

Investigations of Phase Structure Transformation and VUV Excitation of YPO₄:Tb Synthesized by Solution Precipitation Route

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Tb-doped YPO₄ has been synthesized by a mild and simple solution precipitation approach. pH value of synthesis has a significant influence on the formation and crystallinity of YPO₄:Tb. Phase transformation occurs in the annealing process. Vacuum ultraviolet (VUV) excitation of Tb-doped YPO₄ is investigated and possible luminescence mechanism under VUV excitation is illustrated.

Lanthanide phosphates represent a class of materials with significant technological importance, and are extensively applied as laser, ceramic, sensor, phosphor, and heat-resistant materials.^{1–3} Lanthanide phosphate compounds are synthesized by different methods such as sol–gel, hydrothermal, precipitation, and high-temperature solid-state reaction.^{4–6} Their physicochemical properties, such as the chemical composition, the crystal structure, the grain size and morphology, and the electronic and luminescent properties, depend strongly on the synthesis routes and parameters.⁷

Among various lanthanide phosphate compounds, the lanthanide doped lanthanide phosphates are extremely suitable for applications as phosphors owing to the transition between energy levels of lanthanide ions. In the past several decades, the spectroscopic properties of lanthanide ions in UV–vis regions have been widely investigated,^{8,9} and the theory about the energy levels and energy level transitions in UV–vis regions has been established, which provides a basis for the development of luminescent materials. Very recently, the development and application of mercury-free lamps and plasma display panels (PDPs) induce considerable research interest in VUV region.^{10,11} However, the luminescence property and mechanism under VUV excitation have not been well understood yet. In this letter, we report the synthesis of YPO₄:Tb by solution precipitation method and its phase transformation in the annealing process. More importantly, VUV excitation of Tb-doped YPO₄ is investigated, and its possible luminescent mechanism in VUV excitation is illustrated.

Ultrapure lanthanide oxide Y₂O₃ and Tb₄O₇ were dissolved in concentrated nitric acid to form 0.5 M solution, together with which, the (NH₄)₂HPO₄ solution of the same mol concentration was dripped into a vessel in different pH conditions at room temperature to form white precipitate. The precipitate obtained was ripened at 50 °C for 4 h, filtered and washed for 3 times with distilled water, then dried at 80 °C. The dried precipitate was annealed at various temperatures in reducing atmosphere.

All the measurements were performed at room temperature. XRD studies were conducted on a Rigaku D/max-2000 X-ray powder diffractometer using Cu Kα radiation. The excitation

spectra were measured by using a vacuum ultraviolet monochromator and a deuterium (D₂) lamp and were normalized to that of sodium salicylate. The emission spectra were obtained under 147-nm excitation.

The effect of annealing temperature on the phase structure of the product synthesized in the acidic condition is investigated. As shown in Figure 1, for the as-prepared sample, all of the peaks could be indexed to the monoclinic YPO₄·2H₂O:Tb, and this structure remains for the sample annealed at 150 °C. As the annealing temperature increases to 200 °C, the diffraction peak recognized as tetragonal structure appears, as marked by a symbol in Figure 1, this means that the phase transformation from YPO₄·2H₂O:Tb with monoclinic structure to YPO₄:Tb with tetragonal structure occurs, which is described as [YPO₄·2H₂O:Tb]_{monoclinic} → [YPO₄:Tb]_{tetragonal} + 2H₂O; when the annealing temperature reaches 250 °C, the phase with monoclinic structure has almost totally disappeared. Above results indicate that this phase transformation process spans a temperature range from 150 to 250 °C. With further increase of annealing temperature up to 800 °C, the YPO₄:Tb phase remains tetragonal structure, but the diffraction peaks intensity is enhanced with temperature, indicating crystal growth of YPO₄:Tb.

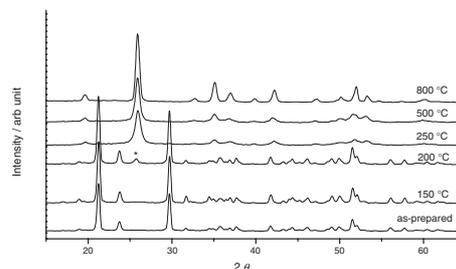


Figure 1. X-ray diffraction patterns of the sample synthesized in the acidic solution after annealing at various temperatures.

Figure 2 shows the XRD patterns of the as-prepared samples synthesized in different pH conditions and those annealed at 500 °C. When the synthesis is conducted in the alkaline condition (pH = 9), the resulting product is almost amorphous. However, the synthesis is carried out in the acidic (pH = 2) or neutral condition (pH = 7), YPO₄·2H₂O:Tb with monoclinic structure is observed. Furthermore, the as-prepared sample synthesized in the acidic condition has higher crystallinity than that synthesized in the neutral condition. This indicates that the acidic condition is helpful to the formation of YPO₄·2H₂O:Tb with high crystallinity. The as-prepared sample synthesized in the alkaline solution after annealing is almost amorphous yet, even at a higher annealing temperature, 500 °C, as shown in Figure 2. This

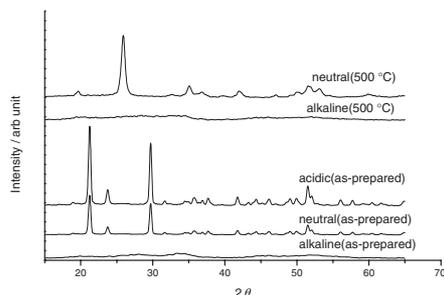


Figure 2. X-ray diffraction patterns of the samples obtained in different pH conditions and those annealed at 500 °C.

means that YPO₄:Tb could not be obtained in the alkaline condition.

