ATLANTIS PRESS
Advances in Engineering Research, volume 103
Proceedings of the 3rd International Conference on Material Engineering and Application (ICMEA 2016)

Facile Synthesis and Luminescence Properties of Uniform $Pbwo_4:Tb^{3+}$ Hierarchical Ellipsoidal Particles

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Keywords: $PbWO_4:Tb^{3+}$, Ellipsoidal Particles, Hydrothermal Synthesis, Luminescence Properties.

Abstract. Monodisperse $PbWO_4:Tb^{3+}$ hierarchical ellipsoidal particles have been fabricated through a hydrothermal method by using trisodium citrate and SDBS as surfactants. The as-obtained $PbWO_4:Tb^{3+}$ are well-dispersed with narrow size distribution and are assembled by many closely packed nanoparticles. The as-obtained $PbWO_4:Tb^{3+}$ ellipsoidal particles exhibit intense green emission under ultraviolet excitation, which might find potential applications in fields of optical displays, optoelectronic devices, and light emitting diodes.

Introduction

In recent years, the scheelite-type tungstates with a general formula AWO_4 (A = Ca, Sr, Ba, Pb) have been extensively investigated due to their potential applications such as phosphors, batteries, scintillators, and solid-state lasers [1,2]. As a member of the tungstate family, $PbWO_4$ exhibits high potential in various applications such as scintillator in high-energy physics, laser and stimulated-Raman-scattering active media [3-6]. On the other hand, it is well established that the scheelite-type AWO_4 tungstates are considered to be excellent candidates for the matrix of lanthanide activator ions (Ln^{3+}). However, compared with other AWO_4 tungstates, there have been few reports for the synthesis of Ln^{3+}-doped $PbWO_4$ luminescent materials. The previous studies merely investigated the Eu^{3+} [7,8] and Yb^{3+}/Er^{3+}-doped $PbWO_4$ phosphors [9] and other Ln^{3+}-doped $PbWO_4$ luminescent materials are seldom reported. Thus, it is highly desirable and of significance to fabricate uniform and well-dispersed spherical Ln^{3+}-doped $PbWO_4$ phosphors with promising properties.

During the past few decades, self-assembled nano/micrometer-sized inorganic materials with particular size, morphology, and hierarchy were of great interest in the areas of materials science and device fabrication. The optical, electrical, magnetic, or catalytic properties of the inorganic functional materials strongly depend on their morphologies, particle size, and structures [10]. Many synthesis methods have been developed to synthesize the inorganic hierarchical particles, such as precipitation, microemulsion, sol-gel processes, chemical vapor technique, combustion, and so forth. Among them, the hydrothermal route has been proved to be an effective and convenient synthesis technique for fabricating various inorganic functional materials with well-defined architectures [11]. Moreover, the complexing agents or surfactants generally play an crucial role in determining the final morphology of the hierarchical nano-/microstructures during the hydrothermal process [12].

In this paper, uniform and well-dispersed $PbWO_4:Tb^{3+}$ hierarchical ellipsoidal particles have been fabricated by a facile hydrothermal route with trisodiun citrate and sodium dodecyl benzenesulfonate (SDBS) as surfactant. Moreover, the luminescent properties of $PbWO_4:Tb^{3+}$ were extensively investigated, which may find potential applications in optical displays, optoelectronic devices, and light emitting diodes.

Experimental Section

In a typical synthesis, 1.9 mmol of $Pb(NO_3)_2$ and 0.1 mmol $Tb(NO_3)_3$ aqueous solution was added into 20 mL of deionized water. Then 2 mmol (0.588 g) of trisodiun citrate ($C_6H_5Na_3O_7 \cdot 2H_2O$) and 2 mmol (0.697 g) of sodium dodecyl benzenesulfonate (SDBS, $C_{18}H_{29}NaO_3S$) were introduced into the above solution under stirring. Subsequently, 4 mmol of Na_2WO_4 solution was slowly added to the above solution. The pH value was adjusted to 4.0 by HAc solution. The mixing solution was transferred into a Teflon-lined autoclave, sealed, and heated to 160 ^oC for 12 h. Then the autoclave was cooled to room temperature naturally. The as-obtained precipitates were separated by centrifugation, washed with deionized water and ethanol in sequence, and then dried in air.

