AIP Applied Physics Letters

Experimental demonstration of the relationship between the OH− content and photoluminescence in Tb-doped YPO4·2H2O

Weihua Di, Xiaojun Wang, Baojiu Chen, Shaozhe Lu, and Xinguang Ren

Citation: Appl. Phys. Lett. **88**, 011907 (2006); doi: 10.1063/1.2158703
View online: http://dx.doi.org/10.1063/1.2158703
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v88/i1
Published by the American Institute of Physics.

APPLIED PHYSICS LETTERS **88**, 011907 (2006)

Experimental demonstration of the relationship between the OH^- content and photoluminescence in Tb-doped $YPO_4 \cdot 2H_2O$

Weihua Di,[a] Xiaojun Wang, Baojiu Chen, Shaozhe Lu, and Xinguang Ren
Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China

(Received 20 September 2005; accepted 30 November 2005; published online 3 January 2006)

Tb-doped $YPO_4 \cdot 2H_2O$ was synthesized via a simple wet-chemical route. Both the crystallinity of samples and the concentration of OH^- adsorbed at the surface were experimentally controlled by adjusting the reaction time. An abnormal phenomenon that photoluminescence efficiency decreases with the increase of crystallinity demonstrates enormously adverse effect of OH^- on photoluminescence, especially, as the OH^- content reaches a critical value, the luminescent efficiency decreases more drastically. This strong dependence of photoluminescence on the OH^- content indicates that to control the OH^- content in a limited range or to reduce the OH^- effect as much as possible is an efficient way to improve photoluminescence efficiency. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2158703]

Luminescent materials doped with rare-earth ions have been extensively investigated in the past few decades because of their technological applications in lighting,[1] displays,[2] x-ray photography,[3] lasers,[4] and amplifiers for fiber-optic communication.[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.

One of the concerns for the luminescent materials is the luminescent efficiency, which is related to several factors, including size, shape, structure, crystallinity, and phase purity of synthesized materials.[8–11] The efficiency of luminescent materials can directly affect the qualities of devices, in which the luminescent materials are used. Therefore, considerable efforts have been made to design some ideas, such as energy transfer,[12,13] doping,[2,14] structure transformation,[9] quantum cutting,[15] for improving the luminescent efficiency. As we have known, the wet-chemical route, such as sol-gel,[16] precipitation,[17] hydrothermal method,[18,19] can control size, shape, structure, crystallinity very well by tuning the synthetic parameters such as reaction time, solution concentration, and solution pH. Therefore, a great deal of interest has been focused on the synthesis using the wet-chemical route and characterization of materials.[18,20,21] Since the wet-chemical synthetic route is carried out in the aqueous solution, there are a few amounts of ions, especially OH^- ions, to be adsorbed at the material's surface and be coordinated with rare-earth ions.[13,17,20] It is well known that OH^- possesses high vibration frequency, and thus always acts as luminescent quenchers in the luminescent materials doped with rare earth ions.[13] A few researchers have just simply mentioned the influence of OH^- on the luminescence in their reports,[16,20,21] but have not investigated the effect of the OH^- content on the luminescence yet, since they does not find a way to change the OH^- content regularly. As a matter of fact, to understand the relationship between the OH^- content and photoluminescence is essential in optimizing the luminescent efficiency. Furthermore, it is a challenging step to attempt to regularly change the OH^- content involved in the sample for the investigation on the relationship between the OH^- content and photoluminescence.

In this letter, we manage to experimentally control the regular change of the OH^- content, and then investigate the relationship between the OH^- content and photoluminescence. Thus, a quantitative concept on the influence of OH^- on photoluminescence can be impressed in one's mind.

Tb-doped $YPO_4 \cdot 2H_2O$ was synthesized via a simple wet-chemical route. Appropriate amounts of high purity Y_2O_3 and Tb_4O_7 were dissolved in concentrated HNO_3 to form $Y(NO_3)_3 \cdot 6H_2O$ and $Tb(NO_3)_3 \cdot 6H_2O$ solutions, to which, appropriate volume of H_3PO_4 solution was added slowly. The final pH value was adjusted to 6–7 by the addition of aqueous ammonia (NH_4OH). After being well stirred at 60 °C for different times ranging from 0.5 to 10 h, the formed colloidal suspensions were treated by diluted HNO_3 in order to remove a small amounts of rare earth hydroxide impurities, and then filted, washed several times with deionized water, and finally dried at 60 °C in air.

