

Synthesis and characterization of Eu doped Y_2O_3 particles by a glycothermal processing

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Abstract Eu doped Y_2O_3 particles were prepared under high temperature and pressure conditions by precipitation from metal nitrates with aqueous potassium hydroxide. The Eu doped Y_2O_3 particles were obtained at 270°C. The average particle size of synthesized powders was below 1 μ m. The X-ray diffraction pattern shows that the synthesized particles were crystalline. This study has shown that the synthesis of Eu doped Y_2O_3 crystalline particles is possible under glycothermal conditions in ethylene glycol solution. The effects of synthesis parameters, such as the concentration of starting solution, pH of starting solution, reaction temperature and time, are discussed.

Keywords Eu doped Y_2O_3 particles · Glycothermal processing

1 Introduction

Rare earth phosphors were extensively applied in luminescence and display, such as fluorescence lamps, projection television tubes, field emission display (FED), and plasma display panels (PDP) [1, 2]. Among them, the optical properties of europium ions present many interests because they are used as visible and UV radiation sources, some

of them being particularly important for lasers and optical communication devices [3, 4]. Europium is commonly available as trivalent state while doping in matrix, and therefore it is necessary to have some methods of reducing it to the low valent chemical state [5]. Y_2O_3 is a material of interest in ceramic technology for a variety of applications. It belongs to a relatively large group of sesquioxides with the C-type cubic structure, which is a defect analogue of the cubic fluorite structure ($a_{\text{C-type}} \sim 2 \times a_{\text{fluorite}}$) [6, 7].

Eu doped Y_2O_3 is one of the most useful red emitting phosphors with almost 100% quantum efficiency [8]. The luminescence properties of Eu^{3+} doped in Y_2O_3 were reported long ago by Forest and Ban [9, 10], who found the existence of two types of Eu^{3+} sites in Y_2O_3 . Recently, it was also reported that the luminescence spectra of nano-size sample are quite different from bulk type or several micron size samples [11, 12]. The resolution of images is related closely to particle size of phosphors. Smaller particles are favorable for higher resolution. In Eu^{3+} doped Y_2O_3 , the electronic transition from 2p orbital of O^{2-} to the 4f orbital of Eu^{3+} forms excited charge transfer (CT) band, in which excited to luminescence with great efficiency and mostly used as the excitation level for commercial phosphor [13–15].

Over the last decade, many methods for synthesis of Eu doped Y_2O_3 phosphors have been reported, including solution combustion method [16], sol–gel method [17], spray pyrolysis method [18], hydrothermal synthesis [19], and precipitation method [20]. Among the many different methods listed above, hydrothermal synthesis meets the increasing demand for the direct preparation of crystalline ceramic powders and offers a low temperature alternative to conventional powder synthesis technique in the production of anhydrous oxide powders. This technique can produce fine, high purity, stoichiometric particles of single and

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multicomponent metal oxides [21]. Furthermore, if the process conditions such as solution pH, solute concentration, reaction temperature, reaction time, seed materials, and the type of solvent are carefully controlled, ceramic particles of the desired shape and size can be produced [22].

The objective of this study is to prepare the Eu doped Y_2O_3 particles by a glycothermal process, and to investigate the effects of the processing conditions on the formation, morphology, and phase of the powders.

2 Experimental procedure

The preparation sequence of Eu doped Y_2O_3 particles is schematically illustrated in Fig. 1. Eu doped Y_2O_3 precursors were precipitated from 0.05 M $Y(NO_3)_3 \cdot 6H_2O$ and 0.0026 M $Eu(NO_3)_3 \cdot 6H_2O$ solution by slowly adding KOH with rapid stirring in which the pH of starting solutions varied between 7 and 9. The precipitated Eu doped Y_2O_3 precursors were washed by repeated cycles of centrifugation and re-dispersion in water. Washing was performed for a minimum of three times in water. Excess solution was decanted after the final washing and the wet precursor was re-dispersed in 200 ml ethylene glycol under vigorous stirring. The resulting suspension was placed in a 1,000 ml stainless steel pressure vessel. The vessel was then heated to the 270°C at a rate of 5°C/min for 6 h. The reaction products were washed at least five times by repeated cycles of centrifugation and re-dispersion in ethanol and deionized water. The characterization of the recovered powders was observed using X-ray diffraction

