

Effect of OH⁻ on the Luminescent Efficiency and Lifetime of Tb³⁺-Doped Yttrium Orthophosphate Synthesized by Solution Precipitation

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In this work, we use the solution precipitation method to synthesize Tb³⁺-doped yttrium orthophosphate, which is a green-emission luminescent material. The evolution of hydrated yttrium orthophosphate (YPO₄·2H₂O) to dehydrated yttrium orthophosphate (YPO₄) is observed in the heat-treatment process, simultaneously, accompanying the structural transformation from monoclinic churchite-type to tetragonal xenotime-type structure. Furthermore, the luminescent efficiency of Tb³⁺-doped YPO₄ presents a sharp jump at a critical temperature in this heat-treatment process. Interestingly, this critical temperature is close to the structural transformation temperature. The remarkable change of luminescent efficiency seems to be related to the structural transformation. However, the FTIR and fluorescent decay measurements at 10 and 300 K indicate that the OH group is the origin of luminescent efficiency change. OH⁻ ions with high vibration frequency provide an efficient means to quench the luminescence. The comparison of the luminescent efficiency, OH⁻ content, and lifetime of ⁵D₄ of Tb³⁺ between two samples with the same crystal structure proves that the structural transformation has no significant effect on the luminescent efficiency and lifetime. On the basis of these results, it is proposed that correctly preventing OH⁻ ions inside the host matrix or effectively eliminating them may improve the luminescent efficiency greatly. This idea also may be applied to other optical systems.

Introduction

Rare earth ion-doped inorganic compounds represent a family of materials with significant technological importance, and are extensively used as high-performance luminescent devices, magnets, catalysts, time-resolved fluorescence labels for biological detection, and other functional materials based on the electronic, optical, and chemical characteristics resulting from the 4f shell of their ions.^{1–5} Most of their properties are dependent on the sizes, shapes, crystal types, and compositions, which are strongly related to the synthetic routes and parameters.^{6–11}

In the case of the synthesis of rare earth ion-doped inorganic compounds, the wet-chemical route is of considerable superiority over the high-temperature solid-state reaction. First, the doping of rare earth ions through aqueous solution is straightforward, efficient, and highly homogeneous.^{12–14} Huignard et al.¹³ synthesized colloidal solutions of well-dispersed YVO₄:Eu nanoparticles by solution precipitation. They determined the cell volume by refining the tetragonal cell parameter of YVO₄:Eu from X-ray diffraction data and found the volume of the unit cell is linear with respect to the Eu content. This indicated the efficient and homogeneous incorporation of Eu³⁺ into the YVO₄ host matrix by the solution precipitation. Second, the wet-chemical route can provide several adjustable synthetic parameters such as solution pH^{7,10,15–17} and concentration, and reactive temperature^{15–19} and time, by adjusting which of the size, shape, morphology, and structure parameters may be well controlled. Several research teams have reported that the hydrothermal method is used to synthesize rare earth orthophosphates, and that the different shapes of materials are obtained by changing

the solution pH.^{20,21} We found in our previous report²² that the required phase could not be obtained, as the solution pH value exceeds 7 in the synthesis of YPO₄ with solution precipitation method. This indicated that the optimization of the synthetic condition is very important in obtaining the desirable phase. Finally, the synthesis using the wet-chemical route is performed at room temperature or at a low temperature. In this case, one can observe structural evolution from a low-temperature phase to a high-temperature one as the as-synthesized samples are heat-treated,^{23–25} simultaneously, accompanying the property evolution including optical and electronic properties.²⁵ Furthermore, in such a low-temperature synthesis, sometimes, metastable phased materials can be prepared, which cannot be obtained with use of the high-temperature solid-state reaction.^{6,25,26} Jia et al.²⁵ synthesized metastable zircon-type LaVO₄:Eu nanocrystals at a low temperature using an ethylenediamine tetraacetic acid (EDTA) assisted hydrothermal method. The reported result showed the emission intensity of synthesized LaVO₄:Eu with zircon structure is nine times as high as that of LaVO₄:Eu with monazite structure that is prepared via the high-temperature solid-state reaction. In conclusion, the wet-chemical route provides us with many adjustable parameters for selective synthesis to obtain the required materials with desirable size, shape, structure, and properties. Besides, the optimization of synthetic parameters is a key factor in forming the desirable materials.