Figure 1 shows x-ray diffraction (XRD) patterns of samples synthesized in different reaction times ranging from 0.5 to 10 h. For simplicity, the samples synthesized during 0.5, 1, 3, 5, and 10 h are denoted as samples a, b, c, d, and e, respectively. It is noted that, all of the diffraction peaks could be well indexed to the monoclinic $YPO_4 \cdot 2H_2O$ with

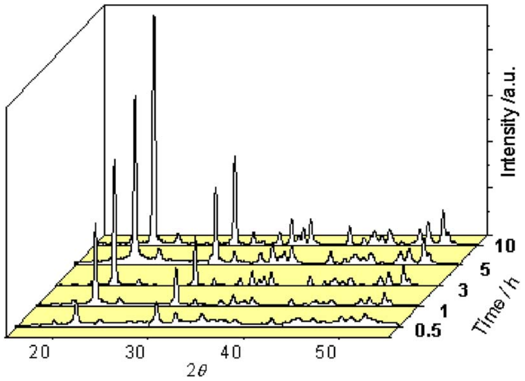

FIG. 1. (Color online) XRD patterns of the samples a, b, c, d, and e. Samples from a to e are synthesized with different reaction times ranging from 0.5 to 10 h, as indicated in this figure. The concentration of Tb^{3+} doped in all these samples is as high as 6 mol %.

---

[a] Electronic mail: weihdi@yahoo.com.cn

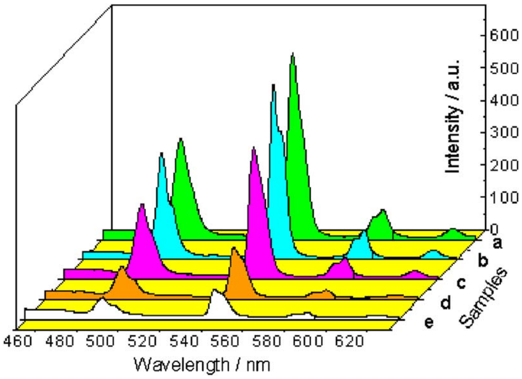

FIG. 2. (Color online) Emission spectra of samples a, b, c, d, and e under 355 nm excitation.

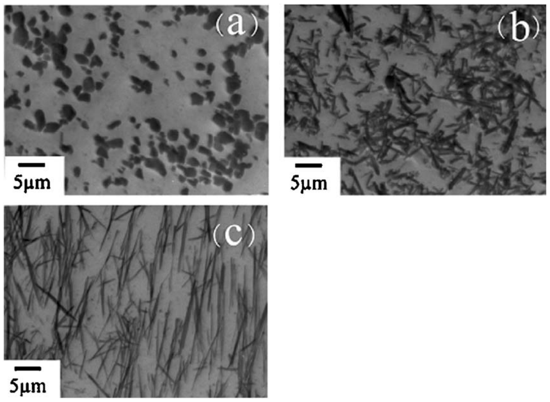

FIG. 4. SEM images of samples. (a) Sample a with the reaction time of 0.5 h; (b) sample c with the reaction time of 3 h; and (c) sample e with the reaction time of 10 h.

churchite-type structure and space group $I2/a$ (JCPDS File No. 85-1842). The intensity of diffraction peak is enhanced with the increase of reaction time, indicating the increase of crystallinity.

Figure 2 presents the emission spectra of the samples a, b, c, d, and e, respectively. All of them consist of lines ranging from 460 to 630 nm, which originate from the transitions between different f-electron states of Tb^{3+}, i.e., between the excited $^5D_4$ to the ^7F_j ($j=6$, 5, 4, 3) ground states.[22] It is worth noting that the luminescent intensity decreases with the increase of reaction time. The earlier XRD data indicate that the crystallinity of the samples enhances with the increase of reaction time. This means that the luminescent intensity decreases as the crystallinity increases. Generally, the enhanced crystallinity contributes to the luminescence.[20,23] Interestingly, in this work, we find that the luminescent efficiency decreases as the crystallinity increases, especially for samples d and e, the luminescent efficiency decrease more drastically, although the crystallinity of these two samples is much higher than that of samples a, b, and c. What on earth results in this abnormal phenomenon?

