

# The contribution of the coordinated water to $^5D_4$ population in $YPO_4$ hydrates doped with low concentration of $Tb^{3+}$

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Received 9 October 2006; in final form 9 January 2007

Available online 17 January 2007

## Abstract

This work reports an interesting result on the photoluminescence of  $YPO_4 \cdot 2H_2O$  doped with low concentration of  $Tb^{3+}$ , which was synthesized at low temperature by aqueous route. In the as-synthesized  $Y_{0.098}PO_4:Tb_{0.002} \cdot 2H_2O$ , in which the hydration water is coordinated to the rare earth ions, the emissions of  $^5D_4$  of  $Tb^{3+}$  are much more intense than the emissions of  $^5D_3$ . After dehydration by annealing, an opposite result is achieved, i.e., the emissions of  $^5D_4$  of  $Tb^{3+}$  are much lower than the emissions of  $^5D_3$ . The Fourier-transform infrared (FTIR) and fluorescent decay spectra demonstrate that the coordinated water molecule in the hydrated sample contributes to the relaxation of  $^5D_3$  to  $^5D_4$ , thus increasing the population of the excited state  $^5D_4$  of  $Tb^{3+}$  in the as-synthesized sample.

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Luminescent materials doped with rare-earth ions have been extensively investigated in the past a few decades because of their technological applications in lighting [1], displays [2], X-ray photography [3], lasers [4] and amplifiers for fiber-optic communications [5]. Very recently, the researchers have also found their potential utility in biological detectors and biotechnology [6,7]. Therefore, interest in rare earth-doped luminescent materials grows continuously.

The size, morphology, and structure are well known to have an impact on the luminescent properties of doped materials [8,9]. To obtain desirable luminescence properties, much effort has been made on the control of morphology and structure. For example, Jia et al. [8] have used an ethylenediamine tetraacetic acid (EDTA) assisted hydrothermal method to synthesize metastable-phased zirconite-type  $LaVO_4:Eu$  nanocrystals at low temperature, whose emission intensity is nine times as high as that of  $LaVO_4:Eu$  with monazite-type structure that is prepared by the high-

temperature solid-state reaction. In addition, the selection of the host matrix is also crucial since the luminescent properties and efficiencies can be strongly affected by various processes caused by the interaction between the rare-earth ions and the vibration of the host, such as nonradiative de-excitation and phonon-assisted energy transfer [10]. Therefore, the search for a suitable host material is a key to tailor the luminescent properties. For example, rare earth fluorides are shown to be good candidates as host materials due to low phonon energy, which decreases the nonradiative rate and thus increases the luminescent intensities [11].

$Tb^{3+}$ -doped materials can show bright blue or green light depending on the  $Tb^{3+}$  concentration [12]. With a very low concentration of  $Tb^{3+}$  doped into host matrix, the transition from  $^5D_3$  of  $Tb^{3+}$  dominates and produces the blue emissions. With an increasing concentration of  $Tb^{3+}$  doped into host matrix, a well-known cross relaxation process from  $^5D_3$  to  $^5D_4$  occurs [13], and thus the emissions from  $^5D_4$  can be observed, which produce the green light.  $Tb^{3+}$ -doped materials, including borates [14], aluminates [15], phosphates [13], fluorides [11] and so on, have been widely investigated in the past a few decades.

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However, the photoluminescence of the hydrated materials doped with low concentration of  $Tb^{3+}$  has not been reported yet, based on our present best knowledge. In this work,  $YPO_4$  hydrates doped with low  $Tb^{3+}$  concentration ( $Y_{0.098}PO_4:Tb_{0.002} \cdot 2H_2O$ ) was synthesized at low temperature by aqueous route, and an abnormal photoluminescence was observed and explained.

The samples were prepared by aqueous precipitation as follows: appropriate amounts of high purity  $Y_2O_3$  and  $Tb_4O_7$  were dissolved in concentrated  $HNO_3$  to form Y(III) and Tb(III) solutions, respectively. Appropriate volume of  $(NH_4)_2HPO_4$  solution was added slowly to above mentioned rare earth (III) solutions under vigorous stirring. The final pH value was adjusted to 1–2 by the addition of aqueous ammonia. The mixtures were vigorously stirred for 10 h at 60 °C. The resulting products were washed with ethanol and distilled water, and centrifuged at 8000 rpm. This process was repeated several times. The obtained precipitates were dried overnight at room temperature. XRD studies were conducted on a Rigaku D/max-2000 X-ray powder diffractometer using  $Cu K\alpha$  radiation. Infrared spectra of powders (FTIR) were recorded in the range of 600–4000  $cm^{-1}$  on a Fourier-transform spectrometer (Perkin Elmer, Spectrum 1, USA) with a resolution of 1  $cm^{-1}$ . The powder samples were mixed with KBr, then pressed into a cylindrical die. The emission spectra at room temperature were measured with a Hitachi F-4500 fluorescence spectrometer. The measurement of fluorescent decay was carried out with a third-harmonic generator pumped by the pulsed Nd:YAG at room temperature.

