Vacuum Ultraviolet Spectra of YVO₄: Tm³⁺

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Abstract: Series of blue phosphors YVO₄: xTm (x = 0.001, 0.003, 0.005, 0.007, 0.01, 0.03, 0.05) were synthesized by the high temperature solid state reaction in this paper. X-ray diffraction shows that the product is a tetragonal zircon structured single phase. The result is consistent with JCPDS standard card (72-0861). The vacuum UV excitation spectrum and emission spectra of the phosphors at room temperature were also detected. The vacuum UV excitation spectrum of YVO₄: xTm includes a continuous banded peak in the range of 120 ~ 350 nm, and there are two significant peaks at 155 nm and 333 nm. Excited by 155 nm, the emission spectrum of YVO₄: xTm consists of two parts. The main emission spectrum at 474 nm is a sharp peak, caused by ³G₄→³H₄ transition of Tm³⁺. The weaker emission peak is at 650 nm, which is generated by ⁴G₄→³H₄ transition of Tm³⁺. In addition, there is a weak band emission centering around 540 nm, which presents broadband emission of VO₄⁻ ions. With the increasing of Tm³⁺ mole fraction (x) from 0.001 to 0.005, the emission intensity gradually increases to a maximum value. Then, as x increases continuously, the emission intensity decreases gradually, presents an obvious concentration quench. By analyzing the spectra of YVO₄: xTm and its luminescent mechanism, it can be derived that YVO₄: Tm³⁺ is a kind of blue phosphor material with high luminous efficiency and color purity under ultraviolet or vacuum ultraviolet excitation.

Key words: blue emitting; YVO₄: Tm³⁺; vacuum ultraviolet

YVO₄: Tm³⁺ 的真空紫外发光性能

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摘要：通过高温固相反应合成 YVO₄: xTm(x = 0.001, 0.003, 0.005, 0.007, 0.01, 0.03, 0.05)蓝色系列粉末状发光材料。经 X 射线衍射分析产物为单相，属四方晶系石结构，其结果与 JCPDS 标准卡(72-0861)相符。检测了材料的真空紫外激发光谱和发射光谱。YVO₄: xTm 的真空紫外激发光谱在120 ~ 350 nm 范围内为连续的
带状峰，在155 nm和333 nm附近有明显的峰值。在155 nm激发下，YVO₃·xTm的发射光谱由两部分组成，其中主发射峰在474 nm附近呈一尖锐的线状，来自Tm⁺⁺的"G₄→̧H₆"跃迁；在650 nm左右有一弱发射峰，来自Tm⁺⁺的"G₅→̧H₆"跃迁。另外，还有一较弱的带状发射，中心位于540 nm左右，来自样品的VO⁺⁺离子的宽带发射。随着Tm⁺⁺摩尔分数x由0.001增加到0.005，Tm⁺⁺发射光谱强度逐渐增加到最大值。之后随着x继续增加，发射光谱强度逐渐下降，呈现明显的浓度猝灭现象。通过对YVO₃·xTm的光谱分析及发光机理进行推导，认为YVO₃·Tm⁺⁺在紫外及真空紫外激发下，是一种具有较高发光效率以及色纯度较好的蓝色发光材料。

关 键 词：蓝光发射；YVO₃·Tm⁺⁺；真空紫外

1 Introduction

Comparing with LCD TV，plasma TV has higher refresh rate，contrast，color saturation and dynamic resolution. Meanwhile，the display size of plasma TV can be produced bigger. According to these advantages，plasma TV is considered to be the best platform for 3D display in recent years. In addition，the advantage in dynamic resolution of plasma TV can solve the double image problem in 3D display. Therefore，3D plasma display technology is more competitive comparing with other displays.

Phosphor is one of the important factors determining the image quality of the PDP display. In order to improve the display characteristics，high property PDP fluorescent powder is necessary. Hence，as one of the important basic researches of PDP device，PDP phosphor becomes a hot spot again in the field of luminescence materials.

