Research Article

Structural and Optical Properties of $\text{ZnWO}_4\text{:Er}^{3+}$ Crystals

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Erbium ion- (Er^{3+} -) doped ZnWO_4 crystals were synthesized via a hydrothermal method with different erbium concentrations. The prepared materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Raman, UV-Vis, and photoluminescence (PL) spectroscopy. For $\text{ZnWO}_4\text{:Er}^{3+}$ crystals, a pure phase of ZnWO_4 was obtained without any evidence of impurity present. The SEM images show that the grain size and morphology of $\text{ZnWO}_4\text{:Er}^{3+}$ material depends on the Er^{3+} -dopant concentration. The UV-Vis spectra of $\text{ZnWO}_4\text{:Er}^{3+}$ compounds exhibited an absorption band at about 323 nm (3.83 eV) stemming from the $[\text{WO}_4]^{2-}$. Other absorption bands centered at 367, 379, 408, 490, and 522 nm are related to Er^{3+} -ion transitions. Room temperature PL spectra of the $\text{ZnWO}_4\text{:Er}^{3+}$ compounds exhibited visible emission at 515–540 and 545–565 nm corresponding to the ${}^2\text{H}_{11/2}$ – ${}^4\text{I}_{15/2}$ and ${}^4\text{S}_{3/2}$ – ${}^4\text{I}_{15/2}$ transitions of Er^{3+} ions, respectively.

1. Introduction

Rare-earth compounds have been widely used as phosphors in high-performance luminescent devices [1–3]. For such applications, rare-earth compounds have been introduced into a variety of host materials, and a lot of research effort has been focused on the development of novel and more facile synthesis procedures and on the tuning of the photoluminescence properties of rare-earth centers. ZnWO_4 is a very promising host material since it is nonhygroscopic and nontoxic, and it exhibits intrinsic photoluminescence properties. In the literature, various studies report on the doping of ZnWO_4 with a variety of rare-earth ions such as Eu [4, 5], Y [6], and Ho [7]. Doping other rare-earth element ions such as the Er^{3+} ion has barely been investigated from a synthesis and photoluminescence point of view. On the other hand, the spectroscopy of the Er^{3+} incorporated in a variety of other host materials has received much attention in the recent

years, focusing especially on the development of green and infrared eye-safe laser [8].

Previously, Er^{3+} -doped ZnWO_4 has been prepared via the Czochralski method [8]; however, this method requires high calcination temperatures. Reports on the hydrothermal synthesis of this material were not found. Furthermore, control of crystal morphology and size as well as the effects of surface area, crystallinity, and dispersion on the luminescent properties of Er^{3+} -doped ZnWO_4 was not discussed in detail. In this work, we report on a facile hydrothermal synthesis procedure at low temperature (180°C) of Er^{3+} -doped ZnWO_4 , and we discuss the effect of the composition on the structural and optical properties.

2. Experiments

Erbium-doped zinc tungstate (ZnWO_4) nanoparticles were prepared by the hydrothermal reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$,

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, and $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ at 180°C for 6 hrs. The typical procedures for the preparation of these samples consist of adding 10 mL of an aqueous solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) to 20 mL of an aqueous solution containing $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (1 mmol) and $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ under vigorous stirring. The volume of this solution was increased to 40 mL by adding distilled water, and the pH of the solution was adjusted to 7 by dropwise addition of a 30% aqueous ammonia solution. After that, the solution was transferred into a Teflon-lined stainless steel autoclave of 100 mL capacity. The autoclave was heated to 180°C for 6 hrs without shaking or stirring, and it was then allowed to slowly cool to room temperature. From this autoclave, a white precipitate was collected and washed for four times with distilled water, after which the solid powder was retrieved. The solid powder was heated at 80°C and dried at this temperature under vacuum for 2.5 hrs before calcination at 700°C for 2 hrs.

Structural characterization was performed by means of X-ray diffraction using a D5005 diffractometer with $\text{Cu K}\alpha$ radiation. The FE-SEM observations were carried out by using a S4800 (Hitachi) microscope. Raman measurements were taken in a backscattered geometry using the Jobin Yvon T 64000 triple spectrometer equipped with a cryogenic charge-coupled device (CCD) array detector, using the 514.5 nm line of an Ar-Ion laser. The absorption spectra were recorded by using the Jasco 670 UV-Vis spectrometer, and the room temperature luminescence spectra were recorded on a spectrofluorometer (PL, Fluorolog-3,) using 325 nm laser excitation.

