



ELSEVIER

July 2002

Materials Letters 55 (2002) 152–157

**MATERIALS
LETTERS**

www.elsevier.com/locate/matlet

Hydrothermal synthesis and photoluminescent properties of ZnWO₄ and Eu³⁺-doped ZnWO₄

Fu-Shan Wen^a, Xu Zhao^a, Hua Huo^a, Jie-Sheng Chen^{a,*}, E. Shu-Lin^b, Jia-Hua Zhang^b

^aState Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Department of Chemistry, Jilin University, Changchun 130023, People's Republic of China

^bLaboratory of Excited State Processes, Chinese Academy of Sciences, Changchun 130021, People's Republic of China

Received 10 September 2001; accepted 24 September 2001

Abstract

Through a hydrothermal reaction route, zinc tungstate (ZnWO₄) crystals with various morphologies and particle sizes have been synthesized using sodium tungstate and zinc acetate as the raw materials. Eu³⁺-doped ZnWO₄ was also obtained from hydrothermal systems and the photoluminescent properties of the products were investigated. Significant energy transfer from WO₄²⁻ groups to Eu³⁺ ions has been observed. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 8078

Keywords: Hydrothermal synthesis; Photoluminescence; Energy transfer; Zinc tungstate, ZnWO₄; Europium-doped

1. Introduction

Zinc tungstate (ZnWO₄) exhibits interesting photoluminescent properties [1] and ZnWO₄ single crystal was first introduced for microwave applications in the middle of the 20th century [2]. Recently, studies concerning light yield, emission spectrum, afterglow, lifetime and optical properties of ZnWO₄ have been reported in literature [3–6]. ZnWO₄ was also found to be an attractive compound for X-ray scintillators with luminescence output and afterglow comparable to those for materials currently in use [7]. One of the

advantages of ZnWO₄ is that the materials used for the preparation of ZnWO₄ are nonhygroscopic, non-toxic and cheaper than those for BGO (Bi₄Ge₃O₁₂), a widely used scintillation crystal [7].

Usually, single-crystal ZnWO₄ is grown by traditional Czochralski technique [8], whereas the powder form of ZnWO₄ is synthesized by solid state method at high temperatures [9]. Hydrothermal synthesis has been successful for the preparation of important solid state materials such as microporous and mesoporous crystals, superionic conductors, chemical sensors, electronically conducting complex oxide, complex oxide ceramics and fluorides, magnetic materials, nonlinear optical materials and luminescence phosphors [10]. In this paper, the hydrothermal synthesis of ZnWO₄ from zinc acetate and sodium tungstate is presented for the first time. Various morphologies and

* Corresponding author. Fax: +86-431-567-1974.

E-mail address: chemcj@mail.jlu.edu.cn (J.-S. Chen).

particle sizes for the ZnWO_4 compound were achieved through this milder synthetic technique.

The scheelite lattice of compounds such as CaWO_4 has been used as a host for the doping of rare earth ions. Botden [11] reported that there exists energy transfer from tungstate to tungstate group and from tungstate to samarium in $\text{CaWO}_4\text{-Sm}^{3+}$ in 1951. But in the wolframite structure compounds such as ZnWO_4 , the study of energy transfer for rare earth-doped ZnWO_4 has not been reported to our knowledge. We doped the ZnWO_4 crystals with Eu^{3+} centers through the hydrothermal method and found a significant energy transfer from WO_4^{2-} groups to Eu^{3+} ions.