The Fourier-transform infrared (FTIR) spectra of samples a, b, c, d, and e are shown in Fig. 3. The peaks at about 1640, 1720 and 2300 cm^{-1}, and a broadband ranging from 2700 to 3700 cm^{-1} are characteristic of the vibration of the OH groups. It can be seen that the vibration intensity of OH group enhances as the reaction time increases. This indicates that the OH^- content increases with the increase of reaction time. In fact, OH^- ions are adsorbed at the surface easily and coordinated with rare earth ions due to the nature of wet-chemical route.[13,17] Usually, the morphologies and the surface states of the samples can affect the adsorption of chemical species at the surface. Figure 4 shows scanning electron microscopy (SEM) images of samples a, c, and e. The sample synthesized with the reaction of 0.5 h has a shape of particles with a size about 1–2 μm, as shown in Fig. 4(a). With the increase of reaction time, the shapes of the samples tend to rods and wires, as shown in Figs. 4(b) and 4(c), respectively. Furthermore, it is obviously seen that the width becomes smaller, and the aspect ratio becomes larger with an increase of reaction time. Such a particle-rod-wire shape evolution results in the increase of surface area and surface energy of samples with an increase of reaction time, thus enhancing the chance of the adsorption of OH^- at the surface based on the knowledge of thermodynamics. This prediction is in good agreement with the FTIR result, as shown in Fig. 3: more is the reaction time, and higher is the OH^- content. Therefore, the reaction time is a parameter, which may control the OH^- content very well by the changes of morphologies and surface states of the samples. It is a preliminary step to control the change of OH^- content for investigation on the relationship between OH^- content and photoluminescence. In addition, the mechanism of the growth of $YPO_4 \cdot 2H_2O$ with reaction time would be interesting, and deserves further exploration.

Figure 5 shows the fluorescent decay curves of the $^5D_4$–$^7F_5$ transition for Tb^{3+} in the samples a, b, c, d, and e at room temperature. It can be seen that the fluorescent decay rate increases from sample a to sample e, resulting in the decrease of fluorescent lifetime of the $^5D_4$ state. As observed in Fig. 3, OH^- vibration frequency occurs in the broad range of 2700–3700 cm^{-1}, which is much higher than other vibra-

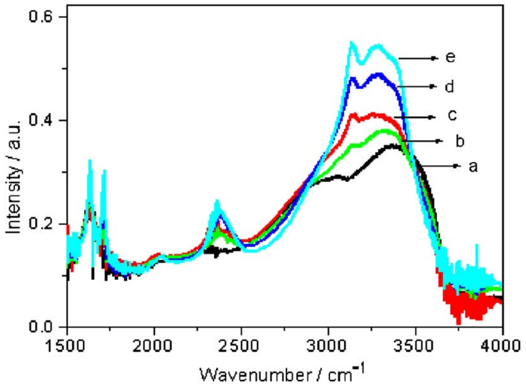

FIG. 3. (Color online) FTIR spectra of samples a, b, c, d, and e.

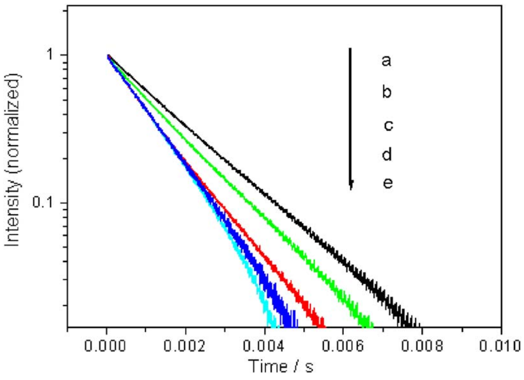

FIG. 5. (Color online) Fluorescent decay curves of the $^5D_4$–$^7F_5$ transition for Tb^{3+} in the samples a, b, c, d, and e at room temperature.