At present，blue phosphor for PDP on the market is mainly Eu⁺⁺ activated aluminate phosphor. Because the multiple aluminate blue powder has serious thermal degradation during the roasting of coated screen，the instability of Eu⁺⁺，and moreover，easy to become Eu⁺³ in the bombardment of VUV irradiation and discharge ion，all of these are harmful for the performance of phosphor. In order to solve this problem，a stable activated ion is needed. Usually the Tm³⁺ doped materials have two emission in the blue region，one is at 450 nm due to the ¹D₂→¹H₄ transition of Tm³⁺，and the other is at 470 nm due to the ¹G₄→¹H₆ transition of Tm³⁺. Besides，though the valence state of Tm ions can be +2，it is hardly as stable as Tm³⁺，thus there is almost no Tm²⁺→Tm³⁺ conversion during either production or application of PDP device，and blue phosphors doped with Tm³⁺ are expected to present higher resistance to aging.

The luminescent material with the yttrium vanadate matrix has good chemical stability and thermal stability because Y³⁺ has full 3d orbital and empty 4d，4f orbital. Previous studies have proved that，due to the high absorption cross section in vacuum ultraviolet and the high energy transfer from matrix to the activation，this luminescent material has high luminescence efficiency and luminous intensity. Tm³⁺ activated rare earth vanadate presents higher color purity and an appropriate fluorescence lifetime，so it is possible to be used in plasma 3D display device as new blue-ray powder.

2 Experiments

2.1 Sample Preparation

Sample was prepared by high-temperature solid state synthesis. Firstly，Y₂O₃ (99.99% )，NH₄VO₃ (AR)，Tm₂O₃ (99.99%)，H₃BO₃ (AR) and other reagents were weighted in agate mortar at a certain molar ratio. Then，the mixed powders were poured into a corundum crucible and calcined at 900 – 1000 °C for 2 – 3 h. The treated sample was then washed with 1：1 aqueous ammonia and deionized water solution. At the end，the sample was dried and calcined at 1 300 – 1 350 °C for 4 – 6 h to obtain YVO₃·Tm phosphor.

2.2 Characterization

The structure of samples were determined by the PW-1700 X-ray diffraction. The vacuum ultraviolet excitation and emission spectra at room temperature (RT) were characterized at the National
Synchrotron Radiation Laboratory in University of Science and Technology of China.

3 Results and Discussion

3.1 Structural analysis

Fig. 1 shows the XRD results of YVO₄: Tm³⁺ sample synthesized by high-temperature solid-state reaction at 1 350 °C. The figure indicates that the synthesized product is a single YVO₄ phase which belongs to tetragonal system, with zircon structure. The result corresponds to JCPDS standard card (72-0861). In YVO₄, each V atom is in the center of the tetrahedron formed by four O atoms, Y atoms are surrounded by eight oxygen atoms, and eight oxygen atoms form two deformed tetrahedron. TmVO₄ and YVO₄ are isomorphic to each other. Therefore, the introduced Tm³⁺ does not change the structure of YVO₄, but diffuses into the lattice, substitutes Y³⁺ and form a luminescent center.

![Fig. 1 XRD patterns of YVO₄: 0.01Tm³⁺ synthesized by the conventional solid state reaction](image)

3.2 Spectra analysis

Fig. 2 presents the excitation spectrum of YVO₄: xTm at RT between 120 – 350 nm and the emission spectra excited by 155 nm and 333 nm at RT, respectively. As shown in the figure, under the monitor of 475 nm, the excitation spectrum of YVO₄: xTm between 120 – 350 nm is a broad band, and has clear peaks at 155 nm and 333 nm. In general, broadband absorption is mainly the absorption of charge transfer state or the absorption of the matrix or may be assigned to lattice defects. But because of the electronic arrangement of Tm³⁺, the charge transfer state was located in higher energy level. Therefore, the absorption in the excitation spectrum is due to VO₄²⁻. Among them, the first peak at 155 nm belongs to the weak absorption band of VO₄²⁻ group. The excitation band near 200 nm can be attributed to 2p (O) → 4f (Y) or 5d transition. In the range of 240 – 380 nm, there is an absorption band which is caused by the transform of VO₄²⁻ from the base state ¹A₂ (¹T₁) to stimulate state ¹A₁ (¹T₁), ¹B₁ (¹E), ¹A₄ (¹E), ¹E (¹T₁), ¹E (¹T₂) of VO₄²⁻. Meanwhile, if VO₄²⁻ is excited, this excitation could result in the transition of charges, and then the electrons transfer from the molecular orbital which shows characteristic of ligands (O) orbital to the orbital that shows characteristics of metal (V) d orbital, and it will produce broadband absorption.