Fig. 1 shows the XRD patterns of the as-synthesized sample and those heat-treated at various temperatures. It is noted that, the as-synthesized sample is well-crystalline, and that all of the peaks could be well indexed to the monoclinic  $YPO_4 \cdot 2H_2O$  with churchite-type structure and space group  $I2/a$  ( JCPDS File No. 85-1842 ). As the annealing temperature increases to 190 °C, an additional

diffraction peak is observed, as marked by a specific symbol in Fig. 1. This means that a new phase is involved in the monoclinic phased  $YPO_4 \cdot 2H_2O$ . Further increasing annealing temperature up to 250 °C, the phase with monoclinic churchite-type structure has almost totally disappeared, and a new phase, all of whose peaks could be well indexed to tetragonal dehydrated  $YPO_4$  with xenotime-type structure and space group  $I4/amd$  ( JCPDS File No. 84-0335 ), is observed. Typical DTA plot of as-synthesized  $YPO_4 \cdot 2H_2O$  is given in the inset of Fig. 1. A well-defined endothermic effect is observed due to dehydration in the temperature range 150–290 °C peaking at 247 °C. This temperature is in good agreement with the structure transition temperature. This indicates that the dehydration really leads to the structural transition from monoclinic churchite-type  $YPO_4 \cdot 2H_2O$  to the dehydrated tetragonal xenotime-type  $YPO_4$ . The above result indicates that the  $YPO_4 \cdot 2H_2O$  phase is metastable, which can commonly not be prepared by high-temperature synthesis route. Metastable-phased materials can usually be prepared under mild conditions at relatively low temperature [16,17].

Fig. 2 presents FTIR spectra of the as-synthesized sample and the sample annealed at 250 °C. In the investigated range of wavelength, the peak at about 650  $cm^{-1}$ , the should at 910  $cm^{-1}$ , and the band around 1050  $cm^{-1}$  are indicative of the characteristic vibrations of phosphate groups [18]. What we are most interested in is the water vibrations, which have a close association with the photoluminescence to be investigated below. For the water vibrations, in addition to the wide bands extending from 2700 to 3700  $cm^{-1}$ , the presences of two bands at 1640 and 1715  $cm^{-1}$  and the band at 755  $cm^{-1}$  indicated in Fig. 2 are indicative of the characteristic of coordinated water [16], i.e., the hydration water molecule in the as-synthesized sample is bonded to the rare earth ions. For the sample annealed at 250 °C, the characteristic vibrations of coordinated water have been completely disappeared due

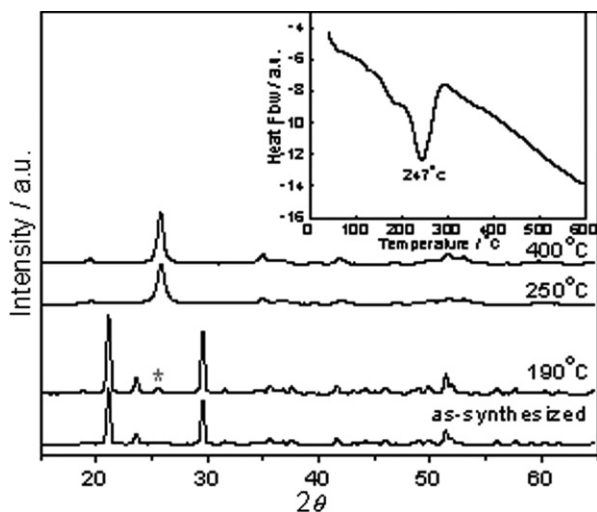


Fig. 1. XRD patterns of the as-synthesized sample and the sample annealed at different temperatures.

