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Low temperature synthesis of nanocrystalline YVO_4:Eu via polyacrylamide gel method

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Abstract

Nanocrystalline europium doped yttrium orthovanadate (YVO_4:Eu) were synthesized by the polyacrylamide gel method. For a comparative evaluation, bulk YVO_4:Eu was prepared by solid-state reaction. On the basis of X-ray powder diffraction, scanning and transmission electron microscopy and luminescence measurements, the polyacrylamide gel method appears to be a more efficient method to prepare the luminescence materials YVO_4:Eu with high homogeneity, purity and luminescence intensity.

Keywords: YVO_4:Eu; Nanocrystalline; Luminescence; Polyacrylamide gel method

1. Introduction

The development of new types of flat panel and projection displays has created a need for optical phosphors with new or enhanced properties. Nanophase and nanocrystalline materials offer new possibilities for advanced phosphor applications because of their enhanced structural, electronic and optical properties [1,2]. YVO_4:Eu is an efficient red-emission phosphor and has been used in fluorescent lights and cathode ray tube (CRT) [3–5]. Recent studies show that nanosized YVO_4:Eu has significant promise in plasma display panels (PDP) [6,7]. Thus, a great deal of research work has been devoted to the method development for the synthesis of YVO_4:Eu particles of varied sizes in a controllable manner. Among them, the most common routes involve colloidal routes [7,8], solution combustion process [9], hydrolyzed colloid reaction [10], urea precipitation [11] and microemulsion-mediated synthetic process [12] and so forth. But until now, the scale-up of nanocrystalline YVO_4:Eu synthesis is still not realized for the confinement of the synthesis methods.

The polyacrylamide sol–gel process was a fast, cheap, reproducible and easily scaled up chemical route for obtaining fine powders of oxide [13]. This method is based on forming an auxiliary three-dimension (3D) tangled network, in which a solution of the respective chelated cations is soaked [14–16]. A steric entrapment of stoichiometric cation solution occurs in nanocavities formed inside the gel, that is, an homogeneous micro-solution with cations in the desired stoichiometry. A series of nanosized composites, such as $La_{1-x}MnO_{3\pm\delta}$ [15], $Zr_{0.84}Y_{0.16}O_{2-\delta}$ [14] and so on, have been successfully prepared by this method.

It was known that transition elements (V, Ni, Mn), rare earth elements (La, Y) and metalloid elements of the *p*-group (Bi) impede formation of the polyacrylamide gel because they react with acrylamide monomers to form complexes in which the element is bonded to their amino group [13]. For this reason, formation of gels containing a great deal of yttrium and vanadium, for example in YVO_4:Eu phase, was impossible. Therefore, in order to avoid this side reaction, a chelating agent (i.e., critic acid, ethylenediamine-tetraacetic) must be used to isolate the cations from the monomers. In our experiment, we adopted critic acid as a chelating agent to form the polyacrylamide gel, consequently the scale-up of nanocrystalline YVO_4:Eu synthesis can be achieved.

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In this paper we used two routes to prepare the YVO4:Eu phases: the usual solid-state reaction (SR) and a polyacrylamide gel method (PG). The concentration of Eu ions in the samples was kept constant at 1 mol% and this value was checked by chemical analysis. The properties of the powders were characterized and estimated by using X-ray diffraction (XRD), infrared absorption (IR) and photoluminescence (PL). Correlation with the microsurface was made by analyzing the surface morphology using scanning electron microscope (SEM) images.

2. Synthesis

2.1. Synthesis I (polyacrylamide gel method)

High-purity Y_2O_3 (99.99%), Eu_2O_3 (99.99%) and NH_4VO_3 (99.9%) were taken as the starting chemicals. Critic acid (CA, 99%) was used as chelating agent. Acrylamide ($CH_2{=}CHCONH_2$, 99%), N,N-methylene-bisacrylamide ($CH_2{=}CHCONHCH_2NHCOCH{=}CH_2$, 99%) and α,α' azoisobutyronitrile (AIBN, $C_8H_{12}N_4$, 98%) were used as polymerization agents for polymerization process.

