

Synthesis and Characterization of PVP/Tb_{4/3}L•7H₂O Luminescent Complex

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Abstract. Rare earth terbium [Tb (III)]-pyromellitic acid [H₄L] luminescent complex has been synthesized in polyvinylpyrrolidone (PVP) matrix by precipitation method. The chemical constitution of the complex has been demonstrated as PVP/Tb_{4/3}L•7H₂O by a combination of elemental analysis, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and Fourier-transform infrared spectroscopy (FT-IR). X-ray diffraction analysis (XRD) has shown that the complex is a new kind of crystal whose structure is totally different from the ligand. The morphology of the complex has been investigated by scanning electron microscopy (SEM). The results have shown that the well dispersed complex has a bulk crystal structure and the diameter of the crystal is about 1-2 μm. Thermogravimetric analysis (TG) has indicated that the luminescent complex is thermally stable below 467 °C. Photoluminescence spectra (PL) have revealed that the complex can emit Tb³⁺ characteristic green fluorescence under ultraviolet excitation.

1. Introduction

Rare earth elements possess the electron configuration with the same outermost electron number and similar 4f electron energy levels, thus the rare earth complexes exhibit many unique chemical and physical properties [1, 2]. It is widely used in optical, electrical, magnetic fields ect [1-7], and regarded as a treasury of new materials [2]. Rare earth luminescent complex has been attracted increasing interest in the development of rare earth functional materials due to its excellent luminescent properties [8-10].

Recently, the synthesis and fluorescence properties of rare earth terbium Tb (III) luminescent complex have been reported in the literatures [3, 11-13]. However, the synthesis and characterization of Tb (III)-H₄L luminescent complex obtained in PVP matrix is rarely published [14, 15]. In this paper, the bulk like Tb (III)-H₄L luminescent complex has been synthesized and the constitution, structure, morphology and properties of the complex have been studied in detail.

2. Experimental Section

2.1. Reagents

Tb₄O₇ (99.95%) was purchased from Baotou Rare Earth Research Institute. Pyromellitic acid was obtained from Beijing Chemical Company. Polyvinylpyrrolidone was purchased from Beijing Yingli Chemical Company. All of the other chemicals were of analytical grade and used as received.



2.2. Characterization

C, H, and N elemental analysis of the sample was carried out with a VarioEL elemental analyzer and Tb^{3+} was determined by TJA POEMS plasma mass spectrometer. FT-IR of the complex was performed on a BIO-RAD FTS135 Fourier-transform infrared (FT-IR) spectrometer using the KBr pellet technique with a wave number range of $4000\text{--}400\text{ cm}^{-1}$. The structure of the complex was measured by a RIGAKU D/max-II B X-ray diffractometer (XRD) using Cu $K\alpha$ radiation ($\lambda = 0.1542\text{ nm}$, $\theta = 2\text{--}60^\circ$). The morphologies of the complex were observed on a JEOL JSM-5600LV scanning electron microscope (SEM). Thermogravimetric (TG) analysis of the complex was performed with TA SDT-2960 analyzer with the temperature range from 10 to 700°C at a rate of $10^\circ\text{C}/\text{min}$ in air. The excitation and emission spectra of the sample were measured by a HITACHI F-4500 fluorescence spectrophotometer with the photomultiplier voltage of 700 V .

2.3. Synthesis and composition analysis of the complex

Firstly, 30.00 mL of $0.05\text{ mol/L H}_4\text{L}$ (1.5 mmol), 12.20 mL $0.08223\text{ mol}\cdot\text{L}^{-1}\text{Tb}^{3+}$ (1.0 mmol) and were dropped in 35 mL of 5% PVP solution respectively. The pH value was adjust to 5 using aqueous ammonia under stirring. Then, the mixture was reacted at 80°C for 2 h . Finally, the precipitate was cooled, centrifugated, washed, dried at 80°C for 2 h and the white powder was obtained. The filtrate drops are not precipitated with dropping ammonia water, which proves that the Tb^{3+} reaction is complete.