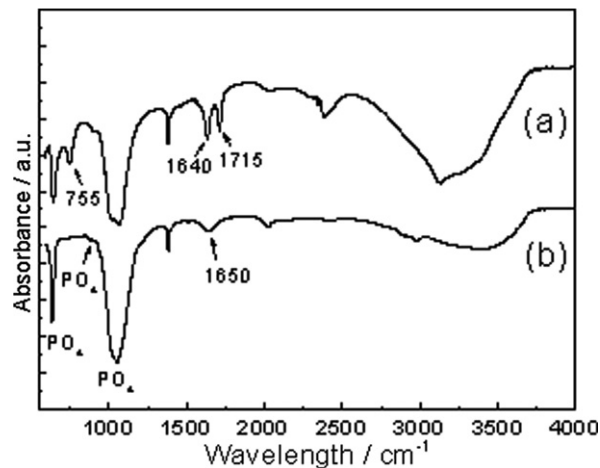


Fig. 2. FTIR spectra of the as-synthesized sample (a) and the sample annealed at 250 °C (b).

to dehydration at this temperature. The band at  $1650\text{ cm}^{-1}$  and the band around  $3400\text{ cm}^{-1}$  are the characteristic vibrations of water molecule in air physically adsorbed at the sample surface, which is completely different from coordinated water in nature.

$\text{Tb}^{3+}$  has a relatively simple 4f-configurational energy level structure: low-energy state,  ${}^7\text{F}_j$  ( $j=6, \dots, 0$ ) and excited states  ${}^5\text{D}_3$  and  ${}^5\text{D}_4$  [15]. Generally, with a very low concentration of  $\text{Tb}^{3+}$  doped into host matrix, the transitions of  ${}^5\text{D}_3$  to  ${}^7\text{F}_j$  dominate and produce the blue emissions [12]. With increasing Tb concentration, the cross relaxation from  ${}^5\text{D}_3$  to  ${}^5\text{D}_4$  occurs due to the interaction between the neighboring  $\text{Tb}^{3+}$  ions [13], which increases the population of  ${}^5\text{D}_4$  energy level, correspondingly, enhancing the transitions of  ${}^5\text{D}_4$  to  ${}^7\text{F}_j$ , which emit green light. In order to observe the  ${}^5\text{D}_3$  emissions of  $\text{Tb}^{3+}$ , low concentration  $\text{Tb}^{3+}$ -doped  $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Y}_{0.098}\text{PO}_4:\text{Tb}_{0.002} \cdot 2\text{H}_2\text{O}$ , was synthesized in this work.

Fig. 3 shows the emissions spectra of the as-synthesized hydrated sample and the dehydrated sample annealed at  $250\text{ }^\circ\text{C}$ . Both consist of lines ranging from 350 to 630 nm, which originate from the transitions between different f-electron states of  $\text{Tb}^{3+}$ , i.e., from the excited  ${}^5\text{D}_3$  and  ${}^5\text{D}_4$  to the  ${}^7\text{F}_j$  ground states, respectively. Among which, the emissions at 380, 416, 436, 458, and 472 nm originate from the transitions from  ${}^5\text{D}_3$ , and those at 490, 544, 588, and 622 nm originate from the transitions from  ${}^5\text{D}_4$ , [13] as indicated in Fig. 3. Interestingly, one can observe a noticeable difference in the relative emission intensity of  ${}^5\text{D}_3$  and  ${}^5\text{D}_4$  for these two samples. For the as-synthesized sample, relatively weak emission from  ${}^5\text{D}_3$  and relatively strong emission from  ${}^5\text{D}_4$  are observed, but for the annealed sample, an opposite result is achieved, i.e., relatively strong emissions from  ${}^5\text{D}_3$  in contrast to those from  ${}^5\text{D}_4$ . Taking into account that both samples contain the same nominal  $\text{Tb}^{3+}$  concentration, what results in this noticeable difference in the ratio of  ${}^5\text{D}_3$  emissions to  ${}^5\text{D}_4$  emissions between these two samples? The earlier XRD and FTIR spectra show the presence of coordinated water in the as-synthesized hydrated sample, but the coordinated water is completely removed due to the dehydration in the sample annealed

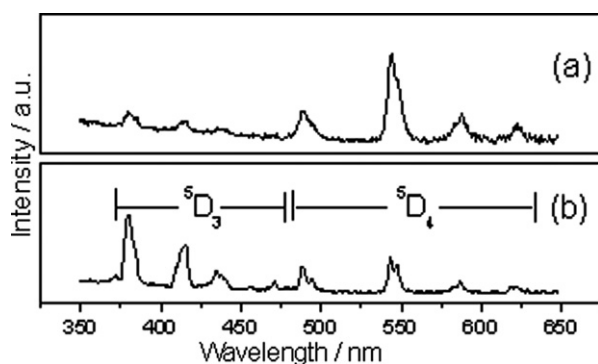


Fig. 3. Emission spectra of the as-synthesized sample (a) and the sample annealed at  $250\text{ }^\circ\text{C}$  (b) under 355-nm excitation.