3. Results and Discussion

Figure 1 shows the diffraction patterns of the pure ZnWO_4 and $\text{ZnWO}_4:\text{Er}^{3+}$ with different erbium concentrations after the calcination. The pure zinc tungstate diffractogram is in good accordance with the standard JCPDS card (no. 73 0554; no. 89-0447) [9, 10]. The different Er^{3+} -doped ZnWO_4 exhibits almost the same XRD patterns as those of the undoped ZnWO_4 . An expanded view of the (111) peak of these different materials on the right shows that the diffraction peaks are slightly shifted to lower angles. This observation suggests that Er^{3+} is successfully substituting Zn^{2+} in the lattice and that Er^{3+} is homogeneously incorporated into the lattice. The minor lattice expansion resulting from the Er^{3+} incorporation is reasonable considering the relative ionic radius of Zn^{2+} (0.74 Å) and Er^{3+} , (0.89 Å) [11] as shown in Figure 2. In pure ZnWO_4 crystals, zinc ions occupy octahedral position ($Z = 8$) of the wolframite structure [12], and, when doped in ZnWO_4 , Er^{3+} should replace Zn^{2+} to be in O_h position [8].

Figure 3 shows the SEM images of pure ZnWO_4 and Er^{3+} -doped ZnWO_4 materials prepared by the hydrothermal route at 180°C from the solution of pH 7 with various doping concentrations (2, 4, 6, 8, 10, and 15 mol%). It is clear that the morphologies and dimensions of the samples strongly depend on the doping concentration. SEM micrographs for the pure ZnWO_4 crystals show an average length of about

FIGURE 1: XRD patterns of ZnWO_4 and Er^{3+} -doped ZnWO_4 samples.

FIGURE 2: Cell parameter versus Er content.

50 nm (Figure 3(a)). However, when Er^{3+} ions were doped with concentration of 2 mol%, the resulting powder consists of nanorods with a diameter of about 20 nm and a length ranging from 100 nm to 250 nm (Figure 3(b)). With increasing Er-doping concentration, the size of the rods becomes more inhomogeneous, and the length of crystals decreased (Figures 3(c)–3(e)). When the erbium concentration was raised to 15 mol%, nanoparticles tend to aggregate into large pigment particles (Figure 3(f)).

ZnWO_4 materials have a monoclinic wolframite structure with C_{2h} point group symmetry and $\text{P2}/c$ space group. It has two formula units per unit cell. The W–O interatomic distance is substantially smaller than that of Zn–O; therefore, to a first-order approximation, the lattices can be separated into internal vibrations of the octahedra and the external vibrations in which an octahedron vibrates as a unit. Group theory analysis for wolframite-type ZnWO_4 predicts 36 lattice modes, of which 18 even vibrations ($8A_g + 10B_g$) are Raman active [13]. The recorded Raman spectra of $\text{ZnWO}_4:\text{Er}^{3+}$

FIGURE 3: SEM images of different Er^{3+} -doped ZnWO_4 samples: (a) 0%, (b) 2%, (c) 4%, (d) 6%, (e) 8%, and (f) 15%.

FIGURE 4: Raman spectra of $\text{ZnWO}_4:\text{Er}^{3+}$ crystals. The inset shows a zoom on the peak at 907 cm^{-1} .

crystals with various erbium doping (0–15 mol%) are shown in Figure 4.

In fact, all expected lines of 907 , 787 , 709 , 679 , 547 , 408 , 343 , 276 , 193 , and 162 cm^{-1} are observed in the Raman spectra shown in Figure 4. In particular, the presence of six internal vibration modes (stretching modes) of A_g and B_g (907 , 787 , 709 , 679 , 547 , and 408 cm^{-1}) should be noted as an important property of monoclinic wolframite ZnWO_4 ; the vibration modes arise from the six internal stretching modes caused by each of the six W-O bonds in the WO_6 octahedrons [14]. Note that the highest-frequency line at 907 cm^{-1} corresponding to the A_g mode has a linewidth of about 9 cm^{-1} for all samples.

When the particle size decreases to the nanometer scale, the effect on the vibrational properties of these materials might occur. A volume contraction occurs within the nanoparticles that are due to the size-induced radial pressure, which leads to increases in the force constants as a result of the decreases in the interatomic distances. In vibrational transitions, the wavenumber varies approximately in proportion to $k^{1/2}$, where k is the force constant. Consequently, the Raman bands shift towards a higher wavenumber due to the increasing force constants [15].