Element analysis data (the theoretical calculation number is included in the brackets): C, 20.02% (20.41%); H, 2.42% (2.72%); Tb, 37.85% (36.04%). It can be estimated that the constitution of the complex in PVP matrix is $\text{PVP/Tb}_{4/3}\text{L}\cdot 7\text{H}_2\text{O}$.

3. Results and Discussion

3.1. FT-IR analysis

From the standard FT-IR spectrum of pyromellitic acid H_4L (Sadler standard spectra 15238K), It can be seen that the stretching vibration band of carbonyl group in carboxyl group ($\nu_{\text{C=O}}$, $1700\text{--}1680\text{ cm}^{-1}$), the stretching vibration band of hydroxyl group in carboxyl group ($\nu_{\text{O-H}}$, $3300\text{--}2500\text{ cm}^{-1}$) and the out-of-plane bending vibration band of hydroxyl group ($\delta_{\text{O-H}}$, $950\text{--}890\text{ cm}^{-1}$), the inner-plane bending oscillation of hydroxyl group ($\delta_{\text{O-H}}$, $1440\text{--}1395\text{ cm}^{-1}$), and $\nu_{\text{C=O}}$ coincidence band of C=O , ($\nu_{\text{C=O}}$ $1320\text{--}1210\text{ cm}^{-1}$). The peaks of $\nu_{\text{C=O}}$, $\nu_{\text{O-H}}$ and $\delta_{\text{O-H}}$ (outplane) are the three characteristic peaks in the standard FT-IR spectrum of pyromellitic acid (H_4L).

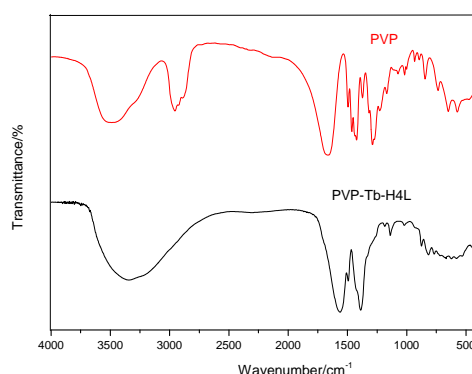


Figure 1. FTIR Spectrum of PVP and $\text{PVP/Tb}_{4/3}\text{L}\cdot 7\text{H}_2\text{O}$

From the standard FT-IR spectrum of $\text{Tb}_{4/3}\text{L}\cdot 7\text{H}_2\text{O}$ (Fig. 1), it can be found that the three characteristic peaks of $\nu_{\text{C=O}}$, $\nu_{\text{O-H}}$, $\delta_{\text{O-H}}$ in the H_4L disappeared, whereas, the characteristic peaks of

$\nu_{\text{COO}^-}^{\text{as}}$ and $\nu_{\text{COO}^-}^{\text{s}}$ are observed at 1557 cm^{-1} and 1392 cm^{-1} , respectively. This indicates the formation of Terbium pyromellitic acid complex. Meanwhile, the appearance of the out-of-plane bending vibration band of C-H ($\delta_{\text{C-H}}$, $650\text{--}900\text{ cm}^{-1}$) is caused by the out-of-plane bending vibration of benzene ring. The stretching vibration bands of hydroxyl group of the complex ($\nu_{\text{O-H}}$, 3376 cm^{-1} and 3393 cm^{-1}) can be attributed to the existence of water molecules in the complex.

3.2. XRD analysis

The XRD patterns of PVP/ $\text{Tb}_{4/3}\text{L}\cdot 7\text{H}_2\text{O}$ and PVP are shown in Fig 2. The diffraction peak positions, peak intensities and lattice distance of the complex are totally different from H_4L (No. 13-882 in JCPDS cards), and PVP. It can be demonstrated that a new complex is formed by banding Tb^{3+} with ligands together. Moreover, the sharp peaks of the complex show that the complex is crystalline.

