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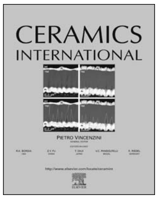

A new molybdate host material: Synthesis, upconversion, temperature quenching and sensing properties

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ABSTRACT

A new upconversion (UC) host material $YbMoO_4$ with 0–100 mol% Er^{3+} doping was obtained using a facile coprecipitation method. A pure tetragonal phase of $YbMoO_4$ was synthesized, which was dependent on the pH value of the reaction mixture and the sintering temperature. The existence of pentavalent molybdenum was confirmed in $YbMoO_4$ by thermal-reduction of hexavalent molybdenum. Under a 976 nm laser diode excitation, both green and red UC emissions were observed from Er^{3+}:$YbMoO_4$, which corresponded to the $^2H_{11/2}/^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} with the strongest luminescence appearing at a mole ratio of Er:Yb = 1:10. The two-photon absorption UC process was responsible for the green and red emissions. The temperature-dependent green UC emission of Er^{3+}:$YbMoO_4$ was observed, which was rationalized using the thermal quenching model. The fluorescence intensity ratio (FIR) of green UC emissions was studied as a function of temperature and its high thermal sensitivity implied that the Er^{3+}:$YbMoO_4$ material is a promising prototype for applications in optical temperature sensing.

1. Introduction

Over the past few years, much effort has been devoted to the upconversion (UC) luminescence of rare-earth ion doped materials because of their wide application [1–4]. Excellent works have been performed to improve the luminescent properties of UC materials, including addition of a sensitizer [5,6], changes in the environment of the luminous center [7,8], size/shape/phase control of the host materials [9,10] and so on. The choice of an efficient host material is the most direct and effective method for enhancing the UC properties. For example, $NaYF_4$ has been known as the most efficient UC matrix due to its low phonon energy and crystalline surroundings [11–13]. Compared to fluoride, the main benefits of the oxide materials are a wide transparency range, good thermal conductivity, isotropic optical properties and high thermal, mechanical and chemical stability, which can bear execrable conditions such as high temperature and a corrosive environment. Until now, various UC phosphors of oxide matrices have been reported including Al_2O_3, TiO_2, $Yb_3Al_5O_{12}$, $Yb_2Ti_2O_7$ etc [3,14–16]. Among the oxide materials, molybdate has a relatively low maximum optical phonon energy, which can suppress the non-radiative multi-phonon relaxation processes that are responsible for a considerable reduction of the emission intensity [17]. The materials $CaMoO_4$, $PbMoO_4$, $NaLa(MoO_4)_2$, and $Yb_2Mo_4O_{15}$ have been studied as the luminescent matrix [18–21]. To date, the valence state of Mo ions has been hexavalent in the reported molybdate UC matrix. However, there are multiple valence states for Mo ions and the synthesis conditions have an important influence on the formation of the various valence states of Mo ions. The molybdate UC matrix with various valence state of Mo may possess exclusive physical properties including phonon energy, energy band and crystal field environment, which would have a significant effect on the luminescence behavior of this material when doped with rare earth ions. In the study reported in this paper, a new phase of molybdate $YbMoO_4$ containing pentavalent molybdenum was prepared under a thermal-reducing synthetic condition using a facile coprecipitation method. The resulting properties of the $YbMoO_4$ UC when doped with Er^{3+} ions were investigated to determine the extent of the UC properties of this molybdate material. In this work, a simple synthesis route for synthesizing Er^{3+} doped $YbMoO_4$ phosphors was demonstrated and its UC properties were characterized along with its potential application for temperature sensing application.

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2. Experimental

2.1. Materials

All chemicals were obtained from commercial suppliers and used without further purification. Rare earth nitrates ytterbium nitrate ($Yb(NO_3)_3 \cdot 5H_2O$, 99.9%) and erbium nitrate ($Er(NO_3)_3 \cdot 5H_2O$, 99.9%) were purchased from Aladdin Chemistry Co Ltd in Shanghai, China. Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $\geq 99\%$) with hexavalent molybdenum and sodium hydroxide (NaOH, $\geq 98\%$) were purchased from Sinopharm Chemical Reagent Co Ltd in Shanghai, China.