at  $250\text{ }^\circ\text{C}$ . The difference of photoluminescence mentioned above is probably related to the coordinated water. FTIR spectrum of as-synthesized sample shows high vibrational frequency of OH groups in the range from  $2700$  to  $3700\text{ cm}^{-1}$  due to the presence of coordinated water. The energy separation between  ${}^5\text{D}_3$  and  ${}^5\text{D}_4$  is about  $6500\text{ cm}^{-1}$ , which may be bridged well by only two OH phonons. Based on the theory of multiphonon relaxation, this makes the  ${}^5\text{D}_3$ - ${}^5\text{D}_4$  relaxation process by the bridge of OH phonons highly probable. Therefore, the population of the excited state  ${}^5\text{D}_4$  of  $\text{Tb}^{3+}$  originates from two channels for the as-synthesized sample. On one hand, it results from the energy transfer from  ${}^5\text{D}_3 \rightarrow {}^5\text{D}_4$  of one  $\text{Tb}^{3+}$  to  ${}^7\text{F}_6 \rightarrow {}^7\text{D}_0$  of another  $\text{Tb}^{3+}$ , a cross-relaxation process, as indicated in Fig. 4a; on the other hand, it results from the  ${}^5\text{D}_3 \rightarrow {}^5\text{D}_4$  relaxation through the decay of OH phonon, as indicated in Fig. 4b. These two processes contribute to the increase of the population of the excited state  ${}^5\text{D}_4$  of  $\text{Tb}^{3+}$ , and correspondingly, decrease the  ${}^5\text{D}_3$  population for the as-synthesized hydrated sample. But for the annealed sample, due to the removal of coordinated water, only a single cross-relaxation process from  ${}^5\text{D}_3 \rightarrow {}^5\text{D}_4$  to  ${}^7\text{F}_6 \rightarrow {}^7\text{F}_0$  is contributive to the population of the excited state  ${}^5\text{D}_4$ . Therefore, the ratio of the population of  ${}^5\text{D}_4$  to that of  ${}^5\text{D}_3$  in the as-synthesized hydrated sample is much higher than that in the sample annealed at  $250\text{ }^\circ\text{C}$ . This may well explain the difference in the ratio of  ${}^5\text{D}_3$  emissions to  ${}^5\text{D}_4$  emissions in these two samples.

As a matter of fact, the relaxation of  ${}^5\text{D}_3$  to  ${}^5\text{D}_4$  by the coordinated water can be estimated by the fluorescent decay of  ${}^5\text{D}_3$ . The fluorescent decay curves of  ${}^5\text{D}_3$  for these two samples are given and compared in Fig. 5. As expected, the luminescence of  ${}^5\text{D}_3$  of these two samples shows nonexponential decay behavior. For the sample annealed at  $250\text{ }^\circ\text{C}$ , this nonexponential decay originates primarily from the cross relaxation due to the interaction between

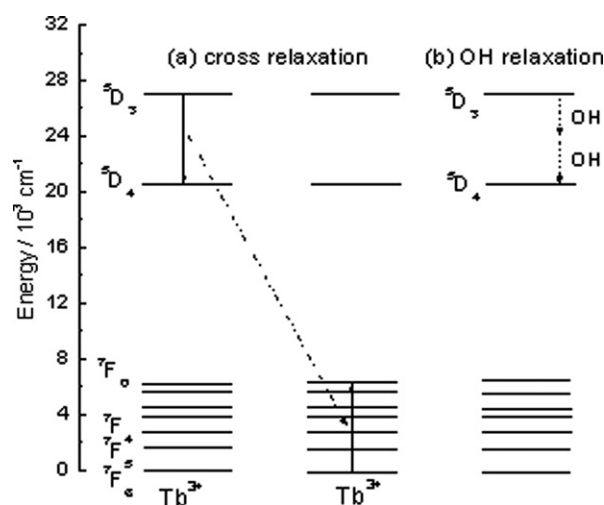


Fig. 4. Schematic images for the  ${}^5\text{D}_3 \rightarrow {}^5\text{D}_4$  cross-relaxation process between neighboring  $\text{Tb}^{3+}$  (a) and the  ${}^5\text{D}_3 \rightarrow {}^5\text{D}_4$  relaxation for a single  $\text{Tb}^{3+}$  by OH phonon vibration (b).

