Optical properties of porous YVO₄:Ln (Ln = Dy³⁺ and Tm³⁺) nanoplates obtained by the chemical co-precipitation method

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ABSTRACT

The present research describes a simple low-temperature synthesis route for obtention of porous YVO₄:Dy and YVO₄:Tm nanoplates via a chemical co-precipitation method using commercially available Y₂O₃, NH₄VO₃, Tm₂O₃, Dy₂O₃ and ethylene glycol as the reacting precursors. To investigate the effect of heating temperatures on the pore size and morphology of nanoplates-like powders, the as-synthesized YVO₄:Ln were thermally treated at 300 and 600 °C for 2 h which is much lower than that of the conventional preparation methods. The obtained samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and photoluminescent (PL) spectroscopy. The photoluminescence measurement revealed that the luminescence intensity was significantly increased with increasing annealing temperature that causes increase of crystallinity and pore size of the porous nanoplates. From PL spectra, it was found that porous YVO₄:Dy nanoplates have characteristic emission peaks due to the 4F⁹/₂ → 6H_{13/2} and 4F⁹/₂ → 6H_{5/2} emission transitions of Dy³⁺. The experimental results have showed that the host YVO₄ transfers the adsorbed energy to thulium ions and strong blue emission at 475 nm assigned to 3H₄ → 1S₀ transition was observed.

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1. Introduction

Yttrium orthovanadate (YVO₄) is one of the most promising inorganic luminescent materials having a zirconia-type tetragonal structure and has a wide practical application in many devices involving the artificial production of light and display fields at present [12,22–27]. A rapid development in the manufacturing of modern field emission displays has created a new demand for a few well-known phosphors with improved properties such as high brightness, high density, high stability, long lifetime, etc. Thus a number of research groups have directed their investigations towards this goal by different approaches. YVO₄ with lanthanide ions have been extensively studied for high luminescent performance owing to abundant emission colors based mainly on f-f transition [3,28]. In the second half of the last century, Levine and Palilla [4] first reported that YVO₄ can be modified by Eu³⁺ to be used as a red phosphor in color television, the cathode ray tube and the high-pressure mercury lamp due to its high luminescence efficiency upon electron-beam excitation. Yttrium orthovanadate activated by trivalent dysprosium (YVO₄:Dy) is a well-known phosphor with high efficiency [5]. The emission color of the luminescence is close to white because of the yellow (4F⁹/₂ → 6H_{13/2}) and blue (4F⁹/₂ → 6H_{15/2}) emissions of Dy³⁺. In general, a whitish color turns to yellow in host lattices. Good physical, optical, and mechanical properties have made YVO₄:Nd an excellent crystal for high power, stable, and cost-effective diode-pumped solid-state lasers [6,29]. Recent research results have demonstrated that Yb³⁺-doped YVO₄ has longer lifetime and higher quantum efficiency than its counterpart Nd-doped materials [7]. The passively Q-switched c-cut Nd: Cd₄G₆ O₄:V₄O₄ crystal has large energy storage capacity and indicate the shortest pulse width, largest pulse energy, and highest peak power [30]. Er³⁺-doped YVO₄ has been considered to be a very attractive potential laser material in the eye safe region around 1.6 µm [8]. In addition, the holmium–doped yttrium orthovanadate crystal was shown to be an effective solid-state saturable-absorber Q switch for a flash-lamp-pumped Y₃Al₅O₁₂:Ti,Er laser operating at 2.017 µm [9]. To avoid the drawbacks of currently available sulfide-based blue phosphors, modification of YVO₄ with thulium ions have been attempted because of its stability under high excitation density, appropriate lifetime and color rendering properties [10]. According to Saito et al. [11], YVO₄:Tm has a smoother and more intense absorption profile for the pump band, which offers advantages for diode-laser pumping, in comparison with the earlier Tm³⁺ lasers.