![Fig. 2 (a) VUV excitation spectrum of YVO₄: xTm at RT, λₑₑₑ = 475 nm. (b) Emission spectrum of YVO₄: xTm at RT, λₑₑₑ = 155 nm. (c) Emission spectrum of YVO₄: xTm at RT, λₑₑₑ = 333 nm.](image)
Therefore, the broadband excitation between 240 – 350 nm in figure should be formed by both of the absorptions.

The emission spectrum is consisted of two parts under 155 nm excitation, including the main emission peak at 474 nm which is very sharp due to the \( ^{1}G_{4} \rightarrow ^{3}H_{6} \) transition of Tm\(^{3+}\). On the other hand, a weaker emission peak at 650 nm is attributed to the \( ^{1}G_{4} \rightarrow ^{3}H_{1} \) transition of Tm\(^{3+}\). In addition, there is a weaker ribbon emission center at 540 nm, which corresponds to the broadband emission of VO\(^{3+}\) ions from the sample. It is consistent with result of the excitation under 333 nm\(^{[19]}\). With the increasing of Tm mole fraction, the broadband emission peak at 540 nm gradually weakened because of self-quenching of VO\(^{3+}\) and luminescence quenching of Tm\(^{3+}\). At the same time, with the increasing of Tm mole fraction, the emission of Tm\(^{3+}\) increases and reaches its maximum when \( x = 0.005 \), then there is a characteristic concentration quenching phenomenon. Similar results could be found when it is excited at 333 nm (Table 1).

**Table 1** Emission peak position and intensity of YVO\(_4\):xTm (\( x = 0.001, 0.003, 0.005, 0.007, 0.01, 0.03, 0.05 \))

| \( x \) | \( \lambda_{ex} = 155 \text{ nm} \) | | \( \lambda_{em} = 333 \text{ nm} \) |
|---|---|---|---|---|---|
| | Peak1/\text{nm} | Intensity/\text{a. u.} | Peak2/\text{nm} | Intensity/\text{a. u.} | Peak1/\text{nm} | Intensity/\text{a. u.} | Peak2/\text{nm} | Intensity/\text{a. u.} |
| 0.001 | 474 | 4 313 | 537 | 1 867 | 475 | 19 289 | 544 | 139.29 |
| 0.003 | 474 | 5 841 | 529 | 1 062 | 475 | 23 547 | 546 | 105.56 |
| 0.005 | 474 | 9 124 | 539 | 1 059 | 475 | 39 938 | 543 | 102.07 |
| 0.007 | 474 | 6 865 | 539 | 482 | 475 | 38 343 | 526 | 84.718 |
| 0.01 | 474 | 6 688 | 536 | 432 | 475 | 38 787 | 544 | 78.582 |
| 0.03 | 474 | 2 777 | 543 | 291 | 475 | 37 314 | 546 | 80.577 |
| 0.05 | 475 | 1 709 | 544 | 225 | 475 | 24 767 | 549 | 67.702 |

