

Synthesis of nanocrystalline $\text{YVO}_4\text{:Eu}$ red emission phosphor with high fluorescence intensity by hydrothermal method using original vanadium–peroxo-citrate complex

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Vanadium peroxo-citrate complex was used for the first time for synthesis of $\text{YVO}_4\text{:Eu}$ red emission phosphor material by hydrothermal method. It was found that particles size can be efficiently controlled in the range of 60–400 nm by changing concentration of the solution utilized for the hydrothermal process. The nanocrystalline powders of $\text{YVO}_4\text{:Eu}$ prepared at 200°C for 2 h with post-synthesis heat treatment at 1000°C exhibited high fluorescence intensity comparable or better than one of the best commercially available $\text{YVO}_4\text{:Eu}$ phosphor synthesized by conventional solid state reaction method and having much larger grain size.

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1. Introduction

Eu^{3+} -doped YVO_4 ($\text{YVO}_4\text{:Eu}$) is one of the most important phosphor materials, which currently finds a variety of applications in cathode ray tubes (CRTs),¹⁾ fluorescent lamps,²⁾ and scintillator in medical image detectors.³⁾ Moreover, submicron $\text{YVO}_4\text{:Eu}^{3+}$ has significant promise for high definition TVs based on plasma display panels (PDP).⁴⁾ Comparing to the bulk materials, the application of nanosized phosphors has attracted considerable attention after the reported increase of quantum efficiency with decreasing particle size because of quantum confinement.^{5)–7)} Especial interest is paid to the possible applications of YVO_4 nanoparticles in biomedical imaging⁸⁾ since bright fluorescence can be efficiently excited by the conventional UV light sources, and yttrium vanadate has considerably less toxicity than CdS or CdSe nanoparticles currently used for the same purpose. Moreover, markers with different emission colors can be easily created by use of different rare-earth activator ions, e.g. Eu (red),^{9),10)} Sm (orange),^{9),11)} Dy (yellow),^{9),11),12)} Tm (blue),¹³⁾ Er (green).^{9),14)}

Active development in these two directions demands new synthetic methods suitable for preparation of YVO_4 nanosized materials, and it is expected that such nanosized phosphors should demonstrate brightness and color purity at least comparable to the current commercial products prepared by conventional solid state reaction. The latter requirement is especially difficult to address because usually submicron particles experience substantial fluorescence quenching due to higher concentration of surface defects.¹⁵⁾ Considering the environmental aspects and energy cost, the new synthetic methods should in addition operate at low temperatures, and they should yield the final product after short reaction times compared to conventional routes. Therefore, hydrothermal method appears to be the most promis-

ing synthesis approach due to the ability of controlling chemical homogeneity, purity, particles morphology, and phase composition of the powders under moderate conditions.

Hydrothermal method was successfully applied by Byrappa et al.^{16),17)} for growth of neodymium-doped YVO_4 single crystals. They have studied the influence of various experimental conditions including type of mineralizer, solution pH and process temperature on the growth of $\text{YVO}_4\text{:Nd}$ single crystals for possible laser applications. H. Wu et al.¹⁸⁾ demonstrated that hydrothermal method can be used for the synthesis of YVO_4 microcrystals as well, and strongly acidic solution favors formation of crystals with well-defined facets, while basic media results in precipitation of flakes of 5–50 nm size. $(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5$ nanowires and porous silicon as templates allowed X. Wu et al.¹⁹⁾ to prepare YVO_4 in the form of nanorods and microtubes by the hydrothermal method. The same group has succeeded in controlled preparation of rod-, olive- and pineapple-shaped nanocrystals of $\text{YVO}_4\text{:Eu}$ when different templates such as V_2O_5 nanowires, and cetyltrimethylammonium bromide (CTAB) were applied.²⁰⁾

In this work, we successfully prepared nanocrystalline $\text{YVO}_4\text{:Eu}$ red phosphor by a hydrothermal method using vanadium–peroxo-citrate complex for the first time as a starting reagent. The basic idea of this work was to explore the potential and chemistry of the vanadium peroxo-citrate complex for the synthesis of multi-component phosphors materials in the nanometer size range by hydrothermal method. The proposed technique allowed for the efficient particle size control, and prepared nanocrystalline $\text{YVO}_4\text{:Eu}$ red phosphor materials demonstrated high luminescence intensity.