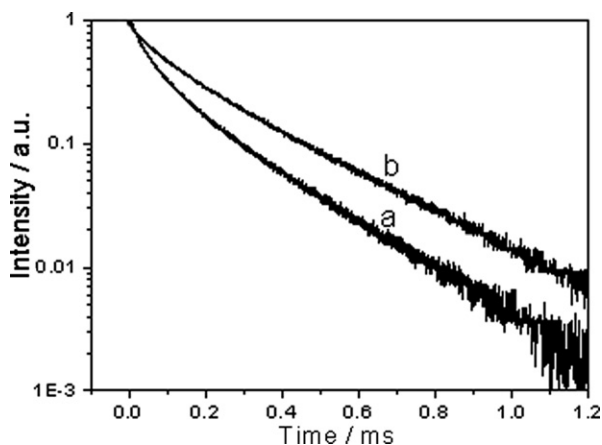


Fig. 5. Fluorescent decay curves of the  ${}^5\text{D}_3$  of  $\text{Tb}^{3+}$  in the samples before (a) and after dehydration (b) under 355-nm excitation.

$\text{Tb}^{3+}$  ions, from  ${}^5\text{D}_3 \rightarrow {}^5\text{D}_4$  of one  $\text{Tb}^{3+}$  to  ${}^7\text{F}_6 \rightarrow {}^7\text{F}_0$  of another  $\text{Tb}^{3+}$ . However, it is worth noting that the luminescence decay deviates much more from single-exponential behavior for the as-synthesized sample (Fig. 5b), in contrast to the annealed sample. This indicates that, except for the cross relaxation, there should exist another nonradiative relaxation route that can also leads to the depopulation of  ${}^5\text{D}_3$  for the as-synthesized sample. As demonstrated earlier, in the as-synthesized sample, the hydration water coordinated to the rare earth ions presents the intense vibration in the range from 2700 to 3700  $\text{cm}^{-1}$ , and the energy separation of  ${}^5\text{D}_3$ – ${}^5\text{D}_4$  matches the two OH phonons well. Thus, the  ${}^5\text{D}_3 \rightarrow {}^5\text{D}_4$  decay by OH phonon relaxation becomes probable. Therefore, in the as-synthesized sample that contains the coordinated water, the cooperative contributions of the cross relaxation and OH phonon relaxation decrease the population of  ${}^5\text{D}_3$  considerably, but relatively increase the population of  ${}^5\text{D}_4$ . This may support the result on the difference in photoluminescence of the samples before and after dehydration.

The decay rate  $W$  for excited level  ${}^5\text{D}_3$  of  $\text{Tb}^{3+}$  ion in crystalline matrices may be approximated by the sum of a radiative transition rate ( $W_{\text{R}}$ ), multiphonon relaxation rate ( $W_{\text{MP}}$ ) and the cross-relaxation rate between  $\text{Tb}^{3+}$  ( $W_{\text{CR}}$ ). Thus,  $W$  can be written as

$$W = W_{\text{R}} + W_{\text{MP}} + W_{\text{CR}}$$

In the dehydrated  $\text{YPO}_4:\text{Tb}$ , the excited levels of  ${}^5\text{D}_3$  are depopulated by radiative transition and cross-relaxation processes. However, in the as-prepared  $\text{YPO}_4:\text{Tb}2\text{H}_2\text{O}$  containing coordinated water, there increases another pathway depopulating the  ${}^5\text{D}_3$  level by the interaction of the  ${}^5\text{D}_3$  level of  $\text{Tb}^{3+}$  with the vibrations of coordinated water due to the energy matching. This is evidenced by

the variations of optical spectra (Fig. 3) and fluorescent decay (Fig. 5). Furthermore, from a large change of the ratio of  ${}^5\text{D}_4$  emissions to  ${}^5\text{D}_3$  emissions before and after dehydration, it is not difficult to conclude that the coordinated water possesses a large contribution to the relaxation of  ${}^5\text{D}_3$  of  $\text{Tb}^{3+}$  to  ${}^5\text{D}_4$ .

In summary, we have used the aqueous route to synthesize low concentration  $\text{Tb}^{3+}$ -doped  $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$ , in which the hydration water is coordinated to the rare earth ions. In the as-synthesized sample, in addition to a well-known cross-relaxation process, an additional process, the  ${}^5\text{D}_3 \rightarrow {}^5\text{D}_4$  relaxation by coordinated water vibration, also contributes to the increase of  ${}^5\text{D}_4$  population. This ultimately leads to unusual photoluminescence phenomenon, that is, the ratio of the emissions from  ${}^5\text{D}_4$  to the emission from  ${}^5\text{D}_3$  in the as-synthesized sample is much higher than that in the sample annealed at 250  $^\circ\text{C}$ , in which, the coordinated water is removed completely.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 50502031, 50572102) and The Young People Foundation of Jilin Province (Grant No. 20060522).

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