The PG process used to prepare nanosized YVO4:Eu is as follows. At first, 0.903 g of Y_2O_3 (4.0 mmol), 0.0142 g of Eu_2O_3 (0.04 mmol) and 0.945 g of NH_4VO_3 (8.08 mmol) were dissolved in 40 mL of dilute HNO_3 (2 mol/L) to prepare the solution. After their dissolution, the cations of transition (V), rare earth (Y, Eu) elements were complexed by the addition of critic acid, in the ratio of 1:1 and the pH was adjusted to 6–7 to ensure the cations complex completely and stirred continuously to convert them to stable V- and Y, Eu-CA complexes. Subsequently, the monomers of acrylamide (3 g) and the cross-linker N,N-methylene-bisacrylamide (0.429 g) were added into the clear solution, in proportions indicated in Ref. [13]. The resulting solution was heated in a water bath and during the whole process, the system was continuously stirred. The solution became gradually transparent with rising temperature. When the temperature reached about 80°C, a small amount of compound initiator AIBN ($C_8H_{12}N_4$) was added to the solution and polymerization occurred quickly and transparent polymeric resin was obtained without any precipitation. At last, the gel was dried at 100°C for 24 h to yield a xerogel. The xerogel was heated in a laboratory furnace at 300°C to burn out the organic residues and calcined at higher temperature (600–1200°C) to obtain different samples.

2.2. Synthesis II (solid-state reaction)

The stoichiometric amounts of Y_2O_3 (0.224 g, 0.99 mmol), Eu_2O_3 (0.0352 g, 0.01 mmol) and NH_4VO_3 (0.234 g, 2 mmol) was mixed with ethanol in an agate mortar. The mixture was calcined at 800°C for 10 h in air. After grinding the powders were pressed into pellets and calcined at 1000°C, 1100°C and 1200°C for 10 h in air, respectively.

2.3. Experimental section

The diffractometer employed was a Rigaku D/MAX RB X-ray diffractometer using Cu$K\alpha$ ($\lambda = 1.5418$ Å) Cu radiation. IR spectra were obtained on a JASCO FTIR 480 plus spectrophotometer with the KBr pellet technique. C, H, N contents in the calcined powders were obtained on a PE2400CHN elemental analyzer.

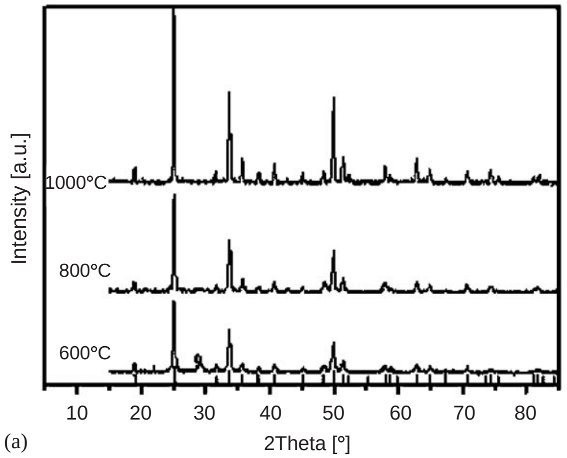
The SEM images were performed on a KYKY-1000B scanning electron microscope. Micrographs were recorded using JEM-2000Ex transmission electron microscope (TEM) under a working voltage of 100 kV. Specimens were prepared by dispersing small amounts of the powder in ethanol.

The luminescence spectra were taken on a JASCO FP-6500 spectrofluorimeter equipped with a 450 W xenon lamp as the excitation source at room temperature. Relative luminescence efficiencies were estimated by using the 320 nm radiation.