The sample was characterized by powder X-ray diffraction (XRD) performed on a D8 Advance diffractometer (Bruker). Fourier transform infrared spectroscopy (FT–IR) spectrum was measured with a Perkin–Elmer 580B infrared spectrophotometer. The morphology of the sample was inspected using JSM-7500F cold field scanning electron microscope (JEOL). Photoluminescence (PL) excitation and emission spectra were recorded with a Hitachi F-7000 spectrophotometer. The luminescence decay curves were obtained from a Lecroy Wave Runner 6100 Digital Oscilloscope (1GHz) using a tunable laser as the excitation (Continuum Sunlite OPO). All measurements were performed at room temperature.

Results and Discussion

Fig. 1 shows the XRD patterns of the $PbWO_4:Tb^{3+}$ sample. The diffraction peaks of the sample are well indexed to the tetragonal scheelite-type $PbWO_4$ (JCPDS No. 85-1857, space group: *I*41/*a*, No. 88). No impurity peaks can be detected, indicating that the pure tetragonal phase of $PbWO_4$ formed and the Tb^{3+} ions were effectively doped into the $PbWO_4$ host. Moreover, the diffraction peaks of the sample are very sharp and strong, which means that the products exhibit high crystallinity. This is important for phosphors, because high crystallinity generally means less traps and stronger luminescence.

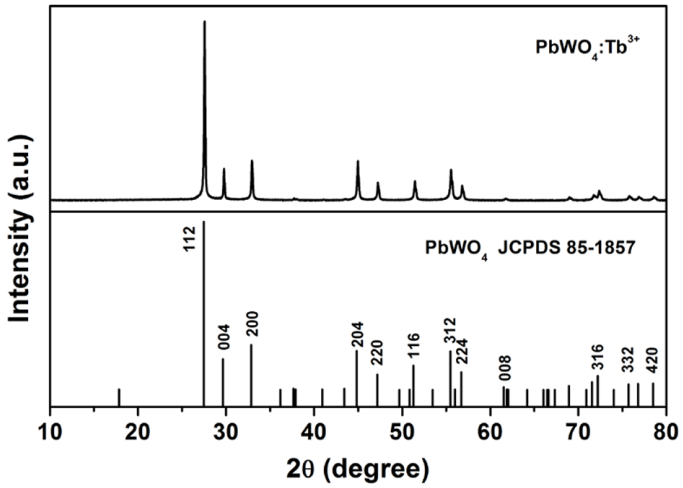

Fig. 1 XRD pattern of the $PbWO_4:Tb^{3+}$ sample.

The FT-IR spectrum was further used to investigate the $PbWO_4:Tb^{3+}$ sample (Fig. 2). The intense peak centered at 792 cm^{-1} is ascribed to the F_2 (ν_3) antisymmetric stretching from the W–O stretching vibration, and the weak peak at 479 cm^{-1} can be attributed to ν_3 bending vibration of W–O [13]. The result confirms the presence of WO_4^{2-} groups in the product, and provides additional evidence for the formation of $PbWO_4$. Moreover, the absorption bands centered at 3409 (1614) and 2362 cm^{-1} are attributed to the adsorbed water and CO_2 on the surface of the sample.