Inorganic nanocrystals have already exhibited unique size- and shape-dependent electrical, magnetic and optical properties due to potential quantum confinement effect and low dimensionality [12]. Recently, many efforts have been developed for the
fabrication of porous nanостructures which give fascinating properties to a material differing from the solid counter parts [13,14]. If the porous nanostructure and luminescence property can be combined together, the porous nanomaterials would be useful as an ideal candidate for the photoluminescence applications due to their surface plasmonic properties and catalytic activities. Till date, low-temperature morphology controllable soft chemical methods have been employed to fabricate well-dispersed fine YVO4, i.e. hydrothermal synthesis [15], hydrolyzed colloidal reaction technique [16] and induced precipitation [17]. However, all reported methods produced solid nanoparticles without any pores. To the best of our knowledge, no report on the synthesis and luminescence properties of porous YVO4:Ln (Ln=Dy, Tm) nanoplates has been published. Therefore, in this paper, we demonstrate a simple approach for the synthesis of porous YVO4:Ln nanoplates by chemical co-precipitation method to regulate both the pore size and morphology of nanoparticles. Furthermore, the optical properties were investigated in details.

2. Experimental

All chemical reagents were analytical purity and purchased from Beijing Chemical Reagents Company (China) and used without further purification.

Nanosized Y0.98VO4:Ln0.02 (Ln=Tm, Dy) were synthesized by chemical co-precipitation method. The stoichiometric amounts of Y2O3, Tm2O3 and Dy2O3 were dissolved in 20 ml HNO3 (6 mol/l) at room temperature to obtain a transparent solution. 5 ml ethylene glycol (C2H4O2) was added into the solution as a complex agent, followed by introducing the stoichiometric amount of NH4VO4 as a source of vanadium ions. The mixture was continuously stirred at room temperature for 20 min. Subsequently, 25 ml of ammonia (NH4OH) solution was slowly dropped into the homogenous solution under vigorous stirring to adjust its pH to 9–10. The resultant solution was preheated in a thermostated water bath at 80°C for 6 h. Then the as-synthesized precipitate was collected, washed with distilled water and absolute ethanol several times, and dried in vacuum at 80°C for 6 h. The as-synthesized powders were heated at 300 and 600°C for 2 h at a heating rate of 10°C/min in a laboratory furnace.

The crystal structures of the powders were determined by a powder X-ray diffraction (XRD; D/MAX2550, Rigaku, Japan) with monochromated Cu Kα radiation (λ=1.5406Å) at 40 kV and 50 mA. The transmission electron microscope (TEM) micrographs of the powders were taken with a JEM-2000 Ex transmission electron microscope (JEOL, Tokyo, Japan) under a working voltage of 200 kV. The excitation and emission photoluminescence (PL) spectra were measured using a PerkinElmer 155S fluorescence spectrometer (PerkinElmer, Shelton, USA).

3. Results and discussion

Fig. 1 presents the results of XRD analysis of the as-synthesized at 80°C for 6 h and heated nanocrystalline YVO4:Dy and YVO4:Tm at 300 and 600°C for 2 h although a difference between the XRD patterns of two compositions is not observed. All peaks can be indexed to a pure phase YVO4 (JCPDS Card No.17-0341) with a zirconia-type tetragonal structure belonging to the space group I41/amd, and its lattice parameters are a=b=0.71192 nm and c=0.62898. The presence of a single phase without the presence of any extraneous phases in the samples is confirmed. The results exhibit that pure phase YVO4:Ln can be obtained under the current conditions of chemical co-precipitation method at as low a temperature as 80°C for 6 h. The diffraction intensities of the samples increases with increasing heating temperature up to 600°C which means the samples become a highly crystallized at that temperature.

