



# Facile synthesis of lanthanide vanadates and their luminescent properties



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## ARTICLE INFO

### Article history:

Received 16 October 2014

Received in revised form 13 March 2015

Accepted 20 May 2015

Available online 30 May 2015

### Keywords:

Microwave

GdVO<sub>4</sub>

Europium

Luminescence

## ABSTRACT

GdVO<sub>4</sub>:Eu<sup>3+</sup>, Bi<sup>3+</sup> with tetragonal phase has been successfully synthesized by employing efficient irradiations. The assembly of composites with fine grains based on acoustic energy and microwave radiation requires low temperature (90 °C) and short reaction time (60 min). All the compounds exhibited red emissions and they can be sensitized through the doped Bi<sup>3+</sup> ions. The dependence of pH changes and doping concentration on the fluorescence features has been discussed. The photoluminescence measurements show that the optical properties achieved the best results at pH = 9 for GdVO<sub>4</sub>:Eu<sup>3+</sup> (5 mol%), Bi<sup>3+</sup> (1 mol%) or pH = 7 for GdVO<sub>4</sub>:Eu<sup>3+</sup>.

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## 1. Introduction

Over the past few years, the lanthanide containing phosphors have attracted much attention on account of their unique luminescent properties which were derived from unique intra-4f transitions [1]. It has been found Ln<sup>3+</sup> ions have very special characteristics of sharp optical emissions. They cover a wide spectrographic range and have long-lived lifetimes, which facilitate several applications including displays, phosphors, laser crystal and so on [2]. Among them, lanthanide doped vanadate has been extensively studied owing to the excellent luminescence efficiency, stable physical and chemical properties and the abundant luminous colors [3–5]. Especially gadolinium vanadate has been paid much attention based on better laser performance, higher thermal conductivity, a larger emission or adsorption cross-sections [6,7]. It is also known that the half-filled shell ground state of the gadolinium leads to the phosphors with lowest excited levels and relatively high energy [6,7]. The encapsulated Eu<sup>3+</sup> ions with the parity forbidden characteristics usually exhibits strong red line emissions [7,8]. The resultant composite has high color purity and can be used for the fabrication of red phosphors [9,10].

Recently, numerous methods have been used to achieve these materials, such as solid state reaction, thermal evaporation,

hydrothermal, sol–gel and low-temperature synthesis. The supersonic microwave co-assistance (SMC) method appears as a new preparation technology for solid state material, which is considered to be promising in industrial application due to simple synthetic process, less energy loss, and fast efficiency. In our work, the Eu<sup>3+</sup>, Bi<sup>3+</sup> co-doped GdVO<sub>4</sub> phosphors were synthesized using the supersonic microwave co-assistance (SMC) method. The dependence of pH variation and doped Bi<sup>3+</sup> on the photoluminescence properties has been explored.

## 2. Experimental

Gd<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub> powders were dissolved in nitric acid, to prepare Gd(NO<sub>3</sub>)<sub>3</sub>, Bi(NO<sub>3</sub>)<sub>3</sub>, Eu(NO<sub>3</sub>)<sub>3</sub> powders. NH<sub>4</sub>VO<sub>3</sub> was used as a starting material. GdVO<sub>4</sub>:Bi<sup>3+</sup>, Eu<sup>3+</sup> were synthesized by the supersonic microwave co-assistance (SMC) method. For the synthesis of GdVO<sub>4</sub>:Bi<sup>3+</sup>, Eu<sup>3+</sup>. Microwave power was set as 200 W and reaction temperature was remained to be 90 °C. Supersonic power was 200 W with the reverse duty cycle 2 s. All the operation time was fixed as 60 min. The derived samples were cooled down to room temperature in air. Centrifugation was used to collect the precipitates. After washing twice with distilled water and absolute alcohol, the as-derived sample was dried at 70 °C.

Other samples GdVO<sub>4</sub>:Eu<sup>3+</sup>(0.05) and GdVO<sub>4</sub>:Bi<sup>3+</sup>(0.05), Eu<sup>3+</sup>(0.05) phosphors were prepared at pH = 3, 7, 9 because the acidification of an aqueous system plays an important role in the formation of complex phosphors. Then the concentration of Bi<sup>3+</sup>

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was controlled at 1–9 mol% to explore the influence of  $\text{Bi}^{3+}$  concentration for forming phosphors, and pH was controlled at 9.