Figure 3 shows the VUV excitation spectrum of ⁵D₄–⁷F₅ emission of Tb³⁺ and the emission spectrum under 147-nm excitation. The VUV excitation spectrum consists of several broad bands, among which, the band peaking at 149 nm should be ascribed to the host absorption. Generally, the energy of host lattice absorption is a definite value, i.e., it should not have a considerable change when different activators are doped into the same host. Therefore, in order to confirm the contribution of the band peaking at 149 nm, we measure the VUV excitation spectrum of Eu-doped YPO₄, in which, the band peaking at 149 nm is also observed. This wavelength at about 149 nm is very close to the emission wavelength of Xe discharge, i.e., 147 nm. Other bands in the excitation spectrum of Tb-doped YPO₄ are ascribed to the transitions from the lower energy level of the 4f⁸ configuration to the energy levels of the 4f⁷5d configuration of the Tb³⁺, i.e., ⁷D and ⁹D levels. The transitions between ⁷F_j and ⁷D_j are spin-allowed, and should have high energy; whereas the transitions between ⁷F_j and ⁹D_j are spin-forbidden, and should have low energy. Therefore, the band peaking at 267 nm with low energy is ascribed to the transitions between ⁷F_j and ⁹D_j, and the two strong bands peaking at 187 and 226 nm are ascribed to the transitions between ⁷F_j and ⁷D_j. These two bands are more likely to be due to the splitting of ⁷D_j level. The last two excitation bands in VUV excitation spectrum are also observed in UV excitation spectrum, as shown in Figure 4. Furthermore, their locations are similar. Upon excitation the host absorption at 147 nm and direct excitation the ⁷F_j–⁷D_j transition at 226 nm, their emission spectra under VUV–UV excitation are shown in Figures 3 and 4. The emission lines under VUV and UV excitation are similar. By this result, the luminescence mechanism under VUV excitation may be understood well. Under VUV excitation, the energy is absorbed first by the host, and then transferred to the activators. Therefore, the luminescence efficiency under VUV excitation depends strongly on the host absorption rate on VUV light and the energy transfer rate from the host to the activator. It is worth noting that Tb-doped YPO₄ phosphor exhibits a strong host absorption in the VUV range, however this absorption in the VUV range is not as strong as the highest 4f–5d transition band of the Tb³⁺ in the UV range.

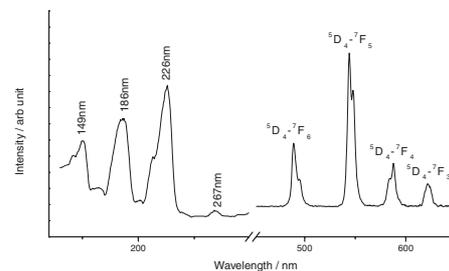


Figure 3. VUV excitation spectrum of YPO₄:Tb in 130–300-nm range and its emission spectrum under 147-nm excitation.

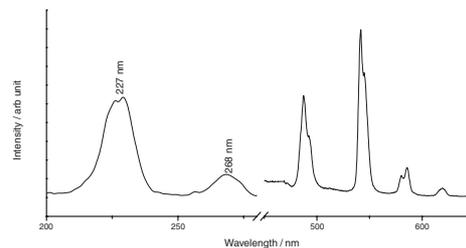


Figure 4. UV excitation spectrum of YPO₄:Tb in 200–280-nm range and its emission spectrum under UV excitation.

More work is required to improve the host absorption for luminescence enhancement under VUV excitation.

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References

- 1 J. B. Davis, D. B. Marshal, and P. E. D. Morgan, *J. Eur. Ceram. Soc.*, **20**, 583 (2000).
- 2 K. Riwozki, H. Meyssamy, H. Schnablegger, A. Kornowski, and M. H. Haase, *Angew. Chem., Int. Ed.*, **40**, 573 (2001).
- 3 S. Nishihama, T. Hirai, and I. Komasa, *J. Mater. Chem.*, **12**, 1053 (2002)
- 4 J. M. Nedelec, C. Mansuy, and R. Mahiou, *J. Mol. Struct.*, **651–653**, 165 (2003).
- 5 G. R. Patzke, F. Krumeich, and R. Nesper, *Angew. Chem., Int. Ed.*, **41**, 2446 (2002).
- 6 M. Kizilyalli and A. J. E. Welch, *J. Appl. Crystallogr.*, **9**, 413 (1976).
- 7 S. Lucas, E. Champion, D. Bregiroux, D. Bgernache-Assollant, and F. Audubert, *J. Solid State Chem.*, **177**, 1302 (2004).
- 8 J.-C. Bourcet and F. K. Fong, *J. Chem. Phys.*, **60**, 34 (1974).
- 9 M. Heike, R. karsten, K. Andreas, N. Sabine, and H. Markus, *Adv. Mater.*, **11**, 840 (1999).
- 10 T. Justel, P. Huppertz, W. Mayr, and D. U. Wiechert, *J. Lumin.*, **106**, 225 (2004).
- 11 K. Y. Jung, E. J. Kim, and Y. C. Kang, *J. Electrochem. Soc.*, **151**, H69 (2004).