Fig. 2(a–c) compares the TEM micrographs of the as-synthesized and heated nanocrystalline YVO4:Dy at 300 and 600°C for 2 h. Clearly, the sample preheated at 80°C for 6 h has roughly plate-like nanoparticles with size of 10–20 nm. The plate-like nanoparticles are composed of many small nanoparticles. After heat treatment of the as-synthesized samples at 300°C, the size of the plate-like nanoparticles became apparently larger (>30 nm) and the porous surface appeared on the plate-like nanoparticles. Further increasing the heating temperature up to 600°C resulted in the formation of relatively larger nanoparticles (>40 nm) with narrow particle size distribution. Evidently, the sample heated at 600°C has a large porous structure than that of the sample heated at 300°C. The increase in pore diameter of the sample is thought to be not only due to crystal growth at higher temperatures at 300 and 600°C, but also due to the output of CO2 into of matrix the C2H2O2. This is also a factor that caused the increase of pore diameter in the YVO4 powders, because of heat treatment thermal promote the decomposition of residuals organics compounds, by the following reaction: 2C2H2O2 + 5O2→4CO2 + 6H2O, due to output CO2 of interior of nanoparticles.

Fig. 2d shows that the YVO4:Tm nanoplates heated at 600°C for 2 h have the porous structure with a pore diameter in the range of about 5 nm. In contrast, the porous nanoplates of YVO4:Ln are different from the nanoparticles synthesized without ethylene glycol [18]. It was found that the environment of the ethylene glycol solution considerably influenced the shape formation of the YVO4:Ln crystals.

Fig. 3 displays the representative excitation spectrum of the as-synthesized YVO4:Dy powders. The excitation spectrum of YVO4:Dy nanoplates monitored at 574 nm consists of a broad band ranging from 200 to 350 nm with a maximum 305 nm and a shoulder at 270 nm and some sharp lines in the longer wavelength region. The former is due to the absorption of [VO2+] clusters and the
Fig. 2. TEM images of the as-synthesized (a) and heated nanocrystalline YVO₄: Dy at 300 °C (b) and 600 °C (c) for 2 h and heated nanocrystalline YVO₄: Tm at 600 °C (d) for 2 h.

Fig. 3. Excitation spectrum of the as-synthesized YVO₄:Dy³⁺ under 574 nm emission.

latter to the f-f transitions within Dy³⁺ ⁴F₉ configuration [19,31]. The absorption of [VO₆]⁺ is ascribed to a charge transfer from the oxygen ligands (O²⁻) to the central vanadium atom (V⁵⁺). In crystalline YVO₄, the original Td symmetry of [VO₆]⁺ clusters is reduced to D₂d by the crystal field, which causes a splitting of the degenerate energy levels of [VO₆]⁺ clusters [20]. For the existing of two excitation bands, the reason may be attributed to the distortion of the nanosized YVO₄. It is well known that YVO₄ belongs to the tetragonal zirconia structure and Y³⁺ is located at a site (D₂d) deviated from an inverse center in YVO₄ host. In addition, the particle size of the as-prepared samples is in nanometer dimension, which can also induce the distortion of YVO₄. All can arouse different V–O bond of [VO₆]. Thus there are two excitation bands existing in excitation spectra [20,21]. Besides this, in the longer wavelength region (350–450 nm), weaker excitation band also appears originated from the f-f transition of Dy³⁺. All the excitation spectra of the as-synthesized YVO₄:Tm also showed the similar features and the representative one is illustrated in Fig. 4. The excitation spectrum monitored at 475 nm consists of two strong absorption bands in the
short ultraviolet region (200–350 nm) centered at 211 and 279 nm, respectively. The strong wide band centered at 279 nm originates in transitions towards the charge transfer from the oxygen ligands to the central vanadium atom inside the $[\text{VO}_6]^-$, which are almost similar shape for all samples. The small peaks in the range of 211 nm are attributed to the host absorption band. In the longer wavelength (350–450 nm), the f–f transitions are too weak to be analyzed.