Figure 5 shows the diffuse reflectance spectra of the $\text{ZnWO}_4:\text{Er}^{3+}$ sample with Er concentrations of 4 mol%. Five distinct absorption peaks at wavelength 367 , 379 , 408 , 490 , and 522 nm in the absorption spectrum are attributed to transitions from ground state to excited states of Er^{3+} ions: $^4\text{I}_{15/2} \rightarrow ^2\text{K}_{15/2}$, $^4\text{I}_{15/2} \rightarrow ^4\text{G}_{11/2}$, $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{9/2}$, $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{7/2}$, and $^4\text{I}_{15/2} \rightarrow ^2\text{H}_{11/2}$, respectively [16]. In addition, the absorption spectrum consists of a broad intense band at around 264 nm which is contributed by the $[\text{WO}_4]^{2-}$ group.

ZnWO_4 material is an indirect-gap semiconductor [17, 18]. For a crystalline semiconductor, the optical absorption near the band edge follows the following equation: $ah\nu = A(h\nu - E_g)^{1/n}$, where a , ν , E_g , and A are the absorption coefficient, the light frequency, band gap, and constant, respectively [19]. For the ZnWO_4 , n was determined to be 2. Using this equation to calculate, the band gap of the crystal Er^{3+} -doped ZnWO_4 (4 mol%) was roughly estimated to be 3.83 eV , while those of other $\text{ZnWO}_4:\text{Er}^{3+}$ compounds (2%–15%) were determined to be between 3.82 and 3.85 eV .

PL spectra of $\text{ZnWO}_4:\text{Er}^{3+}$ with Er^{3+} concentration of 2, 4, 6, 8, and 15 mol% under 325 nm excitation were shown in Figure 6. Three emission lines centered around

FIGURE 5: Absorption spectra of $\text{ZnWO}_4:\text{Er}^{3+}$ (4 mol%).

wavelengths 537, 550, and 562 nm were observed in the PL spectra of the $\text{ZnWO}_4:\text{Er}^{3+}$ nanoparticles. The emissions at 515–540 and 543–565 nm correspond to the ${}^2\text{H}_{11/2} - {}^4\text{I}_{15/2}$ and ${}^4\text{S}_{3/2} - {}^4\text{I}_{15/2}$ transitions of Er^{3+} ions, respectively [20]. The transition ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ at 550 nm is suitable for green laser [8]. The absorption spectra in Figure 4 confirmed that this erbium emission can result only from the energy transfer from the UV-excited tungstate groups to the erbium ions.

4. Conclusions

A hydrothermal synthesis procedure for the generation of erbium-doped ZnWO_4 materials has been developed. For $\text{ZnWO}_4:\text{Er}^{3+}$ crystals, a pure ZnWO_4 phase was obtained without any evidence of impurities present; however, small distortions in the lattice parameters because of the difference in size between erbium and zinc could be observed. The c -parameter changes from 0.5734 nm to 0.575 nm, while the a - and b -parameters do not almost change. The Raman peak of these materials shifts to lower frequency with increasing Er-dopant concentration which again supports the successful substitution of Zn^{2+} by Er^{3+} in ZnWO_4 lattice. The SEM images clearly show that the grain size and morphology of $\text{ZnWO}_4:\text{Er}^{3+}$ material depends on concentration of the doped Er^{3+} ion. The absorption spectra of $\text{ZnWO}_4:\text{Er}^{3+}$ show a combination of the tungstate absorption in combination with the Er^{3+} -ion transitions at 367, 379, 408, 490, and 522 nm. From these measurements, the band gap of Er^{3+} -doped ZnWO_4 was estimated to be about 3.83 eV. Room temperature PL spectra of the $\text{ZnWO}_4:\text{Er}^{3+}$ compounds exhibited emission in the visible ranges 515–540 and 545–565 nm stemming, respectively, from the ${}^2\text{H}_{11/2} - {}^4\text{I}_{15/2}$ and ${}^4\text{S}_{3/2} - {}^4\text{I}_{15/2}$ transitions of Er^{3+} ions.

Our work suggests that the idea of using ZnWO_4 doped with Er^{3+} could be a plausible strategy to develop a green laser.

FIGURE 6: PL spectra of $\text{ZnWO}_4:\text{Er}^{3+}$ with different molar concentrations of Er^{3+} .

Conflict of Interests

We declare that there is no conflict of interests regarding the publication of this article.

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