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Structure-induced change of luminescent properties in the hydrated and dehydrated YPO_4:Tb

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Abstract

The wet-chemistry route is used to synthesize well-crystalline hydrated YPO_4:Tb, which cannot be obtained by conventional routes. The phase transformation from the hydrated YPO_4:Tb with monoclinic churchite structure to the dehydrated YPO_4:Tb with tetragonal xenotime structure occurs in the annealing process. The structural change induced by the phase transformation results in a remarkable difference in the luminescent efficiency. The correlation of the structure with the luminescent property is well investigated. Based on these results, it is proposed that the structural control is an efficient way to modify the luminescent properties.

Keywords: Wet-chemical route; YPO_4; Luminescence; OH

1. Introduction

Rare earth ion doped compounds have attracted great interest due to a wide variety of applications, including phosphors [1,2], lasers [3], scintillators [4], and amplifiers for fiber-optic communication [5]. Rare earth phosphates doped with rare earth ions are mainly used as phosphors in lighting and display applications. For example, Ce and Tb co-doped $LaPO_4$ is used in fluorescent lamps as an emitter of green light due to its high chemical stability and high luminescence quantum efficiency [6,7]; and, recently, Tb activated YPO_4 has been a new type of efficient phosphor used in plasma display panels owing to high absorption and strong resistance to vacuum ultraviolet light radiation [8,9].

For these materials, the composition and microstructure of the host play important roles in controlling the chemical, physical, optical, and electronic properties of materials [10–12]. It is shown that the composition and structure are strongly affected by the synthetic routes and parameters. In the case of the synthesis of rare earth phosphates, solid-state and wet-chemistry routes have been involved to date. Generally, wet-chemistry synthetic routes, such as sol–gel [13,14], precipitation [9,15,16], and hydrothermal method [11,17] are superior to solid-state reaction. Wet-chemistry routes may provide several adjustable synthetic parameters such as pH value, reaction temperature, ripening time, and solution concentration, by which, the size, shape, morphology, and structure of synthesized materials can be effectively controlled. Therefore, it is expected that materials with novel or enhanced properties could be synthesized based on wet-chemistry technique. Additionally, the compound prepared by solid-state reaction is very difficult to achieve compositional homogeneity. However, wet-chemistry synthetic route can achieve molecular-level reaction, thus a good homogeneity is obtained; especially for doped rare earth phosphates used as luminescent materials, the doped ions are able to be uniformly dispersed in the crystal lattice, which contributes to the enhanced luminescent properties. Furthermore, conventional solid-state reaction needs a high-temperature calcination for long in order to get a well-crystalline phase. But the synthesis by wet-chemistry route is commonly at a relatively low temperature. In this case, the structure and property evolution from a low-temperature phase to a high-temperature one can be

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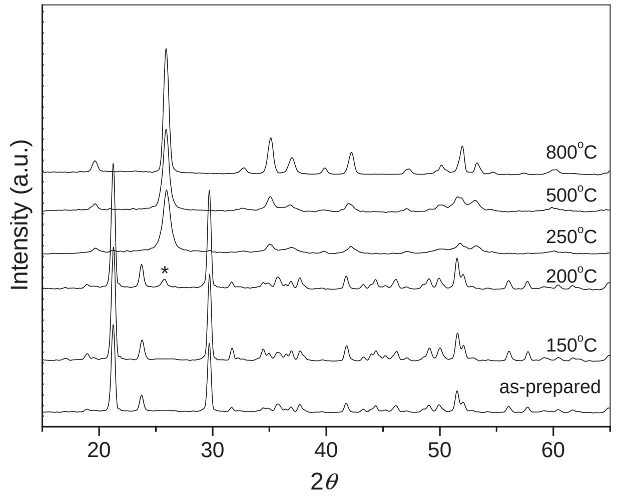

Fig. 1. XRD patterns of the as-synthesized product and those annealed at various temperatures.

observed. Therefore, it provides an efficient means to control the structure and properties with each other. In conclusion, wet-chemistry route seems to provide an alternative and intriguing strategy to generate synthetic tunability, structural and quantitative tailoring, material diversity.