The emission spectra of as-synthesized and heated Dy$^{3+}$ doped YVO$_4$ at 300 and 600 °C for 2 h are shown in Fig. 5. The emission spectra show similar trend for all as-synthesized and thermally treated samples. The spectral peaks at 482.5 nm (blue color) and 574 nm (yellow color) correspond to $^4H_{9/2} \rightarrow ^6H_{15/2}$ and $^4H_{9/2} \rightarrow ^6H_{13/2}$ emission transitions of Dy$^{3+}$ have been observed, respectively. The $^4H_{9/2} \rightarrow ^6H_{12/2}$ transition is magnetically allowed and hardly varies with the crystal field strength around the dysprosium ion. On the other hand, the $^4H_{9/2} \rightarrow ^6H_{13/2}$ transition is a forced electric dipole transition being allowed only at low symmetries with no inversion center. When the Dy$^{3+}$ ion is located at low-symmetry local sites with no inversion centers, $^4H_{9/2} \rightarrow ^6H_{13/2}$ emission transition is often prominent in its emission spectrum. Because Dy$^{3+}$ is located at a site of D$_{2d}$, which is deviated from an inverse center in the host of YVO$_4$, the intensity of its yellow emission is stronger than that of its blue emission. Although the major peak positions in the emission spectrum are identical to each other, the intensity patterns are much different. The emission intensity of porous YVO$_4$:Dy nanoplates heated at 300 °C increase little compared with the as-synthesized YVO$_4$:Dy nanoplates. When the heating temperature reached 600 °C, the emission intensity of YVO$_4$:Dy nanoplates is almost four times higher than the intensity of the as-synthesized YVO$_4$:Dy nanoplates. However, the luminescent properties of normal nanoplates synthesized without porous were independent of the heating temperature showing the same peak and intensity [20].

The emission spectra of the as-synthesized and heated nanocrystalline YVO$_4$:Tm at 300 and 600 °C for 2 h in the range 350–585 nm obtained upon 279 nm excitation are represented in Fig. 6. All the spectral peaks are approximately the same and a strong blue emission centered at 475 nm is observed, which is corresponded to the $^1G_4 \rightarrow ^4H_6$ transition. YVO$_4$:Tm prepared under the current conditions can emit a relatively a high pure and strong blue light, which is relative to the high efficiency of the host-to-guest energy transfer. The influence of pore size on the emission intensity of YVO$_4$:Tm nanoplates was also investigated. Although all the peak positions in the emission spectra are identical with each other, the intensity of all the peaks increased gradually with increasing pore size at different annealing temperatures. The peculiar luminescent properties of YVO$_4$:Dy and YVO$_4$:Tm are possible because of the distinct porous structure of the nanocrystals.

4. Conclusion

In summary, we have demonstrated a facile route to synthesize porous YVO$_4$:Ln (Ln = Dy, Tm) nanoplates using NH$_4$VO$_3$, Y$_2$O$_3$, Tm$_2$O$_3$ and Dy$_2$O$_3$ and ethylene glycol as the reacting precursors. The influence of heating temperatures on the pore size and morphology of the as-synthesized product was investigated. The photoluminescence measurement showed that the luminescence intensity of the porous YVO$_4$:Ln nanoplates was enhanced with increasing pore size of the nanocrystals after thermal treatment at 300 and 600 °C for 2 h. From PL spectra, it was found that porous YVO$_4$:Dy nanoplates have characteristic emission peaks due to the $^4F_{9/2} \rightarrow ^4H_{11/2}$ and $^4F_{9/2} \rightarrow ^4H_{15/2}$ emission transitions of Dy$^{3+}$. The experimental results have showed that the host YVO$_4$ transfers the adsorbed energy to thulium ions and strong blue emission at 475 nm assigned to $^1G_4 \rightarrow ^4H_6$ transition was observed. These materials may find industrial applications due to special properties, simplicity of process, low cost, and availability of raw materials. This method may be extended to synthesize other phosphors with controllable porous nanostructure.
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References