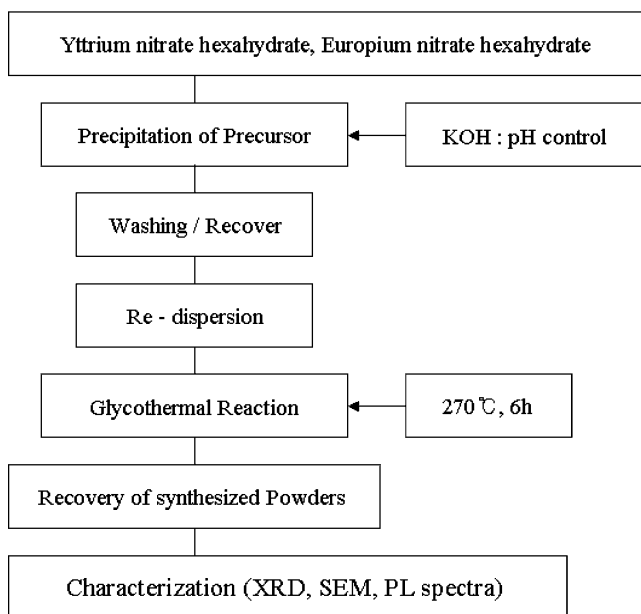


Fig. 1 Experimental flow chart of synthesized Eu doped Y_2O_3 particles by a glycothermal processing

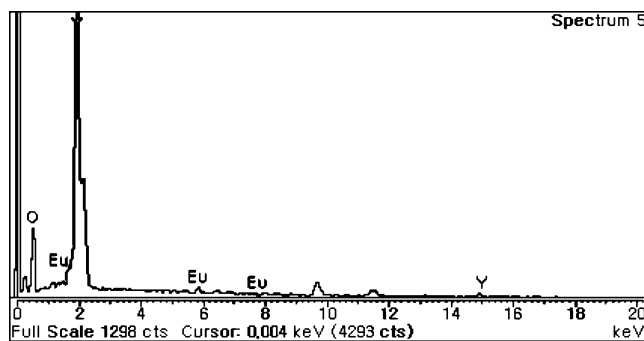


Fig. 2 EDS analysis of synthesized powders at 270°C by a glycothermal processing. (pH 7)

(XRD, X’pert MPD 3040), scanning electron microscope (SEM, JSM-5610), and Photoluminescence spectra (Spectra physics, Ar-laser 488 nm).

3 Results and discussion

Glycothermal process conditions such as pH, reaction temperature and time, have significant effects on the formation, phase component, morphology and particle size of Eu doped Y_2O_3 particles. Figure 2 shows the chemical composition of synthesized particles at 270°C by a glycothermal processing. It was found that the atomic percent of europium and yttrium was 4.7% and 95.3%, respectively. This result is similar to the chemical composition of yttrium (atomic percent 95%)/europium (atomic percent 5%) solution prepared to synthesize particles in an aqueous solution.

Figure 3 shows the X-ray diffraction pattern of Eu doped Y_2O_3 particles synthesized at 270°C by a glycothermal processing. The crystalline phase of the synthesized

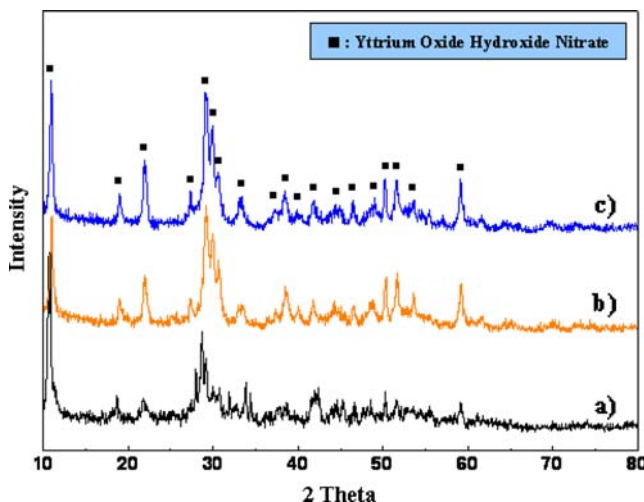


Fig. 3 XRD patterns of synthesized powders at 270°C by a glycothermal processing; (a) pH 7 (b) pH 8 (c) pH 9

powders was yttrium oxide hydroxide nitrate. Eu doped Y_2O_3 should be formed by a condensation reaction at higher temperature because reaction is not complete. Figure 4 shows the X-ray diffraction pattern of Eu doped Y_2O_3 particles synthesized at $270^\circ C$ after heat treatment at $600^\circ C$. The phase of the synthesized powders was crystalline. It was found that the peak intensity of the Eu doped Y_2O_3 decrease as the pH increase. This may be due to the grain size of the synthesized decreased with pH solution was increased (Figs. 5 and 6).