3. Results and discussion

3.1. X-ray powder diffraction

The XRD patterns of YVO_4:1%Eu (polyacrylamide gel method) sintered at different temperatures between 600°C and 1000°C are shown in Fig. 1(a). Compared with the characteristic YVO_4 pattern (JCPDS 17-0341), the patterns of the powder obtained at 600°C shows the coexistence of other crystalline phases (e.g., Y_2O_3, V_2O_5) which are transformed at higher temperature into YVO_4 At 800°C, the XRD pattern shows YVO_4 to be the only crystalline component, which is significantly lower than the crystallinity temperature of the samples prepared by SR (>1000°C) [17]. The reasons for the lower crystallinity temperature of the PG synthesis may be attributed to two aspects. Firstly, the PG synthesis provides a molecular level mixing of elements because the metal ions are completely dissolved in polymeric resin during the process. This fact reduces the diffusion path (up to nanometric scale) for obtaining the desired material and, as a consequence, needs lower temperature synthesis than by SR [15]. In addition, in this polyacrylamide gel, there are a great deal of polymers and NO_3^- existing. It is well known that the polymers can act as fuels and NO_3^- as an oxidant. That is, during the pre-calcination process, the fuel can be ignited at low temperature (about 300°C) and reach high temperatures in a short period of time, which can possibly accelerate the



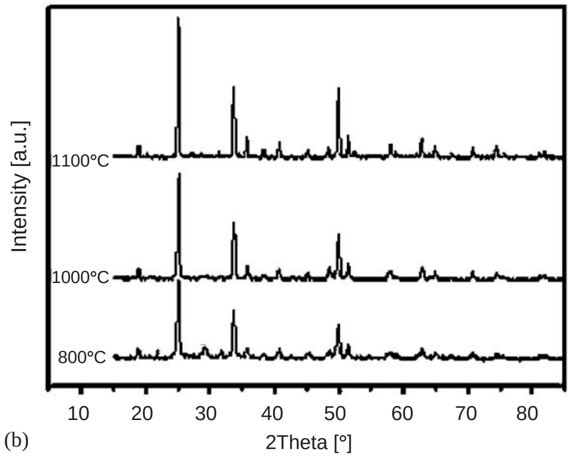


Fig. 1. Temperature dependent XRD traces of $Y_{0.99}VO_4:Eu_{0.01}$ obtained by: (a) PG method and (b) SR routes (O indicate peaks due to Y_2O_3, V_2O_5). The vertical lines correspond to the JCPDS 17-0341.

crystallization process [18]. Further heat treatment indicated no thermal degradation or crystalline of any undesired or contaminating phase could be identified. In both cases the peak pattern corresponds to the characteristic YVO_4 pattern (JCPDS 17-0341) and no formation of the crystalline dopant $EuVO_4$ was observed.

For a comparative evaluation of sol–gel methods and SR, the XRD profiles of the materials obtained by thermolysis of a physical mixture of ammonium metavanadate and yttrium oxide are shown in Fig. 1(b). From the figure, it can be seen the samples prepared by this method need higher heat treatment (1000°C) to obtain the monophase YVO_4:Eu.

3.2. Infrared spectroscopy

It is well known [19,20] that the sol–gel process in which metal hydroxide intermediates are formed, yields materials with residual hydroxyl groups. The hydroxyl groups can quench the luminescence efficiently via non-radiative, de-excitation process due to their high-energy vibration mode ($\sim 3500\,cm^{-1}$) [19].