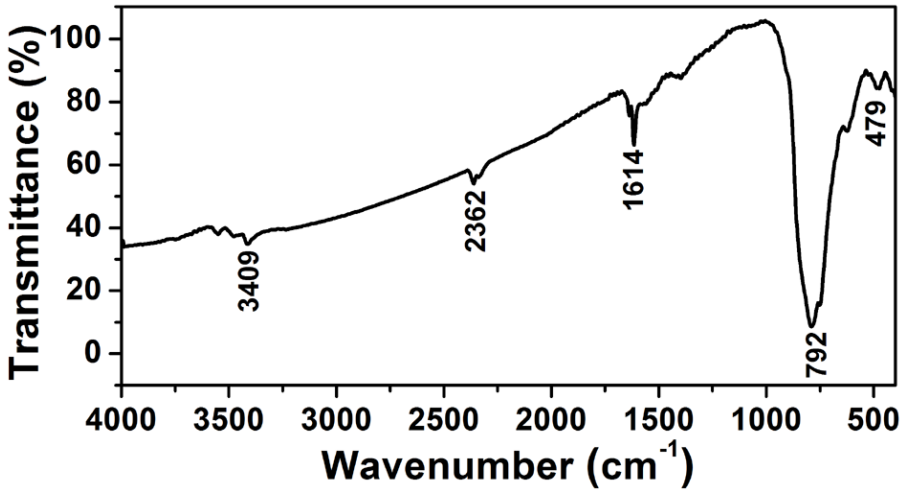

Fig. 2 FT-IR spectrum of the $PbWO_4$:Tb^{3+} sample.

SEM images were used to characterize the morphology of the $PbWO_4$:Tb^{3+} sample. The typical SEM image (Fig. 3a) indicates that the $PbWO_4$:Tb^{3+} sample consists of uniform and well-dispersed ellipsoidal particles, which are approximately 3 μm in length and 2 μm in width. These particles are non-aggregated with narrow size distribution. From the enlarged SEM image (Fig. 3b), one can see that the hierarchical ellipsoids are actually composed of many closely packed nanoparticles, which leads to a relatively rough surface of the sample.

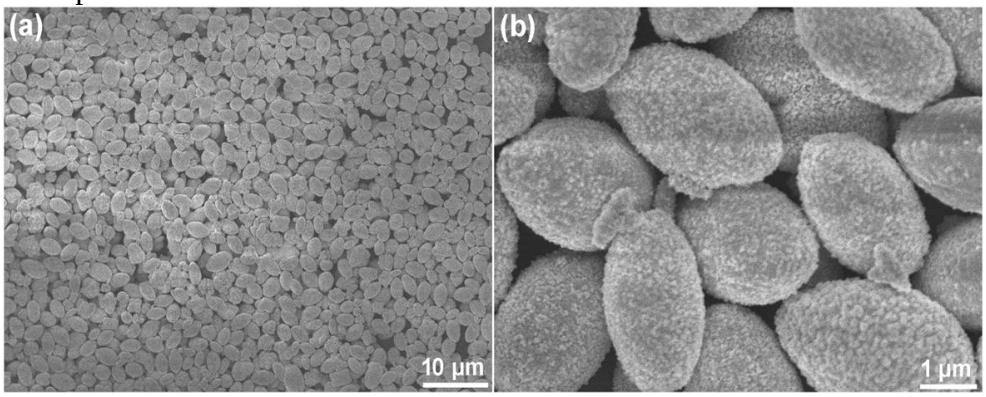

Fig. 3 SEM images of the $PbWO_4$:Tb^{3+} ellipsoidal particles.

The photoluminescence (PL) properties of the as-synthesized $PbWO_4$:Tb^{3+} sample were characterized by the photoluminescence excitation and emission spectra. The excitation spectrum of $PbWO_4$:Tb^{3+} sample (Fig. 4a), which was obtained by monitoring the emission of the Tb^{3+} $^5D_4$–$^7F_5$ transition at 544 nm, is composed of a broad band with a maximum at about 313 nm and some sharp lines. The intense broad band can be attributed to the charge transfer transition within the WO_4^{2-} groups, and the sharp lines are assigned to the characteristic f–f transitions of the Tb^{3+} ions. The presence of the strong band of WO_4^{2-} group in the excitation spectrum means that there an energy transfer exists from the WO_4^{2-} to Tb^{3+} ions. Upon excitation into the WO_4^{2-} groups at 313 nm, the emission spectra of $PbWO_4$:Tb^{3+} sample consists of a group of lines at about 491, 544, 588, and 624 nm, which can be assigned to $^5D_4$–^7F_J (J = 6, 5, 4, 3) transition lines of the Tb^{3+} ions, respectively (Fig. 4b). The characteristic green emission of Tb^{3+} with $^5D_4$–^7F_J transition (544 nm) is the most prominent compared with other transitions. The inset in Fig. 4b shows the luminescence photograph of $PbWO_4$:Tb^{3+} sample under UV excitation in the dark, which exhibits a strong and bright green emission.