According to the study of luminescent properties of Tm\(^{3+}\), the strength of blue emitting of Tm\(^{3+}\) does not only depend on the effectiveness of the energy transfer from the matrix to Tm\(^{3+}\), but also on the competition with other non-blue-emitting. According to the energy levels of Tm\(^{3+}\) as well as its excitation spectra and emission spectra in YVO\(_4\):xTm, we derived the luminescence mechanism of Tm\(^{3+}\) under vacuum ultraviolet excitation. Tm\(^{3+}\) has three excited states which are \( ^{3}P_{0} (35 000 \text{ cm}^{-1}) \), \( ^{1}D_{2} (27 770 \text{ cm}^{-1}) \) and \( ^{1}G_{4} (21 200 \text{ cm}^{-1}) \)\(^{[13]}\), respectively. The excitation energy of matrix in the vacuum ultraviolet region is 64 500 cm\(^{-1}\), which can stimulate emissions of \( ^{3}P_{0} (35 000 \text{ cm}^{-1}) \), \( ^{1}D_{2} (27 770 \text{ cm}^{-1}) \) and \( ^{1}G_{4} (21 200 \text{ cm}^{-1}) \). But the excitation energy of matrix in the ultraviolet region is 30 030 cm\(^{-1}\), which can’t stimulate transmitter of \( ^{3}P_{0} (35 000 \text{ cm}^{-1}) \), but only \( ^{1}D_{2} (27 770 \text{ cm}^{-1}) \) or \( ^{1}G_{4} (21 200 \text{ cm}^{-1}) \). As can be seen from the detected emission spectrum, the \( ^{1}G_{4} \) level emission is absolutely predominant. Photons law shows that one electron can only absorb one photon. YVO\(_4\):Tm\(^{3+}\) vacuum ultraviolet light-emitting mechanism is based on following derivation: First, electron in ground state of the matrix transfers to the excited state by absorbing vacuum ultraviolet or UV, then crosses to the internal through matrix and activator, electron jumps to the \( ^{3}P_{0} \) or \( ^{1}D_{2} \) state of Tm\(^{3+}\), while most of the electrons in the \( ^{3}P_{0} \) and \( ^{1}D_{2} \) state will reach \( ^{1}G_{4} \) quickly by non-radiative transition, and then transfer to different energy levels of Tm\(^{3+}\) from \( ^{1}G_{4} \) level, thus it can send a different light (Fig. 3). So we can deduce that YVO\(_4\) is a good matrix, can effectively absorb energy and transfer it to the active ions Tm\(^{3+}\).
the ultraviolet and vacuum ultraviolet excitation. For this reason, YVO₄: Tm³⁺ is a blue phosphor with higher luminous efficiency and better chromaticity.

4 Conclusion

YVO₄ sample doped with Tm³⁺ was synthesized by high-temperature solid-state reaction at 1350 °C. The product is a single YVO₄ phase which belongs to tetragonal system with zircon structure. The result is consistent to JCPDS standard card (72-0861) . Tm³⁺ does not change the structure of YVO₄, but enters the lattice, substitute Y³⁺ and forms a luminescent center. The excitation spectrum of YVO₄: xTm in the range of 120 – 350 nm is broadband with peaks at 155 nm and 333 nm. The absorption in the excitation spectra is caused by VO₂⁻. The peak at 155 nm belongs to the weak absorption band of VO₂⁻ group. The excitation band near 200 nm can be considered as a result of 2p (O) → 4f (Y) or 5d transition. In the range of 240 – 350 nm, there is an absorption band, due to the transition of VO₂⁻ from the base state ¹A₂ (¹T₁) to stimulate state like ¹A₁ (¹A₁), ¹B₁ (¹E), ¹A₂ (¹E), ¹E (¹T₁), ¹E (¹T₂)[12]. When VO₂⁻ is excited, this excitation can result in transition of charges, and then the electron transfer from molecular orbital which possesses the main characteristic of ligands (O) orbital to the orbital possesses characteristics of the metal (V) d orbital, and it will produce broadband absorption. Therefore, the broadband from 240 to 350 nm should be attributed to both of the absorptions. Under the excitation of 155 nm, the emission spectrum consists of two parts, including the main emission peak at 474 nm, which is very sharp due to ¹G₄→³H₆ transition of Tm³⁺, and a weaker emission peak at 650 nm caused by ¹G₄→³H₄ transition of Tm³⁺. In addition, there is a weaker ribbon emission centering at 540 nm, which is the broadband emission of VO₂⁻.

With the increasing of Tm³⁺ mole fraction, the emission of Tm³⁺ increases and reaches its maximum when x = 0.005, showing a characteristic concentration quenching phenomenon. It is consistent with the results of being excited at 333 nm. By analyzing the spectroscopy of YVO₄: Tm³⁺ and deriving its luminescence mechanism, we believe that YVO₄: Tm³⁺ is a blue phosphor with high luminous efficiency and relatively better chromaticity under the ultraviolet and vacuum ultraviolet excitation.

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