Figure 5 shows the microstructure of Eu doped Y_2O_3 particles synthesized at $270^\circ C$ for 6 h. The average particle size of synthesized powders was in the range of $0.1 \sim 2 \mu m$ with pH of solution were 7, 8, and 9. The average size of the synthesized particles was decreased with pH of solution increased. Figure 6 shows the microstructure of Eu doped Y_2O_3 particles heat treatment at $600^\circ C$. The average particle size of the synthesized powders was decreased because the bonding form was changed from hydroxide to oxide.

Figure 7 shows PL emission spectra of Eu doped Y_2O_3 particles synthesized at $270^\circ C$ for 6 h. The photoluminescence spectra of the Eu doped Y_2O_3 particles were measured by using Ar laser 488 nm. Before heat treatment procedure, a part of emitting light spectrum corresponds with doped Eu^{3+} in cube decision of Y_2O_3 . Because a part of Y_2O_3 has the structure of cubic decision but almost of it remains the form of amorphous phase. This result can know from XRD results [23]. Figure 8 shows PL emission spectra of Eu doped Y_2O_3 particles heat treatment at $600^\circ C$. The spectra was described by the well-known $^5D_0-^7F_2$ line emissions at about 611 nm. This corresponds to the red emission. With increasing the value of pH, the lumines-

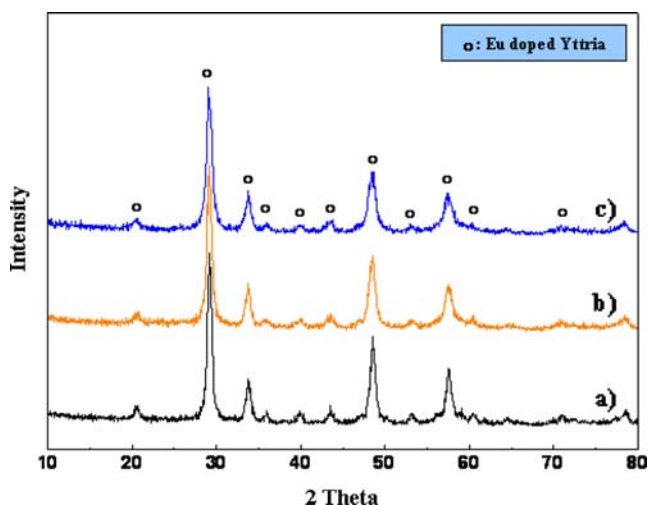


Fig. 4 XRD patterns of synthesized powders at $270^\circ C$ by a glycothermal processing after heat treatment at $600^\circ C$; (a) pH 7 (b) pH 8 (c) pH 9