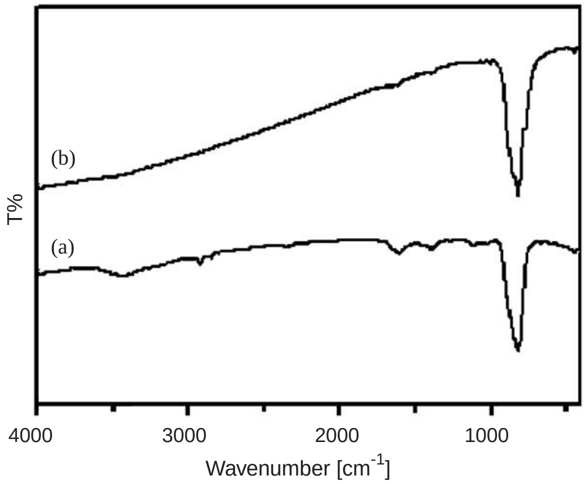


Fig. 2. FT-IR spectra of YVO4:Eu prepared by the polyacrylamide gel method, heat treatment (a)at 800°C and (b) at 1000°C.

Fig. 2(a) shows the FTIR spectrum of YVO_4:Eu samples prepared by polyacrylamide gel method after heat treatment at 800°C for 4 h. The spectrum shows typical spectral characteristic of VO_4^{3-} with strong IR band [21] in the ranges 780–920 cm^{-1}. Additionally, weak frequencies in the ranges 3000–3500 and 1100–1650 cm^{-1} are assigned to C–H, C–O, O–H and nitrate stretching arising from organic residual [22]. After treatment at 1000°C for 4 h the absorption of VO_4^{3-} becomes stronger in the spectrum (Fig. 2(b)) and other weak absorptions almost disappear. The result suggests that these weak absorptions are only due to unreacted organic residues. However, we could still observe weaker bands at 1100–1650 cm^{-1}, which are probably due to the fact that the spectra were not recorded in situ and the absorption of H_2O, CO_2 from the ambient atmosphere has occurred. The presence of organic residues after heat treatment for 4 h at 800°C is also supported by the element analysis which shows a negligible amount of carbon (0.15%), hydrogen (0.12%) and nitrogen (0.06%). Such trifle residues cannot induce the quenching of the luminescence which is also supported by the optical data (see Fig. 6).

3.3. Scanning and transmission electron microscopy

The SEM photograph of the sample recorded at 3500 × magnification (Fig. 3a) shows that the PG sample heated at 800°C exhibits homogeneous aggregates with a flake-like aspect which are composed of a large number of small grains. In addition, pores and voids can also be seen, which result probably from the

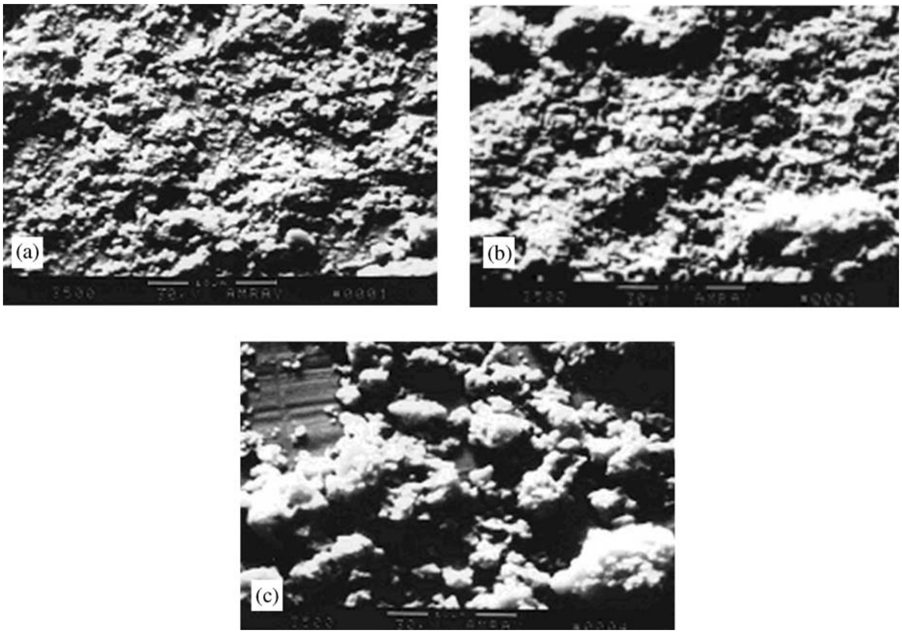


Fig. 3. Scanning electron micrograph of YVO_4:Eu samples obtained by different routes. The PG method (a) heated at 800°C for 4 h, (b) heated at 1000°C for 4 h. The SR method, (c) heated at 1000°C for 10 h; ×3500.