The formation of gadolinium vanadate powder was confirmed by XRD patterns and the measurement was investigated on a Bruker D8 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.1541 \text{ nm}$ ) in the range of  $2\theta = 10^\circ$ – $80^\circ$ . The morphological information and characteristics of the samples were studied by a JSM-6360LV scanning electron microscope (SEM). Fluorescence spectra were measured on a Hitachi-2500 FL Spectrophotometer. Absolute quantum yields were detected at room temperature through an integrating sphere within an Edinburgh FLS920 spectrometer.

### 3. Results and discussion

$\text{Eu}^{3+}$ ,  $\text{Bi}^{3+}$  co-doped  $\text{GdVO}_4$  phosphors are synthesized using a supersonic microwave co-assistance (SMC) method. The rare earth vanadate has a tetragonal structure owing to the system which Gd and V atoms occupied the centers of oxygen tetrahedron. The surrounding oxygen atoms were adjacent to the vanadium. The doped  $\text{Bi}^{3+}$  and  $\text{Eu}^{3+}$  ions replace the site of the  $\text{Gd}^{3+}$  cation when they enter into the tetragonal structure. It is considered that the acidity of the solution will be closely related to the formation of crystal structure [11]. Accordingly, we study the effects of the pH value via the powder XRD pattern compared with JCPDS Card No. 72-0277. The Fig. 1(a) displays powder XRD features of  $\text{GdVO}_4:\text{Eu}^{3+}(0.05)$  at pH = 3, 7 and 9. In this curve, we can find that the rare earth vanadate crystal structure can be perfectly formed at pH = 7 because the sharp diffraction peaks match well with the standard pattern of  $\text{GdVO}_4$ . To investigate the influence of doping  $\text{Bi}^{3+}$  ions on the information of the  $\text{GdVO}_4$  crystal structure, we compare the curves between  $\text{GdVO}_4:\text{Eu}^{3+}(0.05)$  and  $\text{GdVO}_4:\text{Eu}^{3+}(0.05), \text{Bi}^{3+}(0.05)$  at pH = 9 via the Fig. 1(b). It is shown that the insertion of  $\text{Bi}^{3+}$  ions into the host will stimulate the crystal growth and demonstrate the production of tetragonal phase [12].

It has been reported that the pH value has a significant effect on the optical properties for most phosphors [13]. Therefore, we studied the fluorescence spectra at different pH values. The emission and excitation spectra of the  $\text{GdVO}_4:\text{Eu}^{3+}(0.05)$  were monitored at room temperature and the results were given in Fig. 2. The excitation spectra had a broad band between 220 and 400 nm and the peak maximum at pH = 7 was situated at 290 nm ( $\text{Em} = 615 \text{ nm}$ ). The emission spectra exhibited the narrow bands from 4f–4f transitions within  $\text{Eu}^{3+}$  ions in the region of 550–750 nm ( $\text{Ex} = 290 \text{ nm}$ ). It can be observed that the most intensive red

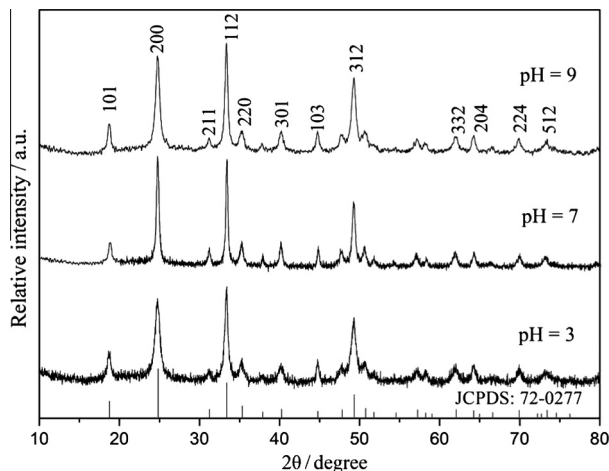


Fig. 1a. XRD patterns of  $\text{GdVO}_4:\text{Eu}^{3+}(0.05)$  prepared at pH = 3, 7 and 9.