2.2. Synthesis of Er^{3+}:$YbMoO_4$

A facile coprecipitation method was used to prepare the $YbMoO_4$ phosphors. The detailed synthesis procedure was as follows: 0.0564 g $Er(NO_3)_3 \cdot 5H_2O$ and 0.5715 g $Yb(NO_3)_3 \cdot 5H_2O$ were first dissolved in 10 ml absolute ethyl alcohol to obtain solution A. Then 0.2472 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was dissolved in 10 ml of deionized water to yield solution B, the pH value of the solution B was adjusted to different values using 1 M NaOH solution. Solution B was added slowly into solution A with continuous stirring. After vigorous stirring for 2 h at room temperature, the resulting solution was dried at 373 K in the oven for 12 h. The formed precipitates were finally annealed at the heating rate of 8 K/min and kept at the sintering temperature of 773, 923 and 1073 K, respectively, for 2 h in air atmosphere, then cooled to room temperature in the furnace. The resulting samples were Er^{3+}:$YbMoO_4$ with mole ratio of Er:Yb=1:10. The Er^{3+}:$YbMoO_4$ phosphors with various mole ratios of Er:Yb were synthesized by the same method for comparison. All of the samples were milled into powders for structural analysis and spectral measurement.

2.3. Characterization techniques

The phase structures of the Er^{3+}:$YbMoO_4$ phosphors were analyzed by a SHIMADZU XRD-6000 X-ray diffractometer (XRD) with Cu Kα radiation, using the scanning mode in 2θ ranging from 10° to 80° with a step length of 0.02° and a rate of 4.0°/min. The surface morphology of the phosphors was observed using an Hitachi S-4800 scanning electron microscopy (SEM) at an acceleration voltage of 5 kV. X-ray photoelectron spectroscopy (XPS) was performed on the samples using a Thermo ESCALAB 250Xi XPS with monochromatized Al Kα ($h\nu = 1486.6$ eV) source. The operating conditions of the X-ray generator were 15 kV and 10.8 mA. Electron Spin-Resonance spectroscopy (ESR) signals of the synthesized materials were recorded at ambient temperature on a Brucker ESR A200 spectrometer. The parameters for the ESR spectrometer were set to center field of 3486.70G, sweep width of 100G, microwave frequency of 9.82 GHz, modulation frequency of 200 kHz, and a power of 10.00 mW. Infrared spectra (IR) were recorded on a Nicolet NEXUS 470 FT-IR Spectrometer in ambient air at room temperature. The IR spectra were collected using KBr pellets from 400 to 4000 cm^{-1} with 4 cm^{-1} resolution and averaged 10 times. The UV/visible/NIR absorption spectra of the samples were measured in the diffuse reflectance mode on a Lambda 750 (Perkin Elmer), combined with an integrating sphere. The UC emissions from the samples were focused onto Jobin Yvon iHr550 monochromator and detected with CR131 photomultiplier tube by a 976 nm laser diode (LD) excitation. The photoluminescence spectra of the samples were excited by a UV 325 nm laser. An in-house fabricated temperature controlling system was used to adjust the temperature of samples from room temperature to 650 K, in which the measuring and controlling accuracy of temperature was about ± 0.5 K.