tion such as PO_4^{3-}.[24] As a result, only a few phonons are required for nonradiative de-excitation of the $^5D_4$ state. OH⁻ ions thus, seem to be very efficient quenchers of the luminescence of Tb^{3+} through multiphonon relaxation. Therefore, the increase of the OH⁻ content from sample a to sample e accelerates the fluorescent decay and lowers the luminescent efficiency. This indicates a relationship of the OH⁻ content with photoluminescence. Furthermore, for samples d and e, the fluorescent decay curves deviate from linear shape, showing the nonexponential behavior of fluorescent decay, which is in good accordance with remarkable decrease of photoluminescence for samples d and e, as observed in Fig. 2. This indicates a strong dependence of photoluminescence behavior on the OH⁻ concentration. As the OH⁻ concentration increases, especially reaches a critical value, the distance between rare earth ions and OH⁻ shortens, which enhances the probability of the interaction between rare earth ions and OH⁻, thus increasing the nonradiative relaxation rate of excited states of Tb^{3+}, just as observed in samples d and e. A few researchers also discussed the effect of OH⁻ on the luminescence in their related reports. For example, Jiang *et al.*[20] reported that the photoluminescence efficiency of YBO_3:Eu prepared by the hydrothermal method was lower than that of the sample prepared by solid-state reaction, since OH⁻ ions in aqueous solutions are easily coordinated to rare earth ions at the surface in the synthesis process using the wet-chemical route. Sabbatini *et al.*[25] reported that the replacement of the OH group by low-frequency OD group diminishes the vibronic deactivation pathway and thus enhances the luminescent efficiency. There are other more examples about the effect of OH⁻ on the luminescence. However, these examples have just made a conclusion that OH⁻ takes the function as multiphonon relaxation centers, and thus affects the lifetime of excited state and the luminescent efficiency. Based on our present knowledge, the investigation on the relationship between OH⁻ content and photoluminescence is conducted for the first time. Our results indicate that there exists little effect of OH⁻ on photoluminescence as the OH⁻ content is lower than a specific value, and that there exist a large exists of OH⁻ on photoluminescence as the OH⁻ content is higher than this specific value. Therefore, to control the OH⁻ content in a limited range or to reduce OH⁻ content as much as possible is an efficient way to improve the photoluminescence efficiency of rare earth ions doped materials synthesized via the wet-chemical route.

As a matter of fact, both crystallinity of the sample and OH⁻ content involved in the sample produce quantitative changes with the increase of the reaction time. As is known, the crystallinity has a positive effect on the luminescence, but OH⁻ has a negative effect on the luminescence. Thus, the net effect on the luminescence is the result of competition of these two effects. However, our experimental result that the luminescent efficiency decreases with the increase of crystallinity indicates strongly adverse effect of OH⁻ on photoluminescence, i.e., the negative effect on photoluminescence resulting from the increase of OH⁻ content is much larger than the positive effect resulting from the increase of crystallinity as the reaction time increases. Therefore, it seems very important that the synthetic parameters such as reaction time, solution concentration, and solution *p*H should be optimized in order to obtain desirable photoluminescence behavior. Also, it is required to develop some posttreatment techniques to reduce the OH⁻ effect for the further improvement of luminescent efficiency.

In conclusion, we designed an experiment on controlling the change of the OH⁻ content, and investigated the relationship between the OH⁻ content and photoluminescence. This work is a vivid example, which makes people clearly aware of largely adverse effect of OH⁻ on the luminescence and strong dependence of photoluminescence on the OH⁻ content. Thus, this work implies that it is required to reduce multiphonon relaxation process in order to improve the luminescent efficiency. Currently, we are engaged in the research towards this direction. One apparent way is to reduce the OH⁻ content by proper adjustment of synthetic parameters; another possible way is to reduce the effect of OH⁻ on photoluminescence by several posttreatment techniques, e.g., coating an inert layer on the surface of the materials or annealing at a suitable temperature.