2. Experimental procedure

2.1 Synthesis of Eu doped YVO_4 powder

Starting materials for synthesis were V_2O_5 (Kanto Chemicals Co., Inc., 99.0%), $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Kanto Chemicals Co., Inc., 99.0%), $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Kanto Chemicals Co., Inc., 99.0%) and H_2O_2 (Santoku Chemical Industries Co., Ltd., 30%). In the

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typical synthesis, V_2O_5 powder (0.5 mmol) was dissolved in the solution composed of hydrogen peroxide (5 ml) and distilled water (15 ml). During this process an exothermic reaction occurred and hydrogen peroxide partially decomposed releasing oxygen gas. A clear yellow solution was obtained after 10–15 min., however oxygen continued to evolve slowly from the solution for about 2 h, and the liquid color gradually turned into red. Then 2 mmol of citric acid was added and the sample was kept at room temperature for another 12 h after which its color changed to blue. Thereafter, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were added into the vanadium peroxo-citrate solution to establish Y:V:Eu mole ratio equal to 1:1:0.05. Next day the total volume was adjusted by distilled water to 100 ml (metal concentration was $C(\text{Y} + \text{V} + \text{Eu}) = 2.05 \times 10^{-3}\text{M}$). The solution was subsequently transferred into a Pyrex test tube, which was sealed in a stainless-steel autoclave and heat treated at 200°C for 15 h. After the autoclave had naturally cooled down to room temperature, the white precipitate was separated from the mother liquor by filtering and the powder was washed with distilled water several times followed by drying at room temperature. The prepared powders were annealed at 1000°C for 2 h. Additionally the effect of the concentration of starting solution on the $\text{YVO}_4\text{:Eu}$ powder characteristics and luminescence properties was investigated employing the solutions with three- and five times higher concentration of metal ions ($C(\text{Y} + \text{V} + \text{Eu}) = 6.15 \times 10^{-3}\text{M}$ and $C(\text{Y} + \text{V} + \text{Eu}) = 10.25 \times 10^{-3}\text{M}$) for hydrothermal synthesis.

2.2 Characterization

The crystallinity and phase purity of the prepared samples were analyzed by powder X-ray diffraction (XRD) using a Rigaku RINT-2200 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406\text{ nm}$) operating at 40 kV–30 mA, at a scanning rate of $2^\circ/\text{min}$ in the 2θ range of 10° – 60° . The morphology of the particles was examined by scanning electron microscopy (SEM, Hitachi S-4100). Excitation and emission spectra were measured by a Hitachi F-4500 fluorescence spectrophotometer.

3. Results and discussion

Figure 1 presents the XRD patterns of the samples prepared by the hydrothermal treatment of solutions with different starting

concentration of metals. All the diffraction peaks could be identified as belonging to the tetragonal zircon-type lattice of $\text{YVO}_4\text{:Eu}$ (JCPDS file 76-1649). No diffraction peaks due to secondary phases were found, which indicates that the YVO_4 products of high purity were successfully synthesized under current experimental conditions. **Figures 2(a)–(c)** show SEM micrographs of $\text{YVO}_4\text{:Eu}$ powders obtained by the hydrothermal method from the solutions with different starting concentrations of metal ions. In the case when $C(\text{Y} + \text{V} + \text{Eu}) = 2.05 \times 10^{-3}\text{M}$ metals concentration was used, the powders were composed of fine particles with diameters of approximately 40–60 nm (Fig. 2(a)). With increasing the starting concentration of metals in the solution the particles morphology undergoes remarkable change (Figs. 2(b)–(c)). The aggregated particles in Figs. 2(b)–(c) are formed by rod-like species with the diameter of about 30 nm and length of 220–250 nm. Moreover, the rod-like particles have internal structure, which seems to be composed of 5–7 cubic nanoparticles of about 40 nm size. Scanning electron microscope images (SEM) of $\text{YVO}_4\text{:Eu}$ powders after anneal-

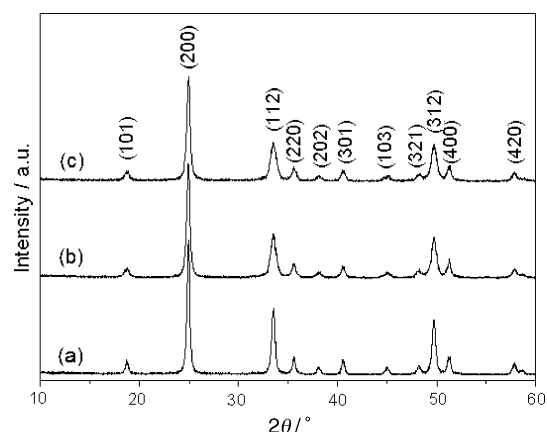


Fig. 1. XRD patterns of $\text{YVO}_4\text{:Eu}$ samples obtained by hydrothermal treatment of solutions with $C(\text{Y} + \text{V} + \text{Eu}) = 2.05 \times 10^{-3}\text{M}$ (a) $C(\text{Y} + \text{V} + \text{Eu}) = 6.15 \times 10^{-3}\text{M}$ (b) and $C(\text{Y} + \text{V} + \text{Eu}) = 10.25 \times 10^{-3}\text{M}$ (c) metals concentration. Metals ratio Y:V:Eu was 1:1:0.05 in all samples.