3. Results and discussions

Fig. 1a shows the XRD patterns of the Er^{3+}:$YbMoO_4$ phosphors with mole ratio of Er:Yb=1:10 synthesized at various pHs. For a pH=5.5, the XRD pattern was characteristic of a tetragonal phase of $YbMoO_4$ (JCPDS No. 35-1471) and MoO_3 and $Yb_2(MoO_4)_3$ based on the presence of tiny diffraction peaks. When the pH value was higher than 7.0, the diffraction peaks of pure $YbMoO_4$ phase could easily be indexed. Fig. 1b shows the XRD patterns of the Er^{3+}:$YbMoO_4$ phosphors with mole ratio of Er:Yb=1:10 at the pH value of 7.0 sintered at various temperatures. The single phase of $YbMoO_4$ formed at the sintering temperature of 773 K. The higher sintering temperatures led to the formation of other new phases of MoO_3 and Yb_2O_3 which coexisted with $YbMoO_4$. The results suggested that the pH and sintering temperature each had a significant influence on the formation of a pure, single $YbMoO_4$ phase. Fig. 1c shows the XRD patterns of the Er^{3+}:$YbMoO_4$ phosphors composed of different mole ratios of Er:Yb at the pH value of 7.0 and sintering temperature of 773 K. For all of the Er^{3+}:$YbMoO_4$ phosphors with different mole ratios of Er: Yb, only a pure phase of $YbMoO_4$ could be found. The main diffraction peak (112) of Er^{3+}:$YbMoO_4$ shifted toward smaller angles with the increasing of Er:Yb ratio, as shown in Fig. 1d. It is noted that the doping concentration of Er^{3+} increased with the increasing of Er:Yb ratio. The substitution of Yb^{3+} by Er^{3+} ions caused the host lattice to expand, because the ionic radii of Er^{3+} is larger than that of Yb^{3+}. The Er^{3+} ions could be completely incorporated into the $YbMoO_4$ lattice at any concentration by this synthesis method and did not change the crystal phase. The lattice constants of Er^{3+}:$YbMoO_4$ phosphors increased nearly linearly with the increase of Er^{3+} doping concentration (Fig. 1e). The inset of Fig. 1e shows the SEM image of Er^{3+}:$YbMoO_4$ phosphor. The average grain size was about 28 nm as calculated by the Scherrer equation, which was lower than the particle size of about 150 nm obtained from the SEM analysis. It could be concluded from this that a single Er^{3+}:$YbMoO_4$ particle consisted of several nanocrystallites.

To verify the valence of the ions in the Er^{3+}:$YbMoO_4$ nanophosphor, the $YbMoO_4$ without Er^{3+} and the Er^{3+}:$YbMoO_4$ samples were examined by XPS. As shown in Fig. 2a, the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ peaks in the spectrum of $YbMoO_4$ could be seen at 231.99 and 235.14 eV, indicating the presence of only one state of molybdenum Mo(V) [22]. The Mo $3d_{5/2}$ and Mo $3d_{3/2}$ peaks of Er^{3+}:$YbMoO_4$ exhibited a slight upshift when compared to those of $YbMoO_4$. The Yb 4d spectrum of $YbMoO_4$ and Er^{3+}:$YbMoO_4$ are shown in Fig. 2b. The Yb 4d spectrum of $YbMoO_4$ could be fitted into four symmetric peaks located at 184.78, 188.26, 192.29 and 198.38 eV. The spectrum was quite similar to the corresponding spectrum of $(YbS)_{1.25}CrS_2$, except for the Yb^{2+} component [23]. This indicated the presence of trivalent of Yb in $YbMoO_4$ phosphors. The four Yb 4d peaks of Er^{3+}:$YbMoO_4$ showed a slight downshift when compared to the spectrum for $YbMoO_4$, because Er^{3+} had lower binding energy than Yb^{3+}. The Er 4d spectrum of Er^{3+}:$YbMoO_4$ shown in Fig. 2c presented only one peak located at 168.35 eV, which was the same as the spectrum of Er_2O_3 [22]. The shift of the binding energy for Mo and Yb in the Er^{3+}:$YbMoO_4$ phosphor could be attributed to the substitution of Yb^{3+} by Er^{3+} in the $YbMoO_4$. Fig. 2d shows the ESR spectra of $YbMoO_4$ and Er^{3+}:$YbMoO_4$. There are four electronic configurations of d0, d1, d2 and d3 which correspond to the four valence state of Mo^{6+}, Mo^{5+}, Mo^{4+} and Mo^{3+}. The Mo^{6+} ion is diamagnetic and will not produce an ESR signal. It is impossible to detect its ESR signal although Mo^{4+} is paramagnetic, because the relaxation speed is too rapid at room temperature. The ESR property of Mo^{3+} is similar to that of Mo^{4+}. However, the ESR signal of Mo^{3+} exists at room temperature, but it is a wide ESR signal located in the lower field. The characterization results of the ESR signals in Fig. 2d indicated

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