escaping gases during calcinations. The fine grains which consist of the aggregates were investigated with the TEM image (Fig. 4). The image showed that grains with spherical morphology are homogeneous and well defined. The grain size is nearly 20 nm. Fig. 3(b) revealed that there is no significant change in the *morphology* even if the PG samples were sintered at temperatures higher than 800°C. In contrast, the SEM images of the SR sample were observed from Fig. 3(c). As can be seen, the grains are partially agglomerated and irregular. The results indicated that the presence of carbon network/cages in the polyacrylamide gel can effectively prevent particles agglomeration even when heat treated at higher temperature.

3.4. Optical measurements

Fig. 5 shows typical PL emission spectra of both SR and PG samples. The measurements were performed under the same conditions for both the luminescent materials. As shown in this picture, the emission spectra were the same with the highest peak position at 619 nm, quite similar to other groups [7,23]. The spectra are dominated by the emission from the europium ions. Due to the absence of an inversion symmetry at the Eu^{3+} lattice site (D_{2d} symmetry), force electric-dipole transitions ${}^5D_0$–${}^7F_{2,4}$ are strong while ${}^5D_0$–${}^7F_{1,3}$, magnetic dipole transitions, are relatively weak. From the emission spectra, it is obvious that the Stark splitting pattern observed in the various Eu^{3+} levels are the same both in SR and PG samples. This suggests that the local

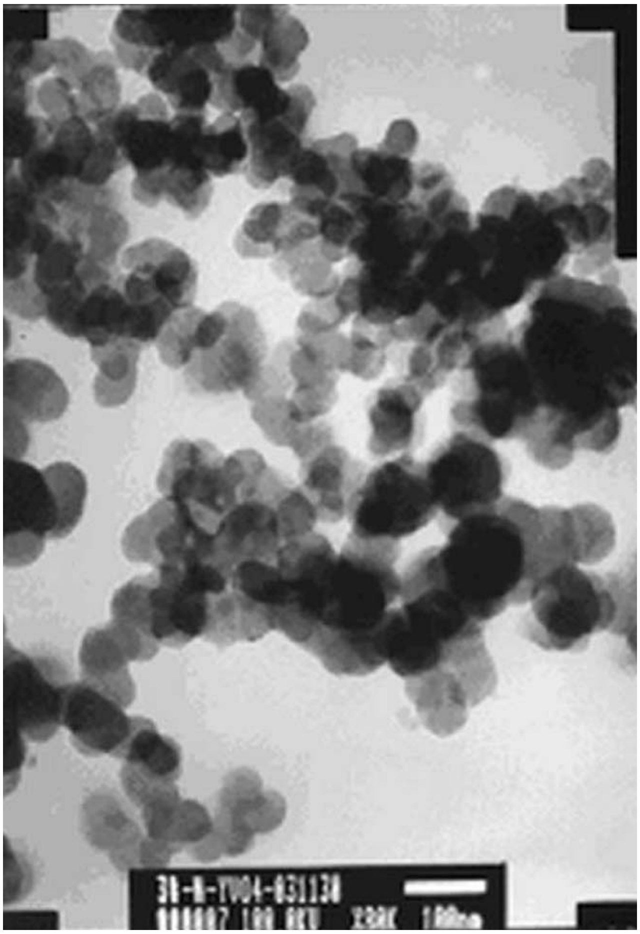


Fig. 4. Transmission electron micrograph of YVO_4:Eu samples obtained by the PG method, calcination at 800°C for 4 h; ×80,000.