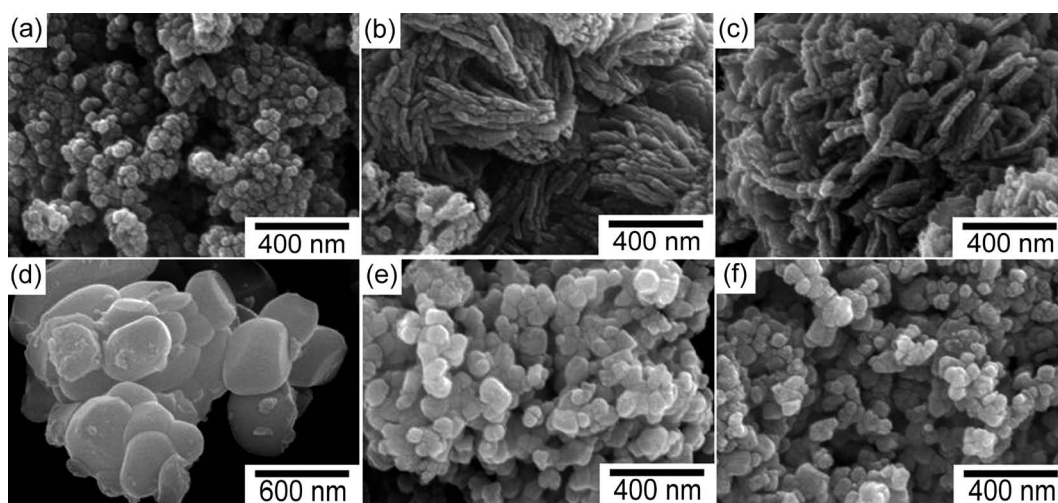


Fig. 2. SEM micrographs of as-prepared (a–c) and annealed at 1000°C (d–f) $\text{YVO}_4\text{:Eu}$ powders obtained via hydrothermal treatment of solutions with different metals concentration: $C(\text{Y} + \text{V} + \text{Eu}) = 2.05 \times 10^{-3}\text{M}$ (a,d); $C(\text{Y} + \text{V} + \text{Eu}) = 6.15 \times 10^{-3}\text{M}$ (b,e) and $C(\text{Y} + \text{V} + \text{Eu}) = 10.25 \times 10^{-3}\text{M}$ (c,f). Metals ratio Y:V:Eu was 1:1:0.05 in all samples.

ing at 1000°C are shown in Figs. 2(d)–(f). Such annealing is necessary to remove residual OH⁻ and carboxylic species from the solid state material that may quench fluorescence intensity of the phosphors. It was found that the powders obtained from C(Y + V + Eu) = 2.05×10^{-3} M solution after annealing consisted of larger grains of ~400 nm. The morphology of YVO₄:Eu powders obtained by using solutions with higher concentration experienced more dramatic transformation yielding nanoparticles with narrow size distribution of ~60 nm size. One may also notice from the set of micrographs in Figs. 2(d)–(f) that final particle size tends to decrease with increase of the metals concentration in the solution used for hydrothermal synthesis.

Figure 3 shows the excitation ($\lambda_{\text{em}} = 618$ nm) and emission spectra ($\lambda_{\text{ex}} = 271$ nm) of the annealed YVO₄:Eu powder synthesized by hydrothermal method followed by calcination at 1000°C for 2 h with metals concentration : C(Y + V + Eu) = 2.05×10^{-3} M. A strong broad band in the range of 250–350 nm was observed in the excitation spectrum, which is assigned to a charge transfer from the oxygen ligands (O²⁻) to the central vanadium ion (V⁵⁺) inside the VO₄³⁻ group, and charge transfer between Eu³⁺ and O²⁻.^{(21), (22)} The emission spectrum mainly consists of peaks assigned to ⁵D₀–⁷F₂ and ⁵D₀–⁷F₁ electron transitions in Eu³⁺ which give rise to strong photoluminescence with a dominant ⁵D₀–⁷F₂ red emission peak at 618 nm.⁽²³⁾

