Synthesis and the Temperature-dependent Luminescent Properties of $\text{SrWO}_4\text{:Eu}^{3+}$
Ultralong Nanowire Phosphors

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Abstract

SrWO₄:Eu³⁺ nanowires with high aspect ratio were prepared by a solvothermal method via a poor solvent induced self-assembly process. The luminescence properties of SrWO₄:Eu³⁺ nanowires were investigated in detail. In the emission spectrum excited at 277 nm, the ⁵D₀→⁷F₂ is much stronger than the ⁵D₀→⁷F₁, indicating that Eu³⁺ ions occupy low symmetry sites in SrWO₄ lattices. The broad excitation band centered at 277 nm is assigned to the overlap of WO₄²⁻ absorption and charge transfer transition between Eu³⁺ and O²⁻. The temperature-dependent luminescent properties are also investigated in a wide temperature range from 100 to 450 K, it reveals that SrWO₄:Eu³⁺ is a potential luminescent thermometer in the temperature range from 310 K to 450 K.

Keywords: Metal tungstates; Nanowires; f–f transitions; Luminescent thermometer

Metal tungstates (XWO_4 , $X=Ca, Sr$) with scheelite structure are an important class of inorganic compounds that have potential applications in various fields, such as phosphors, microwave applications, optical fibers, scintillator materials, catalysis and X-ray intensified screen [1-6]. In recent years, the luminescence properties of tungstates have drawn great attention because of their interesting utilization of phosphors. As a self-activating blue phosphor, the metal tungstates exhibit a broad intrinsic blue emission originated from the charge-transfer transitions between oxygen and tungstate of WO_4^{2-} [7-10]. Moreover, this class of scheelite-like structures is widely used as matrix for the luminescence of rare-earth ions to obtain new optical phosphors [11-17].

In recent years, much attention has been paid to the preparation of rare earth doped $SrWO_4$ nanomaterials, including nanoparticles [18], nanowires [19], string nanobeans [20], nanobelts [21], nanorods [22], and micro-octahedrons [23], however, limited reported on the rare earth doped nanowires with high aspect ratio as luminescent materials to date. It is well known that the dimensionality of nanomaterials plays a critical role in determining the properties of materials. Especially, one-dimensional nanostructures, such as nanowires, nanobelts, and nanotubes, have attracted considerable attention due to their importance in many potential applications. In this paper, we demonstrated a simple method for the synthesis of ultralong nanowire of $SrWO_4:Eu^{3+}$ using sodium oleate as template cooperated with ethanol and cyclohexane as good-poor solvent system. Furthermore, the temperature-dependent photoluminescent properties were also investigated, it reveals that $SrWO_4:Eu^{3+}$ is a potentially useful luminescent thermometer in the temperature range from 310 to 450 K.

In a typical synthesis of $SrWO_4$ nanowires, 0.3 g of NaOH was first dissolved in 0.5

mL of deionized water, and then oleic acid (4 mL), ethanol (0.75 mL), and 8 mL of cyclohexane were added when stirring vigorously, in order to form a good-poor solvent system. Thereafter, the $\text{Sr}(\text{NO}_3)_2$ and Na_2WO_4 solution (0.1 mmol, 0.25 mL) were added subsequently. The mixture was stirred for a few minutes and heated at 180 °C for 12 h. The obtained samples were isolated by centrifugation and washed with ethanol and cyclohexane. The SrWO_4 : Eu nanowires were prepared in the same procedure, except using 0.01 mmol $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ instead the same amount of $\text{Sr}(\text{NO}_3)_2$ in the initial material. Herein, the mixed solution system including oleic acid and cyclohexane served as good solvent and ethanol functioned as a poor solvent in this synthetic system. The good solvents provide a good environment for nanocrystal growth, whereas ethanol increase the supersaturation of the reaction system, affect the interaction among primary crystal nuclei and promote the self-assembly of nanocrystals [24, 25].

Fig. 1a, b shows the SEM images of the as-formed SrWO_4 nanowires with different magnifications. The as-obtained SrWO_4 nanowires with diameters of ~20 nm and length of several tens micrometres, it can be seen that the samples are uniform and flexible. From the TEM image in Fig. 1c, we can see that the as-prepared SrWO_4 nanowires are not smooth; the curved edge of the nanowire further indicated the self-assembled mechanism during the shape formation process. The typical HRTEM image of the SrWO_4 nanowires shows an interplanar distance of 0.298 nm is ascribed to the (004) plane of tetragonal phase SrWO_4 , as shown in Fig. 1d, demonstrating the high crystallinity of the sample.