However, in the synthesis of inorganic luminescent materials, the use of the wet-chemical route can usually introduce a certain number of luminescent quenchers such as OH⁻ and CO₃²⁻.^{13,24,27,28} Such luminescent quenchers have a significant effect on the luminescent efficiency of synthesized materials. This work aims at investigating the effect of OH⁻ on the luminescent efficiency and lifetime of Tb³⁺-doped yttrium

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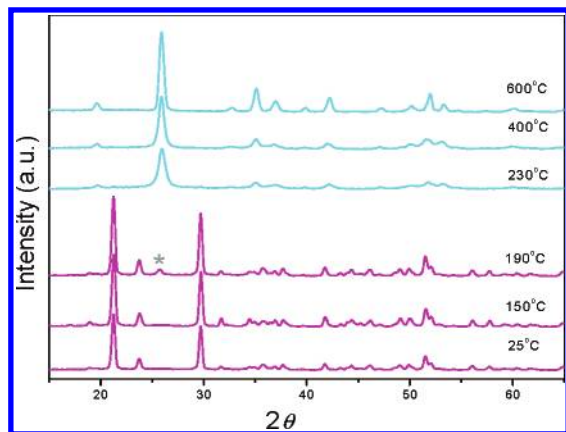


Figure 1. XRD patterns of the as-synthesized sample and those heat-treated at various temperatures.

orthophosphate synthesized by solution precipitation. The measurements of FTIR and the fluorescent decay at 10 and 300 K provide powerful evidence for the influence of OH⁻ on the luminescent efficiency. Results indicate that OH⁻ with high vibration frequency provides an efficient means to quench the luminescence.

Experimental Section

Tb-doped YPO₄ was synthesized by a simple wet-chemistry route. Appropriate amounts of high purity Y₂O₃ and Tb₄O₇ were dissolved in concentrated HNO₃ to form Y(NO₃)₃ and Tb(NO₃)₃ solutions, to which the appropriate volume of H₃PO₄ solution was added slowly. The final pH value was adjusted to 6–7 by the addition of aqueous ammonia (NH₄OH). After the solution was well stirred at 50 °C for 3 h white precipitates were obtained; the solution was then filtered and the precipitates were washed several times with deionized water and then dried at 60 °C in air. The dried precipitates were heat-treated to various temperatures at a speed of 4 °C/min in a reducing atmosphere to prevent the oxidation of Tb³⁺ and kept at that temperature for 1 h.

XRD studies were conducted on a Rigaku D/max-2000 X-ray powder diffractometer with Cu Kα radiation. Infrared spectra of powders (FTIR) were recorded in the range of 1500–4000 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 spectrum at room temperature was measured with a Hitachi F-4500 fluorescence spectrometer. In the measurement of fluorescent lifetime, the samples were put into a liquid-helium-cycling system, where the temperature varied from 10 to 300 K. A 355-nm light generated from the third harmonic generator pumper by the pulsed Nd:YAG laser was used as a general excitation source.