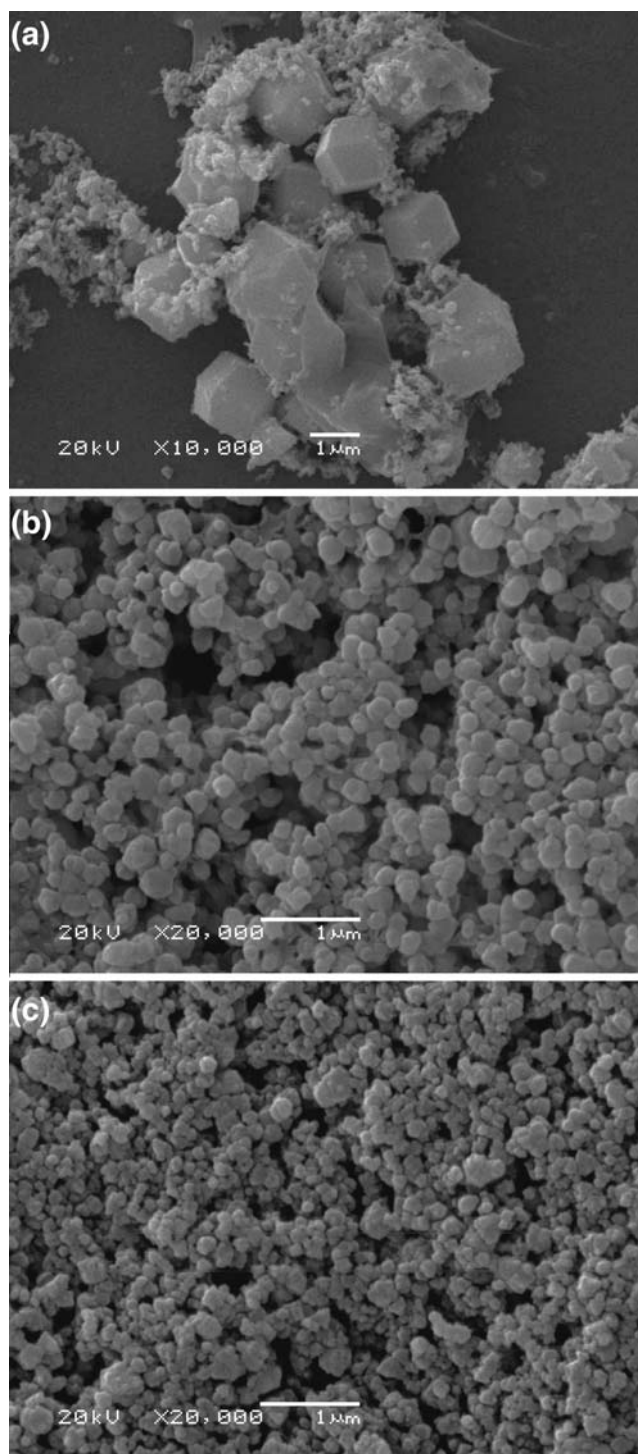


Fig. 5 SEM micrographs of synthesized powders react at $270^\circ C$ for 6 h; a pH 7, b pH 8, c pH 9

cence intensity of synthesized powders was increased. We confirmed that the particle is more decreased, the luminescence intensity is more increased. The origin of these transitions can be understood by considering the energy level diagrams for Eu^{3+} ion in a Y_2O_3 lattice. An Eu^{3+} ion