This work was supported by the National Natural Science Foundation of China (Grant Nos. 50502031, 50172046, 10274083) and the State 863 Project (Grant No. 2002AA311160).

[1] K. Riwotzki, H. Meyssamy, H. Schnablegger, A. Kornowski, and M. Haase, Angew. Chem., Int. Ed. **40**, 573 (2001).
[2] J. C. Park, H. K. Moon, D. K. Kim, S. H. Byeon, B. C. Kim, and K. S. Suh, Appl. Phys. Lett. **77**, 2162 (2000).
[3] G. Blasse and B. C. Grabmaier, *Luminescent Materials* (Springer, Berlin, 1994).
[4] J. R. O'Connor, Appl. Phys. Lett. **9**, 407 (1966).
[5] D. B. Barber, C. R. Pollock, L. L. Beecroft, and C. K. Ober, Opt. Lett. **22**, 1247 (1977).
[6] F. Meiser, C. Cortez, and F. Karuso, Angew. Chem., Int. Ed. **43**, 5954 (2004).
[7] C. Louis, R. Bazzi, C. A. Marquette, J. Bridot, S. Roux, G. Ledoux, B. Mercier, L. Blum, P. Perriat, and O. Tillement, Chem. Mater. **17**, 1673 (2005).
[8] D. Boyer, G. Bertrand-Chadeyron, R. Mahiou, C. Caperaa, and J. C. Cousseins, J. Mater. Chem. **9**,211 (2004).
[9] C. J. Jia, L. D. Sun, F. Luo, X. C. Jiang, L. H. Wei, and C. H. Yan, Appl. Phys. Lett. **84**, 5305 (2004).
[10] W. H. Di, X. J. Wang, B. J. Chen, H. S. Lai, and X. X. Zhao, Opt. Mater. **27**, 1386 (2005).
[11] H. W. Song, L. X. Yu, S. Z. Lu, T. Wang, Z. X. Liu, and L. M. Yang, Appl. Phys. Lett. **85**, 470 (2004).
[12] J. C. Bourcet and F. K. Fong, J. Chem. Phys. **60**, 34 (1974).
[13] H. Mass, A. Currao, and G. Calzaferri, Angew. Chem., Int. Ed. **41**, 2495 (2002).
[14] L. D. Sun, C. Qian, C. S. Liao, X. L. Wang, and C. H. Yan, Solid State Commun. **119**, 393 (2001).
[15] R. T. Wegh, H. Donker, K. D. Oskam, and A. Meijerink, Science **283**, 663 (1999).
[16] D. Boyer and R. Mahiou, Chem. Mater. **16**, 2518 (2004).
[17] W. H. Di, X. J. Wang, B. J. Chen, S. Z. Lu, and X. X. Zhao, J. Phys. Chem. B **109**, 13154 (2005).
[18] H. Meyssamy, K. Riwotzki, A. Kornowski, S. Naused, and M. Haase, Adv. Mater. (Weinheim, Ger.) **11**, 840 (1999).
[19] Z. G. Yan, Y. W. Zhang, L. P. You, R. Si, and C. H. Yan, Solid State Commun. **130**, 125 (2004).
[20] X. C. Jiang, C. H. Yan, L. D. Sun, Z. G. Wei, and C. S. Liao, J. Solid State Chem. **175**, 245 (2003).
[21] A. Huignard, T. Gacoin, and J. P. Boilot, Chem. Mater. **12**, 1090 (2000).
[22] J. Robbins, B. Cockayne, B. Lent, and J. Glasper, Solid State Commun. **20**,673 (1976).
[23] Y. C. Kang, J. R. Sohn, H. S. Yoon, K. Y. Jung, and H. D. Park, J. Electrochem. Soc. **150**, H38 (2003).
[24] Y. P. Fang, A. W. Xu, R. Q. Song, H. X. Zhang, L. P. You, J. C. Yu, and H. Q. Liu, J. Am. Chem. Soc. **125**, 16025 (2003).
[25] N. Sabbatini, S. Dellonte, M. Ciano, A. Bonazzi, and B. Balzani, Chem. Phys. Lett. **107**, 212 (1984).