Results and Discussion

Figure 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-crystallized, and that all of the peaks could be well indexed to the monoclinic YPO₄·2H₂O with churchite-type structure and space group *I2/a* (JCPDS File No. 85-1842). As the annealing temperature increases to 190 °C, a new diffraction peak is observed, as marked by a specific symbol in Figure 1. This means that a new phase is involved in the monoclinic phased YPO₄·2H₂O. With a further increase in the annealing temperature to 230 °C, the phase with the monoclinic structure has almost totally disappeared, and a new

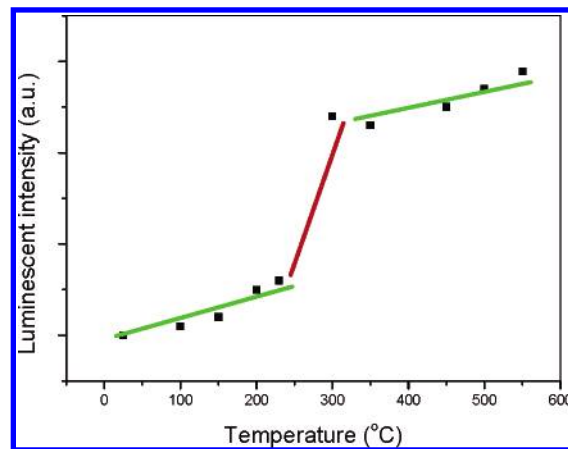


Figure 2. The dependence of luminescent efficiency on the heat-treatment temperature.

phase, all of whose peaks could be well indexed to tetragonal dehydrated YPO₄ 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 with monoclinic churchite-type structure to the dehydrated YPO₄ with tetragonal xenotime-type structure occurs. With a further increase of annealing temperature up to 600 °C, it remains dehydrated YPO₄ with tetragonal xenotime-type structure, but the intensifying and narrowing diffraction peaks are observed, indicating crystal growth of YPO₄ with temperature. The above results indicate that the YPO₄·2H₂O phase is metastable, which commonly can not be prepared by the high-temperature synthesis route. Metastable phased materials can usually be prepared under mild conditions at relatively low temperature.²⁵ Fang et al.²¹ synthesized the YPO₄ via the hydrothermal method, but they did not obtain the metastable YPO₄·2H₂O. This is probably due to the fact that the hydrothermal synthesis is at a higher temperature and at a higher pressure than the solution precipitation used in this work, which is conducted at 50 °C and at ambient pressure. Since Tb³⁺ is located in a different host lattice structure (YPO₄·2H₂O and YPO₄) and experiences a different crystal field, the luminescent properties of Tb³⁺ show a difference, which was reported in our previous work.²⁹

Tb³⁺ has a relatively simple 4f-configurational energy level structure: low-energy state ⁷F_{*j*} (*j* = 6, ..., 0) and excited states ⁵D₃ and ⁵D₄. Generally, with a very low concentration of Tb³⁺ doped into host matrix, the transitions of ⁵D₃ to ⁷F_{*j*} dominate and produce the blue emissions.³⁰ As Tb³⁺ concentration increases, the cross relaxation from ⁵D₃ to ⁵D₄ occurs due to Tb³⁺ ion interaction,³¹ which increases the population of the ⁵D₄ energy level, correspondingly enhancing the transitions of ⁵D₄ to ⁷F_{*j*}, which emit a green light. As the Tb³⁺ concentration reaches a high value, the emissions from ⁵D₃ to ⁷F_{*j*} almost disappear, and the emissions from ⁵D₄ to ⁷F_{*j*} dominate. The concentration of Tb³⁺ doped into YPO₄·2H₂O or YPO₄ host matrix in this work is as high as 6 mol %, thus the luminescence comes from the emissions from ⁵D₄ to ⁷F_{*j*}.

Figure 2 shows the integrated luminescent intensity of as-synthesized sample and those heat-treated at various temperatures. One can see that the luminescent efficiency of the sample heat-treated at 300 °C presents an abrupt jump; however, that of the samples heat-treated below and above this temperature, 300 °C, have no significant change with temperature. It is worth mentioning that this critical temperature, 300 °C, is close to that of the crystal structure transformation related to phase evolution from YPO₄·2H₂O to YPO₄. Therefore, it is assumed that the structural transformation is possibly related to the