This work aims at an investigation on the correlation of phase structure with the luminescent efficiency. Hydrated YPO_4:Tb was synthesized by a simple wet-chemistry route. The as-synthesized product experiences phase transformation during the annealing process, resulting in the formation of different crystal structure. The correlation between the structure and luminescent efficiency before and after phase transformations is investigated.

2. Experimental

Tb-doped hydrated YPO_4 was synthesized by a simple wet-chemistry route. Appropriate amounts of high purity of Y_2O_3 and Tb_4O_7 were dissolved in concentrated HNO_3 to form $(Y,Tb)(NO3)_3$ solution, to which, appropriate volume of $(NH_4)_2HNH_4$ aqueous solution was added slowly. The final pH value was adjusted to be 2. After being well stirred at 50 °C for 5 h, the white precipitates were obtained, and filtered, washed for several times with deionized water, and then dried at 80 °C in air. The dried precipitates were annealed at various temperatures in a reducing atmosphere to prevent the oxidation of Tb^{3+}.

XRD studies were conducted on a Rigaku D/max-2000 X-ray powder diffractometer using Cu K α radiation. The excitation and emission spectra were measured with a Hitachi F-4500 fluorescence spectrometer at room temperature. The fluorescent decay spectrum was measured with a third-harmonic generator pumped by the pulsed Nd:YAG.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-synthesized product and those annealed at various temperatures. It is noted that, the as-synthesized sample is well-crystalline, and all of the peaks could be well indexed to the monoclinic $YPO_4 \cdot 2H_2O$:Tb with churchite structure and space group I2/a (JCPDS File No. 85-1842). This structure remains for the sample annealed at 150 °C. As the annealing temperature increases to 200 °C, a new diffraction peak is observed, as marked by a specific symbol in Fig. 1. This means that the impurity phase is involved in the monoclinic phased $YPO_4 \cdot 2H_2O$:Tb. Further increasing annealing temperature up to 250 °C, the phase with monoclinic structure has almost totally disappeared, a new phase, all of whose peaks could be well indexed to tetragonal dehydrated YPO_4:Tb with xenotime structure and space group $I4_l$/amd (JCPDS File No. 84-0335), is observed. This indicates that the phase transformation from the hydrated YPO_4:Tb with monoclinic churchite structure to the dehydrated YPO_4:Tb with tetragonal xenotime structure occurs. With further increase of annealing temperature up to 800 °C, it remains

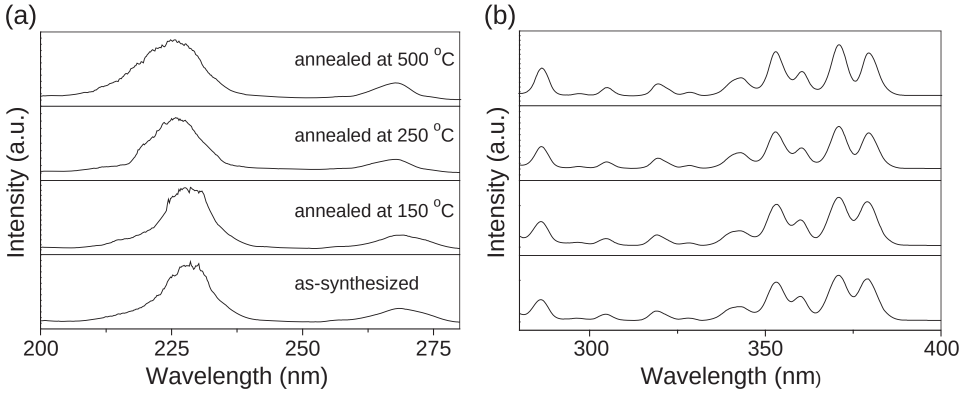

Fig. 2. Excitation spectrum of as-prepared sample and those annealed at various temperatures by monitoring the $^5D_4$–$^7F_5$ emission of Tb^{3+}. The as-synthesized sample and that annealed at 150 °C are monoclinic phased $YPO_4 \cdot 2H_2O$:Tb, and the samples annealed respectively at 250 and 500 °C are tetragonal phased YPO_4:Tb. (a): 4f–5d transition of Tb^{3+}; (b): 4f–4f transition of Tb^{3+}.