terms of their narrow spectral width (5–20 cm^{-1} in a crystalline host) [6–8], long excited-state lifetimes (milliseconds) and relatively low oscillator strengths ($\sim 10^{-5}$–10^{-8}). As for the hosts [9–17], rare-earth orthovanadates and orthophosphates with general formula RMO_4, where R = Sc, Y, La, Gd or Lu and M = V or P, are very important hosts for the luminescence of lanthanide ions. As representative examples in this family, Eu^{3+}-activated YVO_4 is an important commercial red ($^5D_0$–$^7F_2$ of Eu^{3+} at 619 nm) phosphor used in color television, the cathode ray tube and the high-pressure mercury lamp. And $LaPO_4$:Ce, Tb is used as a highly efficient green component in tricolor fluorescent lamps [18]. YPO_4:Ce is an efficient UV-A phosphor applied in tanning lamps [19] and the white YPO_4:Nd, YPO_4:Pr are considered as potential nuclear waste containment hosts [20]. Besides these, Dy^{3+} ion is another good activator and Dy^{3+}-actived YVO_4 is a potential white phosphor because of the yellow band (575 nm) corresponding to the hypersensitive transition $^4F_{9/2}$–$^6H_{13/2}$ ($\triangle L = 2$, $\triangle J = 2$) and the blue band (486 nm) corresponds to the $^4F_{9/2}$–$^6H_{15/2}$ transition. By suitably adjusting the yellow-to-blue intensity ratio (Y/B) value, it is possible to obtain near-white emission with Dy^{3+}-actived luminescence materials. However, the bulk YVO4:Eu^{3+} is usually prepared by solid-state reactions at temperatures above 1300 K [21,22]. To achieve desired phase purity and required particle size, the process of solid-state reaction needs high-temperature treatment and extensive ball milling, which generally introduces additional impurities and defects. For

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improving the drawbacks of the solid-state reaction, on the based solution processes sol–gel method has been investigated [14]. This method has advantages of fine homogeneity, high reactivity of starting materials and lower sintering temperature.

In this paper, we used citrate sol–gel method to prepare the $YP_XV_{1-X}O_4$:Dy^{3+} nanocrystalline phosphor. The luminescence properties of $YP_XV_{1-X}O_4$:Dy^{3+} were investigated by changing the concentration of Dy^{3+}, the molar ratio of P to V and the annealing temperatures, respectively.

2. Experimental section

2.1. Preparation of $YP_XV_{1-X}O_4$:Dy^{3+} phosphor

The phosphor samples $Y_{0.99}Dy_{0.01}VO_4$ and $YP_XV_{1-X}O_4$:Dy^{3+} ($0 \leqslant X \leqslant 1$) were prepared by a citrate sol–gel method. The starting materials were Y_2O_3 (99.99%), Dy_2O_3 (99.99%), NH_4VO_3 (A.R.), $NH_4H_2PO_4$ (A.R.) and citric acid as additives. We use phosphor sample $Y_{0.99}Dy_{0.01}P_{0.5}V_{0.5}O_4$ as a typical example to elucidate the experimental details. First, according to composition in the above formula, stoichiometric weights of oxides were dissolved in dilute nitric acid, and corresponding nitrate solutions were obtained. Then certain amount of citric acid, the molar ratio of which to total metal cation was 3:1, was added into mixed nitrate solution as chelating agent for the metal ions. The PH of the solution was adjusted to 1 with HNO_3 followed by the addition of stoichiometric amount of $NH_4H_2PO_4$ (A.R.) and NH_4VO_3. The solution was continuously stirred at 80 °C for several hours until it turned to sticky blue sol. Then, the sol was dried at 120 °C for 24 h to obtain the brown gel. The gel was ground into powders, put into a furnace for pre-calcination at 500 °C for 2 h, and then calcined at the required temperatures from 800 to 1000 °C for 4 h to obtain the phosphor samples.