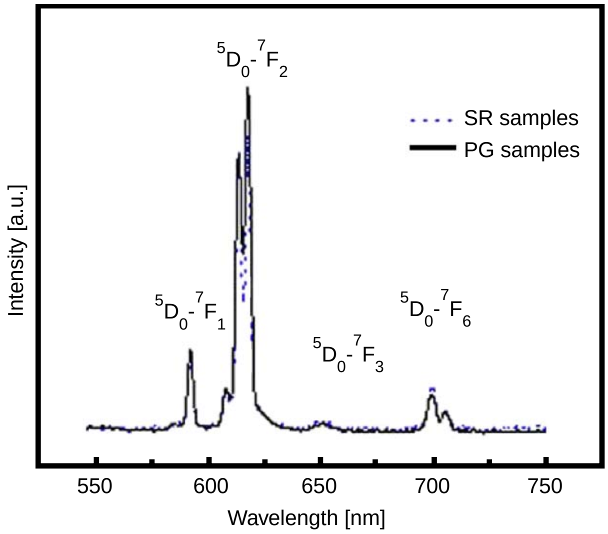


Fig. 5. Luminescence spectra of YVO_4:$Eu_{0.01}$ at 298 K for samples prepared by PG method (800°C for 4 h) and SR method (1000°C for 10 h).

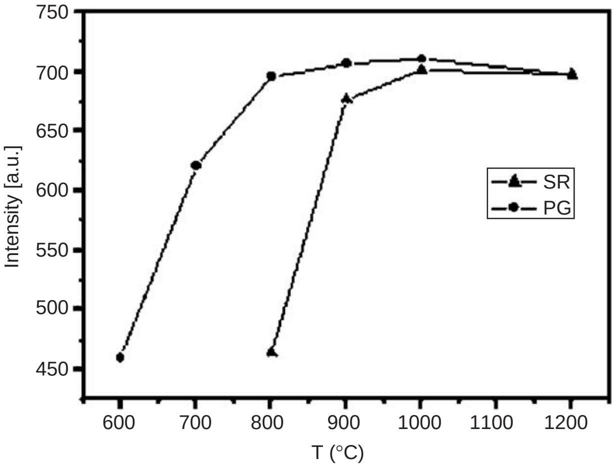


Fig. 6. Evolution at 298 K of the intensities of $^5D_0$–$^7F_2$ luminescence of Eu^{3+} in YVO_4 versus the sintering temperature for the two synthesis method.

symmetries in both nanocrystalline and bulk phosphors are the same [23]. Moreover, in both samples, the relative luminescence intensities of the main transitions are almost the same.

Fig. 6 shows the evolution of the $^5D_0$–$^7F_2$ luminescence intensities recorded at 298 K for YVO_4:Eu against sintering temperature for the two synthesis methods. For the transition, an increase of the sintering temperature leads to an increase of the emission intensity for the two samples. Compared with the other sample, the luminescence intensity of the PG sample reaches the maximum at lower sintering temperature (800°C). However, with the further increase of sintering temperature, the difference between the intensities of the two samples decreases. In particular, when sintered at a temperature higher than 1000°C, the intensities of the samples remain identical.

The results indicate that the sample prepared by the PG method has good phase crystalline at 800°C, whereas sintering to the same extent is achieved only above 1000°C for the other synthesis method.

4. Conclusion

Homogeneous gels achieved by the polyacrylamide gel method have been used for the low temperature synthesis of nanocrystalline europium doped yttrium orthovanadate. It is clear that the polyacrylamide gel method provides a more effective way to prepare nanocrystalline YVO_4:Eu. The advantages of the polyacrylamide gel method, over other methods include lower temperature processing, higher sample homogeneity and purity and easy scale-up. Furthermore, the samples prepared by the polyacrylamide gel method display strong luminescence intensity.

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