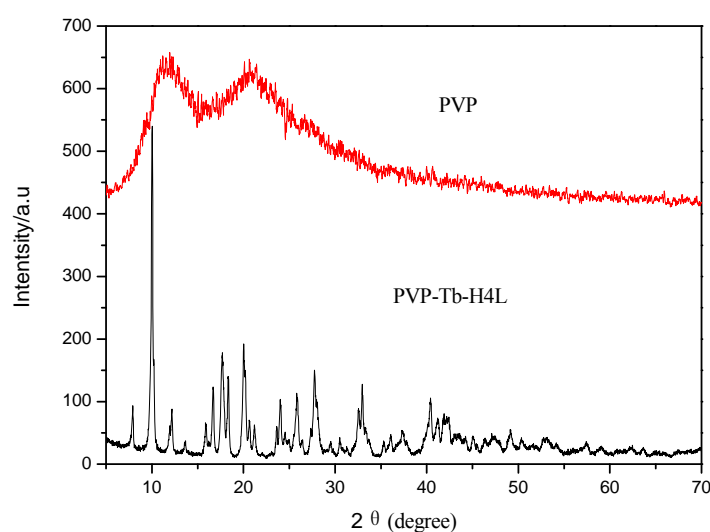


Figure 2 XRD pattern of PVP/ $\text{Tb}_{4/3}\text{L}\cdot 7\text{H}_2\text{O}$

3.3. SEM analysis

The SEM image of the $\text{Tb}_{4/3}\text{L}\cdot 7\text{H}_2\text{O}$ is shown in Fig. 3. It can be seen that the luminescent complex behaves as bulk crystals with high dispersity, and the mean diameter of the spheres is about $1\text{--}2\text{ }\mu\text{m}$.

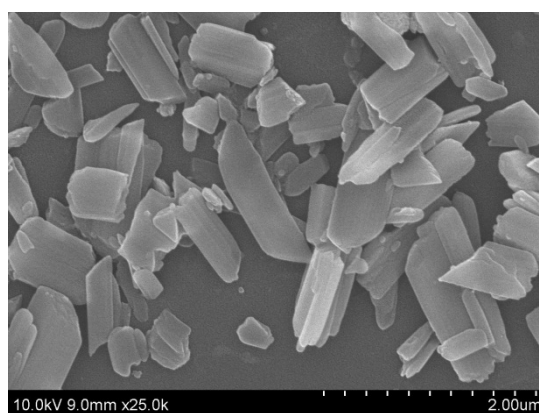


Figure 3. SEM photograph of PVP/ $\text{Tb}_{4/3}\text{L}\cdot 7\text{H}_2\text{O}$

3.4. TG-DTA annlysis

The thermogravimetry and differential thermal analysis (TG-DTA) curve of the $\text{Tb}_{4/3}\text{L}\cdot 7\text{H}_2\text{O}$ is shown

in Fig. 4. The DTA curve of the complex has an endothermic peak at 71 °C, indicating the existence of water molecules. It is noted that the complex decomposed from 50 °C to 483 °C. The mass loss is about 59.53 % (theoretically 58.52 %), which loss of water molecules and ligands in general. There is a strong exothermic peak near 463 °C in the corresponding DTA, where the ligand decomposes. Above 483 °C, decomposition and oxidation process have finished and terbium oxide Tb_2O_3 is generated.

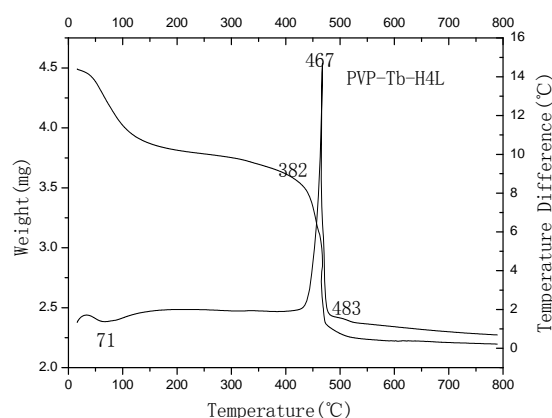


Figure 4. TG-DTA curves of $\text{PVP/Tb}_{4/3}\text{L} \cdot 7\text{H}_2\text{O}$

