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Structure-induced change of luminescent properties in the hydrated and dehydrated YPO₄: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. © 2005 Elsevier B.V. All rights reserved.

Keywords: Wet-chemical route; YPO4; 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 LaPO₄ 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 YPO₄ 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

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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 lowtemperature phase to a high-temperature one can be



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 YPO₄: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 HNO₃ to form (Y,Tb)(NO3)₃ solution, to which, appropriate volume of (NH₄)₂HNH₄ 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 Tb³⁺.

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 YPO₄·2H₂O: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 YPO₄:Tb with xenotime structure and space group I4₁/amd (JCPDS File No. 84-0335), is observed. This indicates that the phase transformation from the hydrated YPO₄:Tb with monoclinic churchite structure to the dehydrated YPO₄: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 ${}^{5}D_{4}-{}^{7}F_{5}$ emission of Tb³⁺. The as-synthesized sample and that annealed at 150 °C are monoclinic phased YPO₄·2H₂O:Tb, and the samples annealed respectively at 250 and 500 °C are tetragonal phased YPO₄:Tb. (a): 4f-5d transition of Tb³⁺; (b): 4f-4f transition of Tb³⁺.



Fig. 3. Emission spectra of the samples annealed respectively at 150 and 300 $^{\circ}\mathrm{C}$ under UV excitation.



Fig. 4. Relative luminescent intensity of as-synthesized and annealed samples.

dehydrated YPO₄:Tb with tetragonal xenotime structure, but the diffraction peaks intensity is enhanced with temperature, indicating crystal growth of YPO₄:Tb. The above results indicate that the hydrated YPO₄:Tb (YPO₄· 2H₂O:Tb) phase is metastable, which can commonly not be prepared by conventional methods [18,19]. Metastable phased materials can usually be prepared under mild conditions at a relatively low temperature [9,20].

Fig. 2 shows the excitation spectrum of as-prepared sample and those annealed at various temperatures by monitoring the ${}^{5}D_{4}-{}^{7}F_{5}$ emission of Tb³⁺. For comparison, the overall excitation spectrum is divided into two parts: one in the range from 200 to 280 nm, represents the 4f–5d transition of Tb³⁺, as shown in Fig. 2(a); the other in the range from 280 to 400 nm, represents the 4f–4f transition of Tb³⁺, as shown in Fig. 2(a), evident spectral shift of YPO₄:Tb from that of YPO₄· 2H₂O:Tb is observed, which is ascribed to the crystal field difference as a result of their different crystal structure. In Fig. 2(b), as expected, this spectral shift is not observed, since 4f shell of Tb³⁺ is well shielded by 5s and 5p shells, resulting in little effect of crystal field on the energy levels.

Fig. 3 shows the emission spectra of the samples annealed respectively at 150 and 300 °C under UV excitation. The reason why these two samples are chosen for the comparison of spectral properties is due to their different crystal structure and small difference in the annealing temperature. Both of them consist of lines ranging from 480 to 630 nm, which originate from the transitions between different f-electron states of Tb³⁺, i.e., between the excited ⁵D₄ to the ⁷F_i (j=6, 5, 4, 3) ground states. The most intense emission is the ${}^{5}D_{4}-{}^{7}F_{5}$ transition peaking around 543 nm, corresponding to the green emission. Both of the spectral shapes have no obvious change, since these transitions occur in the f-electron configuration and 4f shell is well shielded. However, a remarkable difference in the spectral intensity is observed, i.e., the luminescent intensity of $YPO_4 \cdot 2H_2O$: Tb is much lower than that of YPO_4 : Tb. To ascertain this difference, the relative spectral intensity of the as-prepared sample and those annealed at different temperatures is compared and shown in Fig. 4. From it, one can note that the luminescent intensity of the sample annealed at about 250 °C shows a sharp jump. However, the samples annealed below or above this temperature show a very little change in the luminescent intensity with temperature. As observed in Fig. 1, the temperature at about 250 °C is just the transformation temperature from YPO4 · 2H2O:Tb to



Fig. 5. Fluorescent decay curves of the sample annealed respectively at 150 (a) and 300 $^{\circ}$ C (b) by monitoring the $^{5}D_{4}-^{7}F_{5}$ emission of Tb³⁺ at 300 K.

Table 1 Definite values of decay time of as-synthesized sample and those annealed at different temperatures

Sample	1	2	3	4	5	6	7 8	8
Annealing	25	100	150	200	250	300	400	500
temperature (°C)							
Decay time (ms)	2.69	2.65	2.61	3.34	5.54	5.60	5.52	5.66

YPO₄:Tb phase. The above results sufficiently indicate that the remarkable difference of spectral intensity depends less on the annealing temperature, but more on the phase structure. It is believed that, the OH groups coordinated to rare earth ions in the hydrated YPO₄:Tb, due to their highenergy vibrational mode, probably provide an efficient nonradiative decay channel for luminescence centers, causing the radiative emission quenching [21,22]. To clarify this case, we conducted the fluorescent decay time measurement. Fig. 5 presents the fluorescent decay curves of the sample annealed respectively at 150 and 300 °C by monitoring the ${}^{5}D_{4}-{}^{7}F_{5}$ emission of Tb³⁺ at 300 K. It is worth noting that the fluorescent decay curve of the sample annealed at 300 °C, which is YPO₄ phase, can be linearly fitted, but that of the sample annealed at 150 °C, which is YPO₄·2H₂O phase, is not. This indicates the presence of non-radiative process due to OH group in YPO₄·2H₂O phase, which results in the decrease of fluorescent decay time. The definite values of fluorescent decay time of all the samples are listed in Table 1. One can see that the decay time of the as-prepared sample and those annealed below 200 °C show no significant change. But the decay time of the samples annealed in the range of 200-250 °C, during which the phase transformation occurs, shows an obvious increase. Subsequently, the decay time of the samples annealed above 250 °C shows little change with increasing temperature. This total change tendency of decay time observed is the same as that of luminescent intensity. This provides a powerful evidence that the OH group is actually an efficient quenching channel to degrade the luminescent intensity. Therefore, it is concluded that the changes of luminescent efficiency are ascribed to microstructural change induced by phase transformations. Based on these results, it is proposed that the phase microstructure may impart a subtle control to the properties of materials. Therefore mastering the correlation of the microstructure with properties well is beneficial to obtain the novel or enhanced properties of materials.

In conclusion, well-crystalline hydrated YPO₄:Tb, which cannot be obtained by conventional routes, was synthesized by a simple wet-chemistry route. The hydrated YPO₄:Tb phase with monoclinic churchite structure was transfor-

mated to the dehydrated YPO₄:Tb with tetragonal xenotime structure during the annealing process. The structural change induced by the phase transformation results in a remarkable difference in the luminescent efficiency. Based on these results, it is proposed that the structural control is an efficient way to modify the luminescent properties. This idea about the relationship between the microstructure and macro-property may also be applied to other investigated systems.

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