The low and high-magnification SEM images of SrWO_4 : 10 mol % Eu^{3+} nanowires were shown in Fig. 2a and 2b, respectively. From the low-magnification SEM images of

as-formed materials, it can be seen that the samples consist of uniform nanowires with length of several micrometres, which were shorter than the parent nanowires after Eu doping. It also can be observed that the diameter of the as-prepared $\text{SrWO}_4\text{:Eu}^{3+}$ nanowires are range from 20 to 70 nm in the high-magnification SEM image and HRTEM (Fig.S1). After being doped with Eu^{3+} , the length of nanowires decreases substantially, meanwhile, the diameters of nanowires increased slightly. The typical XRD patterns of the SrWO_4 , SrWO_4 : 10 mol % Eu^{3+} nanowires and the standard PDF card of tetragonal phase SrWO_4 (JCPDS no.08-0490) was presented in Fig. 2c. The SrWO_4 belongs to sheelite structure, the W atoms are coordinated to four oxygen atoms to form slightly distorted WO_4 tetrahedron, and Sr^{2+} atoms are bonded to eight oxygen atoms to form SrO_8 octahedron. The radius Sr^{2+} and Eu^{3+} is similar, thus Sr^{2+} ions can be partially substituted by the Eu^{3+} ions in SrWO_4 structure. Compared with the pure SrWO_4 sample, the XRD peaks shift to high degree slightly, which indicated the Eu^{3+} ions were successfully located into the SrWO_4 host lattice. Furthermore, the energy-dispersive X-ray (EDX) results show that the Eu/Sr atomic ratio of the synthesized $\text{SrWO}_4\text{:Eu}^{3+}$ nanowire is about 1:9, which is very close to the reaction raw composition (Fig. 2d).

Fig. 3a shows the excitation spectrum of the $\text{SrWO}_4\text{:Eu}^{3+}$ nanowires monitored at emission wavelength of 612 nm. The excitation spectrum contains a broad excitation band and a series of sharp peaks. The broad excitation band centered at 277 nm is attributed to the combination of WO_4^{2-} absorption and charge transfer transition from O^{2-} to Eu^{3+} (Fig. 3b). The sharp excitation peaks are assigned to f-f transition absorption of Eu^{3+} . The weak peaks at 362 nm and 382 nm are corresponding to

$^7F_0 \rightarrow ^5D_4$ and $^7F_0 \rightarrow ^5G_2$ transition of Eu^{3+} , respectively. The peak at 395 nm is attributed to $^7F_0 \rightarrow ^5L_6$ transition and the peak at 464 nm is assigned to $^7F_0 \rightarrow ^5D_2$ transition. Fig. 4b shows the typical emission spectrum of the $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires excited at 277 nm. The $^5D_0 \rightarrow ^7F_0$ (~535 nm), $^5D_0 \rightarrow ^7F_1$ (~595 nm), $^5D_0 \rightarrow ^7F_2$ (~612 nm), $^5D_0 \rightarrow ^7F_3$ (~654 nm), and $^5D_0 \rightarrow ^7F_4$ (~700 nm) transitions of Eu^{3+} were observed. The luminescence decay curve of the $^5D_0 \rightarrow ^7F_2$ transition for the $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires was also recorded, as shown in Fig. 3c. It is noted that the decay curve can not be fit to a single-exponential function, whereas a biexponential function

$$y = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$

can be fitted well and exhibits two lifetimes of 147.96 and 601.57 μs . The average lifetime (τ_{av}) can be calculated using the following equation

$$\tau_{\text{av}} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$$

Herein, the calculated average lifetime (τ_{av}) is 429.83 μs of Eu^{3+} ion for the nanowires. Fig. 3(d) shows the CIE pattern of the emission spectrum which was obtained under excitation at 277 nm, there is a point located at the red color region of the 1931 CIE diagram with chromaticity coordination (0.645, 0.336). The quantum yield (QY) of our synthesized $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires was measured and shown in Fig.S2, and the QY of the nanowire is 12.28%. To compare with other morphology structure of $\text{SrWO}_4:\text{Eu}^{3+}$, a nano-assembly morphology structure of $\text{SrWO}_4:\text{Eu}^{3+}$ (Fig.S3) was also synthesized and the experiment detail was present in supporting information. At the same test condition, the fluorescence intensity of $\text{SrWO}_4:\text{Eu}^{3+}$ ultralong nanowire is much stronger than that of the nano-assembly (Fig.S4), which shows better photoluminescent property of ultralong nanowires.