The PL decay curve of the Tb^{3+} (544 nm, $^5D_4$–$^7F_5$) ions in $PbWO_4$ host is shown in Fig. 7. It can be seen that all the decay curves can be well fitted into a single exponential function as $I(t) = I_0 \exp(-t/\tau)$ (I_0 is the initial emission intensity at $t = 0$ and τ is the 1/e lifetime of the emission center), and the lifetimes of $PbWO_4$:Tb^{3+} sample is determined to be 0.617 ms. The result basically agrees with other reported Ln^{3+}-activated luminescent materials [14, 15].

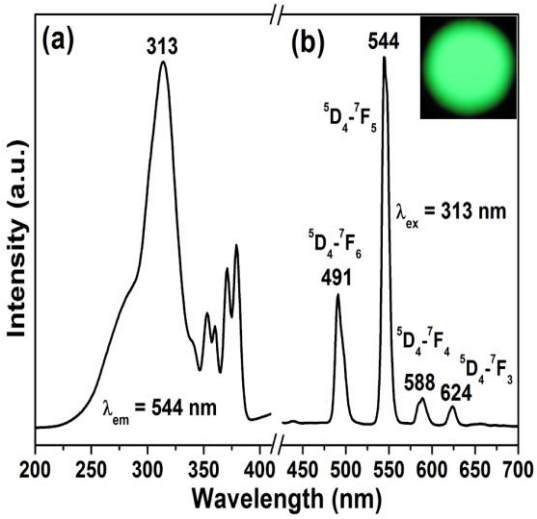

Fig. 4 Photoluminescence (a) excitation and (b) emission spectra of the PbWO4:Tb3+ particles

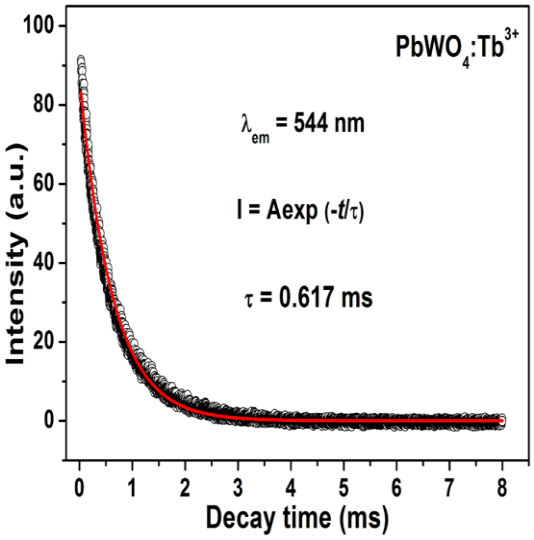

Fig. 5 Decay curve for the as-synthesized PbWO4:Tb3+ sample

Summary

In summary, a facile hydrothermal route has been developed to synthesize uniform and well-dispersed $PbWO_4:Tb^{3+}$ hierarchical ellipsoidal particles, which are composed of many closely packed nanoparticles. The crystal structure, morphology, and luminescence properties were characterized by XRD, FT-IR, SEM, PL, and kinetic decays, respectively. The $PbWO_4:Tb^{3+}$ sample shows intense green emission under ultraviolet excitation. Moreover, this work may provide some insight into the synthesis and design of other well-defined tungstate nano/micromaterials.

Acknowledgments

This research was supported by the National Natural Science Foundations of China (21301046, 51302062), the Second Batch of Top Youth Talent Support Program of Hebei Province, Distinguished Young Scholars Fund of Hebei University (2015JQ04), Key Program of Hebei University Scientific Research Project (ZD2015031), Post-graduate's Innovation Fund Project of Hebei University (X2016087), and Undergraduate Training Programs for Innovation and Entrepreneurship of Hebei University (2016003).

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