Figure 4 compares intensities of the emission peaks at 618 nm, which correspond to ⁵D₀–⁷F₂ transitions of Eu³⁺ ions in YVO₄ host, against one of the best commercially available YVO₄:Eu phosphors. One may notice that the emission intensity increased approximately 3–4 times after additional annealing of the as-prepared powders. Furthermore, emission intensities of the annealed samples strongly correlate with concentration of the starting solutions used for hydrothermal synthesis, and the observed intensity tends to decrease with increase of the starting solution concentration. It is likely that this relationship reflects the correlation between particle size and emission brightness, when phosphors with larger particles in Fig. 2 possess stronger emission intensity. This observation allows to conclude that concentration of metals in the starting solution for hydrothermal synthesis was the predominant factor for the preparation of YVO₄:Eu nanocrystallites with different size, and it affected their luminescence intensity.

In the conventional hydrothermal approach, which utilizes Y₂O₃ and V₂O₅ as starting materials and a mineralizer such as nitric acid, the formation and growth of YVO₄ crystals is relatively slow and it is controlled by solubility, diffusion and crystal growth during the recrystallization under hydrothermal conditions. In contrast, in the proposed synthesis method, the relatively rapid decomposition of the vanadium peroxo citrate complex during heating supplies high concentration of the vanadium containing anions, which triggers formation of YVO₄. Under such conditions, very high supersaturation can be achieved and it leads to the formation of the nanocrystalline product, whose morphology allows to assume that kinetics is determined by the nucleation process and the tiny nuclei agglomerate to minimize free surface energy. Generally, high speed of crystalline phase formation favors high concentrations of defects in the bulk, which is undesirable for the phosphor materials since defects act as non-radiative recombination centers suppressing the material fluorescence brightness. Nevertheless in our particular case even a short heat treatment at moderate temperature resulted in the annealing of defects and led to the substantial improvement of fluorescence intensity.

It is important to emphasize that YVO₄:Eu red emission phos-

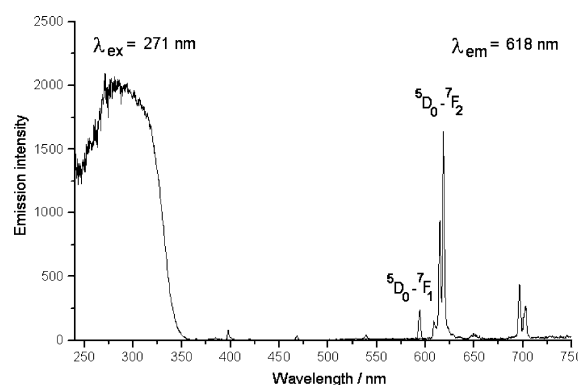


Fig. 3. Excitation and emission spectra of the annealed YVO₄:Eu powder synthesized by hydrothermal method followed by calcination at 1000°C for 2 h with metals concentration : C(Y + V + Eu) = 2.05×10^{-3} M.

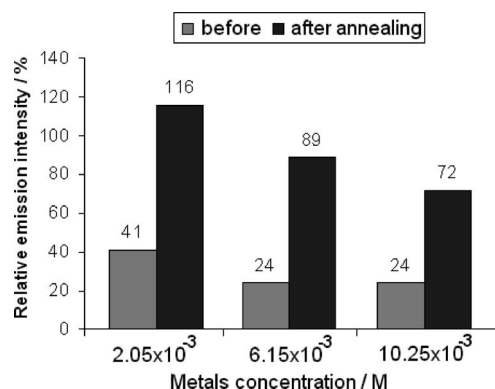


Fig. 4. Relative emission intensities of as-prepared and annealed YVO₄:Eu powders synthesized by hydrothermal method from the solutions with different concentrations. Metals ratio Y:V:Eu was 1:1:0.05 in all samples. 100% corresponds to the emission intensity of one of the best commercially available YVO₄:Eu.

phor material obtained by hydrothermal treatment of the solution with C(Y + V + Eu) = 2.05×10^{-3} M metals concentration demonstrated the best relative emission intensity, which was higher than emission intensity from one of the best commercially available YVO₄:Eu phosphors.

4. Conclusions

In conclusion, the proposed hydrothermal synthesis employing vanadium–peroxo–citrate complex is an excellent solution based method for preparation of nanocrystalline YVO₄:Eu red emission phosphors with high luminescent intensity. Further work on the optimization of the synthesis conditions and investigation of the effect of different hydroxycarboxylic acids on particles morphology and luminescence intensity is currently under way.

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