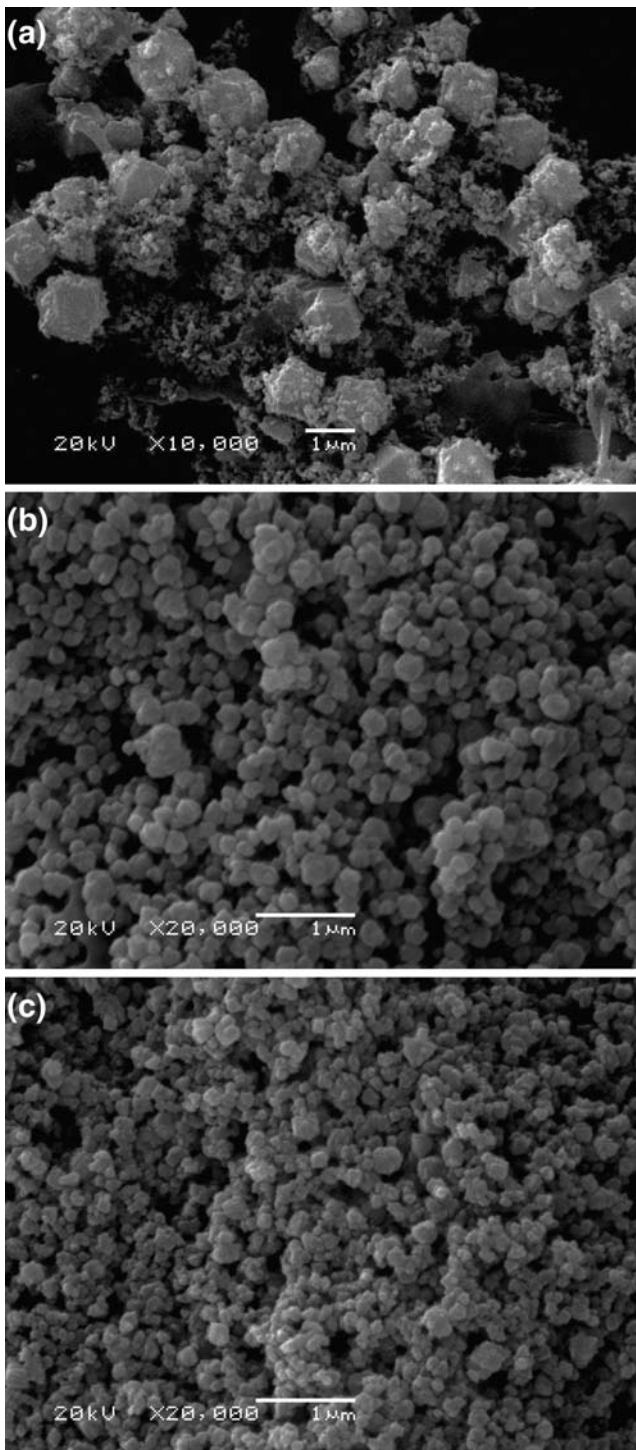


Fig. 6 SEM micrographs of synthesized powders heat treatment at 600°C; a pH 7, b pH 8, c pH 9

in a Y_2O_3 can occupy two types of symmetry sites: a low symmetry site of C_2 and a high symmetry site of C_{3i} . In a unit cell, there are 24 C_2 sites and 8 C_{3i} sites. All things being equal, it is likely that Eu^{3+} ions will occupy these two types of sites with approximately equal probability [24].

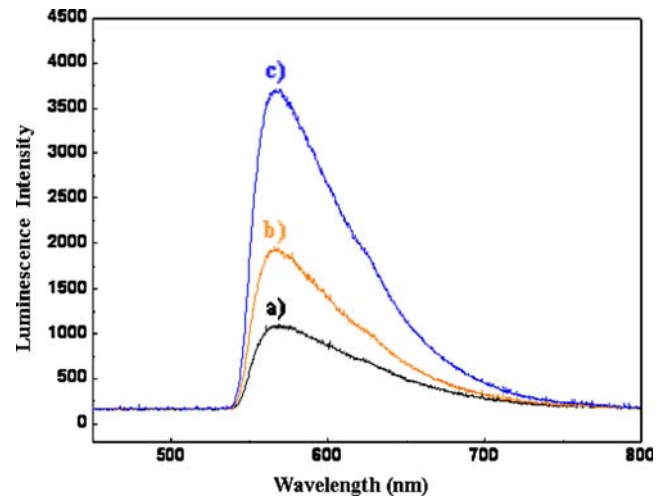


Fig. 7 PL emission spectra of synthesized powders react at 270°C for 6 h; (a) pH 7 (b) pH 8 (c) pH 9

4 Conclusions

Eu doped Y_2O_3 particles were obtained in ethylene glycol solution reaction at 270°C for 6 h. The average particle size and distribution of the synthesized Eu doped Y_2O_3 particles were below 2 μm and narrow, respectively. The average size of the synthesized particles was decreased with pH of solution increased. The phase of the synthesized powder was crystalline. It was found that the $^5D_0-^7F_J$ transitions of Eu^{3+} also appear to occur, and the dominant emission at about 611 nm which is assigned to the $^5D_0-^7F_2$ transition. With increasing the value of pH, the luminescence intensity was increased.

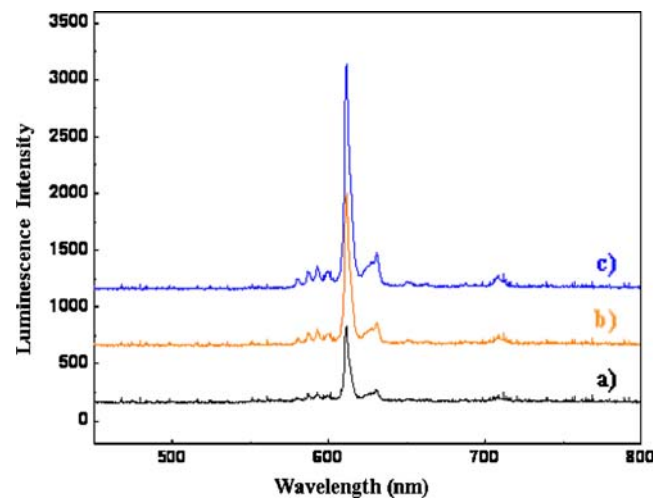


Fig. 8 PL emission spectra of synthesized powders heat treatment at 600°C; (a) pH 7 (b) pH 8 (c) pH 9

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