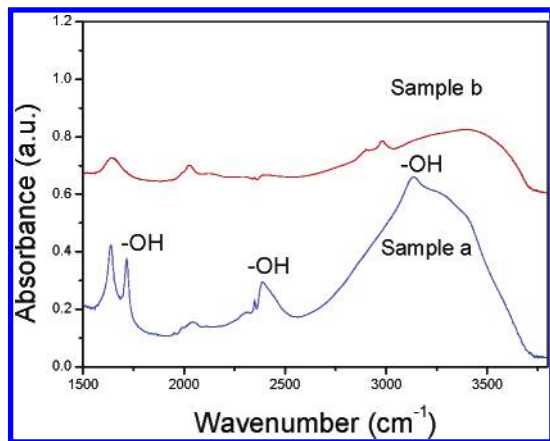


Figure 3. FTIR spectra of samples a and b.

remarkable change of luminescent efficiency. But we have no further evidence to confirm this. Also, it is noted that the $\text{YPO}_4 \cdot 2\text{H}_2\text{O}$ phase with the monoclinic churchite-type structure has been completely transformed to the YPO_4 phase with tetragonal xenotime-type structure at 230 °C, but at which the luminescent efficiency does not show a significant change. Therefore, a question is raised: Is there another factor influencing luminescent efficiency?

To answer this question, the FTIR and fluorescent decay measurements of the samples heat-treated at 230 and 300 °C are conducted. For simplicity, the samples heat-treated at 230 and 300 °C are denoted as samples a and b, respectively, in the following description. Figure 3 presents the FTIR spectrum of samples a and b. The peaks at about 1720 and 2300 cm^{-1} and a broad band ranging from 2700 to 3700 cm^{-1} are characteristic of the vibration of OH groups. While the heat-treatment temperature increases to 300 °C, the vibration intensity of the OH group decreases markedly. In fact, OH^- ions are introduced into the host matrix easily due to the nature of the wet-chemical route. OH^- ions originate from two aspects: on one hand, the synthesis is conducted in the aqueous solutions, and thus OH^- ions come from H_2O ; on the other hand, NH_4OH is used to adjust the solution pH in our experiment, and thus OH^- ions come from NH_4OH . During the reactive process in the aqueous solutions, the intense collision of OH^- ions and rare earth ions creates OH^- ions coordinated to rare earth ions. As a result, a certain number of OH^- ions are incorporated into the host matrix of as-synthesized sample. As the as-synthesized sample is heat-treated to a critical temperature, a quite large number of OH groups can be removed. Figure 4 shows the fluorescent lifetime for the transition of $^5\text{D}_4$ to $^7\text{F}_5$ of Tb^{3+} at 300 K. It is seen that the fluorescent lifetime of sample a is much shorter than that of sample b. The above results illustrate that OH^- ions are the major origin of luminescent efficiency change since samples a and b have the same crystal structure. As is well-known, OH^- vibration frequency occurs in the broad range of 2700–3700 cm^{-1} ,^{32,33} which is much higher than other vibration such as PO_4^{3-} . As a result, only a few phonons are required for nonradiative de-excitation of $^5\text{D}_4$ state. OH^- ions, thus, seem to be very efficient quenchers of the luminescence of Tb^{3+} through multiphonon relaxation. Therefore, the existence of a number of OH groups may well explain both the shorter fluorescent lifetime and the low luminescent efficiency observed in sample a. In sample b, a number of OH^- ions are removed, and thus the probability of the interaction between Tb^{3+} and OH^- decreases largely due to a low concentration of OH^- ions involved.³³ Therefore, remarkably increasing luminescent efficiency and lifetime are observed in sample b. Samples a and