The temperature-dependent photoluminescent properties of $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires were investigated. The temperature dependent emission spectra of $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires from 100 to 450 K are illustrated in Fig. 4a, and the intensities of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (Eu^{3+} , 612 nm) transitions are shown in Fig. 4b. The emission intensity of Eu^{3+} in SrWO_4 nanowires decrease gradually as the temperature increases, which is due to the thermal activation of the nonradiative energy transfer processes. The emission intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} at 612 nm decreases by 92.17% in the range of 100–450 K. It is very interesting that the temperature can be linearly related to $\ln I_{\text{Eu}}$ by the following equation from 310 to 450 K with a correlation coefficient (R^2) of 0.9972 (Fig. 4b).

$$\ln I_{\text{Eu}} = 15.0311 - 0.0116 T$$

The thermometric sensitivity (S) of the $\text{SrWO}_4:\text{Eu}^{3+}$ was evaluated by the equation,

$$S = \frac{\partial(\ln I_{\text{Eu}}) / \partial T}{\ln I_{\text{Eu}}}$$

The maximum sensitivity of $\text{SrWO}_4:\text{Eu}^{3+}$ is $0.12\% \text{ K}^{-1}$ at 450K, which can be comparable to that of the previously reported ratiometric MOF thermometer [26].

In addition, the structure of $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires exhibit very stable. After the temperature dependent fluorescence test, we checked the SEM and TEM of $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires again, the results show the morphology and microstructure is not changed during the test (Fig.S5 and Fig.S6). The reversibility of the $\text{SrWO}_4:\text{Eu}^{3+}$ thermometer was also studied, the temperature-dependent emissions were carried out between 310 and 450 K for three cycles (Fig.S7). The emission intensities of $\ln I_{\text{Eu}}$ during this range for each cycle are nearly unchanged, indicating the relatively good stability and reversibility of this thermometer.

In this work, $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires with high aspect ratio were prepared via a

solvothermal method. In the emission spectrum of the $\text{SrWO}_4\text{:Eu}^{3+}$ nanowires, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ is much stronger than the $^5\text{D}_0 \rightarrow ^7\text{F}_1$, and in the excitation spectrum of the $\text{SrWO}_4\text{:Eu}^{3+}$ nanowires, a broad excitation band assigned to the overlap of WO_4^{2-} absorption and charge transfer transition between Eu^{3+} and O^{2-} and several sharp peaks attributed to f-f transitions of Eu^{3+} ions were clearly observed. Furthermore, the temperature-dependent photoluminescence properties of $\text{SrWO}_4\text{:Eu}^{3+}$ nanowires were investigated, the result exhibits that $\text{SrWO}_4\text{:Eu}^{3+}$ nanowire is a potential luminescent thermometer in the range from 310 K to 450 K.

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Figure Captions

Fig.1 SEM images of the bamboo-like SrWO_4 nanowires: images with low magnification (a) and high magnification (b); TEM(c) and HRTEM (d) images for the as-formed SrWO_4 nanowires.

Fig.2 SEM images for the as-formed $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires: images with low magnification (a) and high magnification (b); (c) XRD pattern of SrWO_4 and $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires, vertical lines at the bottom represent the typical pattern of tetragonal phase SrWO_4 ; (d) EDX spectrum of the $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires.

Fig.3 The emission (a) and excitation (b) spectrum of $\text{SrWO}_4:\text{Eu}^{3+}$, (c) the luminescent decay curve of $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires, (d) the CIE 1931 chromaticity diagram of $\text{SrWO}_4:\text{Eu}^{3+}$ sample.

Fig.4 (a) Emission spectra of $\text{SrWO}_4:\text{Eu}^{3+}$ recorded between 100 and 450 K (excited at 277 nm), (b) temperature-dependent intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Graphical Abstract Figure

$\text{SrWO}_4:\text{Eu}^{3+}$ nanowires with high aspect ratio were prepared via a solvothermal method. The temperature-dependent photoluminescence properties of $\text{SrWO}_4:\text{Eu}^{3+}$ nanowires were investigated, the result exhibits that $\text{SrWO}_4:\text{Eu}^{3+}$ nanowire is a potential luminescent thermometer in the range from 310 K to 450 K.