3.5. Diffuse reflectance spectroscopy analysis

The fluorescence excitation spectrum of $\text{PVP/Tb}_{4/3}\text{L} \cdot 7\text{H}_2\text{O}$ is shown in Fig. 5. The absorption band near 310 nm can be assigned to $\pi \rightarrow \pi^*$ transition of the ligands. The strongest excitation peak is at 310 nm, so the emission spectrum of $\text{PVP/Tb}_{4/3}\text{L} \cdot 7\text{H}_2\text{O}$ is obtained as shown in Fig. 6 using 310 nm as excitation wavelength. There are four groups of emission peaks near 489 nm, 544 nm, 583 nm, 619 nm which are attributed to $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ transition of Tb^{3+} respectively. The strongest peak is at 544 nm and $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition induces the emission of the characteristic green fluorescence of Tb^{3+} .

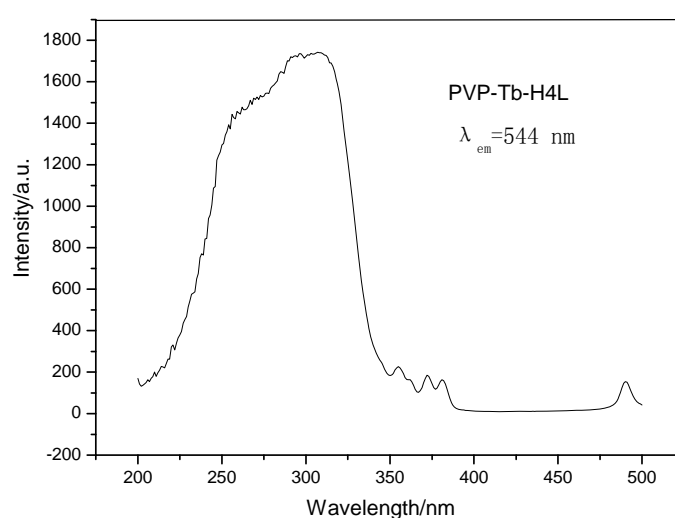


Figure 5. Excitation spectrum of $\text{PVP/Tb}_{4/3}\text{L} \cdot 7\text{H}_2\text{O}$

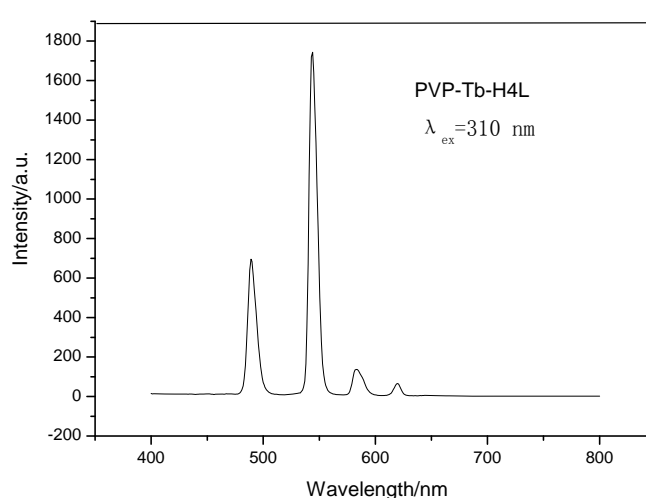


Figure 6. Emission spectrum of PVP/Tb_{4/3}L·7H₂O

4. Conclusion

Terbium [Tb (III)]-pyromellitic acid [H₄L] luminescent complex has been synthesized in PVP matrix by precipitation method. The chemical constitution of the complex has been determined as PVP/Tb_{4/3}L·7H₂O. FT-IR spectrum demonstrates the ligand takes part in the coordination. The complex has been observed as bulk like crystals with good dispersion and 1-2 μm in diameter by XRD and SEM. The complex has fine stability below 467°C proved by TG analysis. The diffuse reflectance spectrum shows that the complex has good optical absorption in ultraviolet region. The complex can emit green fluorescence under the excitation of ultraviolet light 310 nm.

Acknowledgments

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