2.2. Characterization of $YP_XV_{1-X}O_4$:Dy^{3+} phosphor

Transmission electron microscope (TEM) and scanning electron microscope (SEM) were used to observe the morphology and size of the calcined particles. Powder XRD (XRD, 35 kV and 25 mA, $CuK_\alpha = 0.15406$ nm Rigaku/Dmax-IIIA) was used for crystal phase identification and estimation of the crystallite size. Excitation and emission spectra were taken with a Hitachi F-4500 fluorescence spectrophotometer 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 a 298 nm laser (pulse width = 4 ns, gate = 50 ns) as the excitation source (Continuum Sunlite OPO). All the measurements were performed at room temperature.

3. Results and discussion

3.1. Crystallization behaviors and morphology of nanocrystalline $YP_XV_{1-X}O_4$:Dy^{3+} phosphors

YPO_4 and YVO_4 both crystals are tetragonal, space group $I4_1/amd$, $Z = 4$ [23,24]. The cell parameters are: $a = b = 6.8817$ Å; $c = 6.0177$ Å in the case of YPO_4 and $a = b = 7.1183$ Å; $c = 6.2893$ Å in the case of YVO_4. The Dy^{3+} ion occupies a single site with D_{2d} as local site symmetry and is coordinated with eight oxygen atoms. Fig. 1(a) shows the XRD patterns for $YP_XV_{1-X}O_4$:Dy^{3+} ($X = 0$, 0.5, 0.7, 0.9, 1) phosphor samples annealed at 1000 °C and the JCPDS cards for YPO_4 (No. 11-254) and YVO_4 (No. 17-341) as references. In this figure, the diffraction peaks at $2\theta = 25°$ for $X = 0$ and at $2\theta = 25.98°$ for $X = 1$ are due to the (2 0 0) reflection of YVO_4 and YPO_4, respectively. For these diffraction peaks, a small shift towards higher 2θ values with respect to the standard patterns is present. This corresponds to a decrease in unit cell parameters in the phosphor samples, as

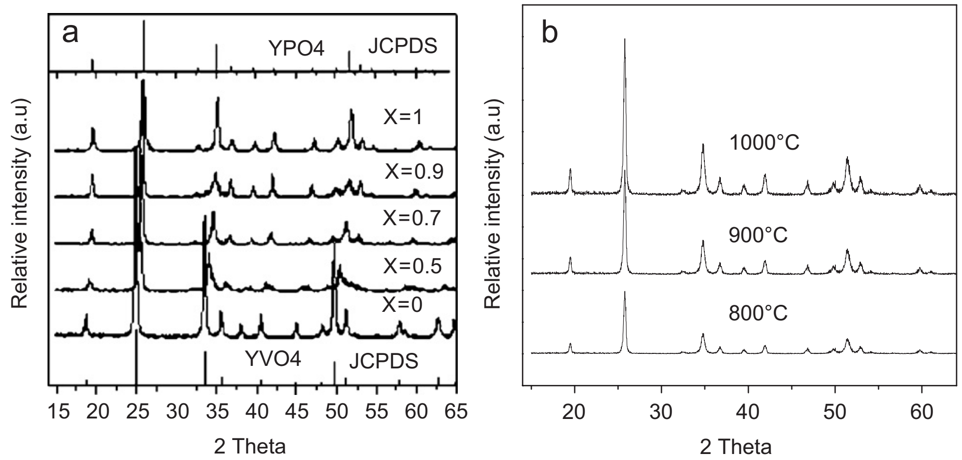

Fig. 1. (a) XRD patterns of the $Y_{0.99}Dy_{0.01}P_XV_{1-X}O_4$ prepared by the citrate sol–gel method calcined at 1000 °C for 4 h. Fig. 1(b). XRD patterns of $Y_{0.99}Dy_{0.01}P_{0.8}V_{0.2}O_4$ precursors sintered at different temperatures.