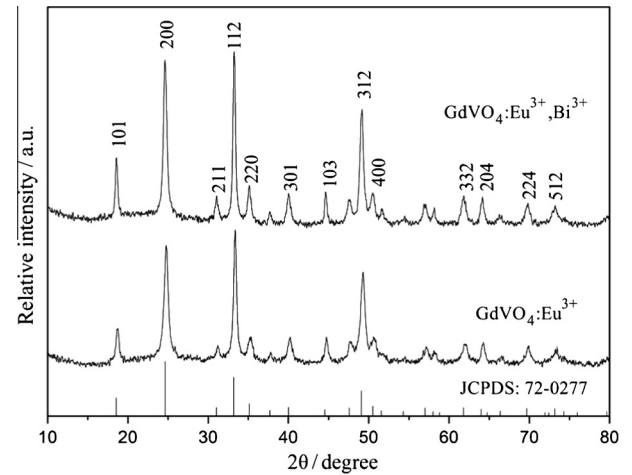


Fig. 1b. XRD patterns of  $\text{GdVO}_4:\text{Eu}^{3+}(0.05)$  and  $\text{GdVO}_4:\text{Eu}^{3+}(0.05), \text{Bi}^{3+}(0.05)$ .

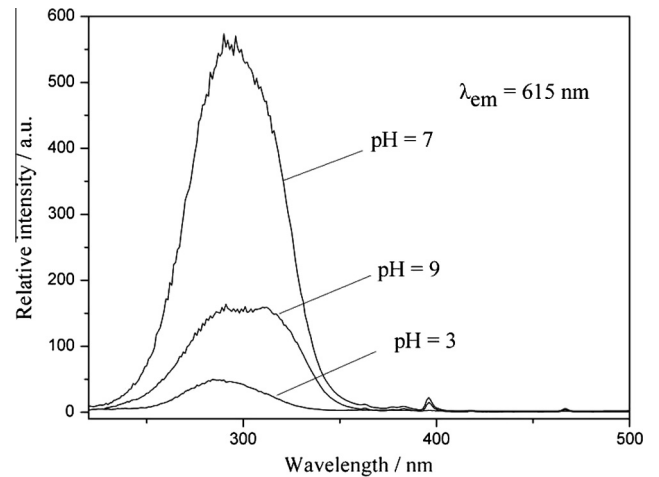


Fig. 2a. Excitation spectra of the  $\text{GdVO}_4:\text{Eu}^{3+}(0.05)$  at pH = 3, 7, 9.

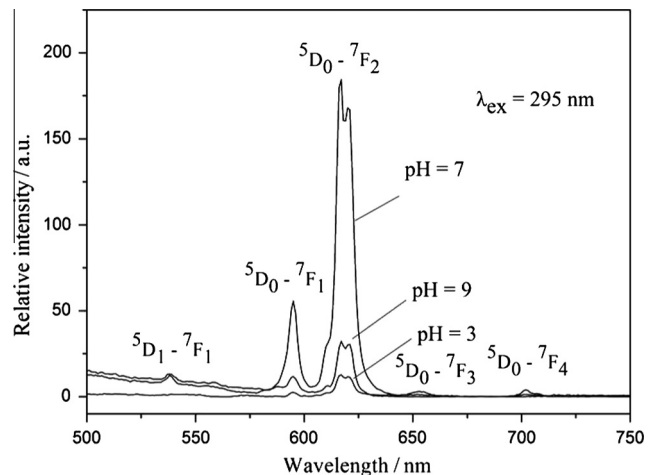


Fig. 2b. Emission spectra of the  $\text{GdVO}_4:\text{Eu}^{3+}(0.05)$  at pH = 3, 7, 9.

luminescence was achieved at pH = 7. It has been well accepted that nonradiative processes will frequently compete with radiative transitions. Based on the collected results, it has been considered that acidic and basic synthetic conditions would lead to higher vibrational frequency of the surroundings (such as hydroxide ions)

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