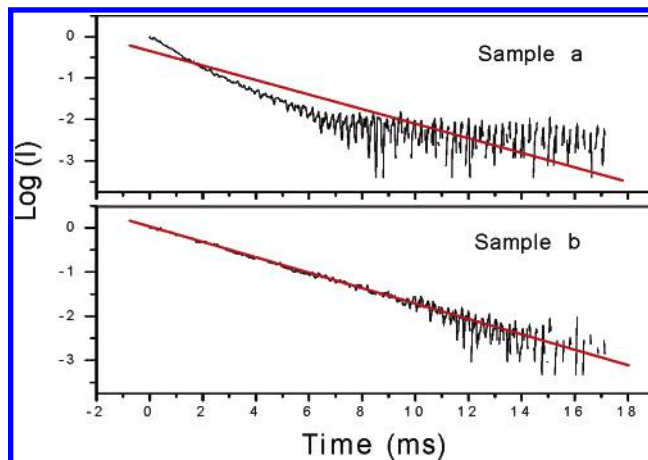


Figure 4. $\text{Log}(I)-t$ curves for samples a and b at 300 K.

b possess the same crystal structure, but their luminescent efficiency and lifetime show a considerable difference. This indicates that the crystal structure has little effect on the luminescent efficiency.

What is plotted in Figure 4 is the $\text{log}(I)-t$ curves of the fluorescent decay for the $^5\text{D}_4-^7\text{F}_5$ transition of Tb^{3+} at 300 K. It is seen that the fluorescent decay curve of sample b, in which a considerable number of OH^- ions are removed, almost goes with a single line, indicating almost single-exponential fluorescent decay. However, the fluorescent decay curve for sample a, in which a large number of OH^- ions are present, deviates from a single line, indicating the presence of nonradiative processes and the fluorescent decay is nonexponential behavior. The nonradiative decay of $^5\text{D}_4$ of Tb^{3+} should include the nonradiative transition of $^5\text{D}_4-^7\text{F}_j$ and the energy transfer from $^5\text{D}_4$ to other Tb^{3+} ions. The above results indicate that the nonradiative transition caused by OH^- ions is a leading contribution to the nonradiative decay processes of $^5\text{D}_4$ of Tb^{3+} , and that the energy transfer from $^5\text{D}_4$ of a Tb^{3+} to another one can be negligible. Regarding the latter, a similar conclusion was made in the report by Riwozki et al.,¹² in which they found that the lifetime of $^5\text{D}_4$ remains unchanged even with a higher concentration of Tb doping in $\text{LaPO}_4:\text{Tb}$, indicating the absence of energy transfer from $^5\text{D}_4$ of a Tb^{3+} to another one. Also, in that report, they found that the luminescence decay of $^5\text{D}_4$ of Tb^{3+} -doped CePO_4 prepared at a low temperature by liquid-phase synthesis deviated from single-exponential behavior, which was explained by energy transfer from $^5\text{D}_4$ of Tb^{3+} to impurity ions. But they did not ascertain the nature and origin of impurity ions. We estimate that those impurity ions are mostly OH^- ions.

To further confirm whether OH^- ions are the major origin of luminescent efficiency evolution or not, the fluorescent lifetime of the $^5\text{D}_4-^7\text{F}_5$ transition at 10 K is measured. It is seen that the fluorescent lifetime at 10 K (3.5 ms) is much longer than that at 300 K (1.87 ms) for sample a. However, for sample b, there does not exist a significant difference in the fluorescent lifetime between that at 10 K (3.72 ms) and that at 300 K (3.6 ms). In fact, the lifetime of $^5\text{D}_4$ of Tb^{3+} , τ , is dominated by the radiative transition rate, W_R , and the nonradiative decay rate, W_{NR} , which can be expressed as $\tau = 1/(W_R + W_{NR})$. Generally, W_{NR} increases remarkably with an increasing temperature, while W_R has little change with temperature.³³ As just discussed above, the nonradiative decay is dominated by nonradiative transition through multiphonon relaxation of OH^- ions. As the temperature is at 10 K, OH^- ions almost cannot perform the function of multiphonon relaxation, which explains a longer fluorescent lifetime at 10 K for sample a containing a number of OH^- ions.

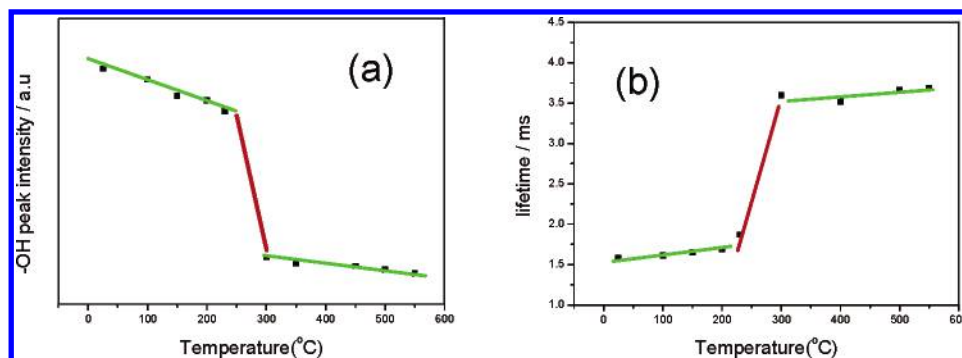


Figure 5. The dependence of OH⁻ content (a) and the lifetime for ⁵D₄-⁷F₅ transition of Tb³⁺ (b) on the heat-treatment temperature.

Regarding why the sharp increase of luminescent efficiency occurs at the critical temperature, 300 °C, this needs further illustration. Panels a and b of Figure 5 show the dependence of OH⁻ content and fluorescent lifetime (⁵D₄-⁷F₅ transition at 300 K) on heat-treatment temperature. It is noted from Figure 5a that 300 °C is just the critical temperature at which the number of OH⁻ ions starts to decrease greatly, and the number of OH⁻ ions does not show an obvious variation below and above this temperature. Combining Figures 2 and 5b with Figure 5a, it is found that 300 °C is also the critical temperature at which not only the fluorescent lifetime of the ⁵D₄-⁷F₅ transition of Tb³⁺ starts to become longer but also the luminescent efficiency starts to become higher. These changes are consistent with each other. In addition, a relationship between OH⁻ content and the lifetime of ⁵D₄ of Tb³⁺, i.e., the dependence of the lifetime on OH⁻ content, can be well established from Figure 5a,b. Thus, we can evaluate the OH⁻ content by the measurement for the lifetime of ⁵D₄ of Tb³⁺.

In conclusion, OH⁻ ions are very efficient quenchers of luminescence through multiphonon relaxation. It is concluded that the origin of the remarkable increase of luminescent efficiency is a significant decrease of OH⁻ ions, but not the crystal structure transformation. Therefore, correctly preventing OH⁻ ions inside the host matrix or effectively eliminating them may improve the luminescent efficiency greatly. This idea also may be applied to other optical systems.

Conclusions

The solution precipitation method is used to synthesize Tb³⁺-doped yttrium orthophosphate. XRD data show the YPO₄·2H₂O phase transitions to the YPO₄ phase in the range of 180–230 °C during the heat-treatment process, simultaneously accompanying the structural transformation from monoclinic churchite-type to tetragonal xenotime-type structure. This indicates that YPO₄·2H₂O is a metastable phase, which can be prepared only under mild conditions at relatively low temperature.

Also, in this heat-treatment process, the luminescent efficiency of Tb³⁺-doped YPO₄ presents a sharp increase at a critical temperature, 300 °C, at which the FTIR and fluorescent lifetime measurements show that both the content of OH⁻ ions and the lifetime for ⁵D₄-⁷F₅ transition of Tb³⁺ present abrupt change. The sample heat-treated at 300 °C shows an almost single-exponential fluorescent decay, and the fluorescent decay of the sample heat-treated at 230 °C largely deviates from single-exponential behavior. But the two samples have the same crystal structure. These results indicate that an abrupt increase of luminescent efficiency results from the remarkable decrease of OH⁻ ions, not from the structural transformation. The lifetime measurement at low temperature further justifies this conclusion.

Therefore, correctly preventing OH⁻ ions inside the host matrix or effectively eliminating them is an efficient means to improve the luminescent efficiency.

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