2. Experimental

The starting materials for the synthesis of ZnWO_4 were $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (A.R.) and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (A.R.). In a typical synthesis procedure, an initial mixture with a molar composition of $\text{Zn}(\text{OAc})_2/\text{Na}(\text{WO}_4)_2/110 \text{ H}_2\text{O}$ was stirred until homogeneous, sealed in a Teflon-lined stainless steel autoclave and heated at 473 K for 4 days under autogenous pressure. The solid product recovered from the reaction system was washed thoroughly with distilled water and dried at room temperature. For the preparation of Eu^{3+} -doped ZnWO_4 , europium nitrate was first added to water followed by the addition of sodium tungstate

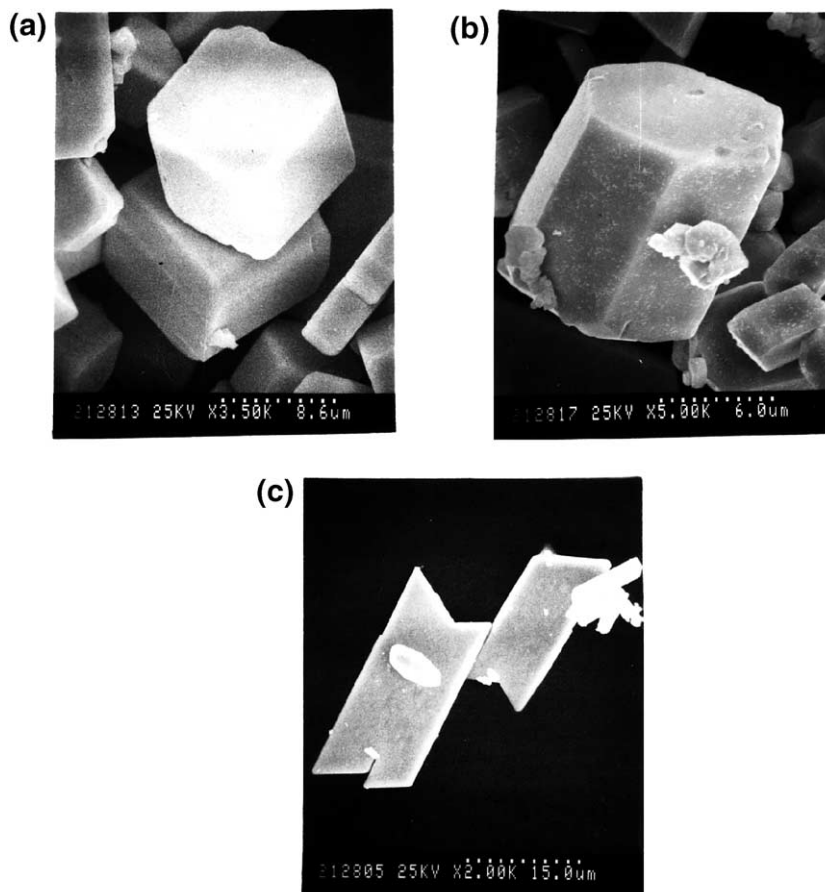


Fig. 1. Scanning electron photographs of ZnWO_4 obtained under different hydrothermal conditions: (a) $\text{H}_2\text{O}/\text{Zn}(\text{OAc})_2 = 50$; (b) $\text{H}_2\text{O}/\text{Zn}(\text{OAc})_2 = 150$; (c) $\text{H}_2\text{O}/\text{Zn}(\text{OAc})_2 = 300$. (a)–(c): $\text{Zn}^{2+}/\text{WO}_4^{2-} = 1$, $T = 453 \text{ K}$, 4 days.

dihydrate. The rest of the procedure was the same as that for the preparation of ZnWO_4 .

For comparison, we also synthesized the Eu^{3+} -doped zinc tungstate by a solid state method. The $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in distilled water followed by the addition of the solution of sodium tungstate. A white precipitate was obtained from the reaction mixture. The precipitate was washed thoroughly with distilled water, dried in air and calcined at 1073 K. The product proved to be ZnWO_4 on the basis of X-ray diffraction.

The powder X-ray diffraction (XRD) was carried out on a Siemens D5005 with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The particle morphologies of the crystals were obtained by scanning electron microscopy using a Hitachi X-650 scanning electron microscope. The luminescence of the samples was measured on a Hitachi-F4500 fluorescence spectrophotometer.

3. Results and discussion

3.1. Hydrothermal synthesis

In the hydrothermal synthesis, the effects of crystallization temperature and time, pH value and concentration on the crystallinity, the morphology and the particle size of the ZnWO_4 crystals have been investigated.

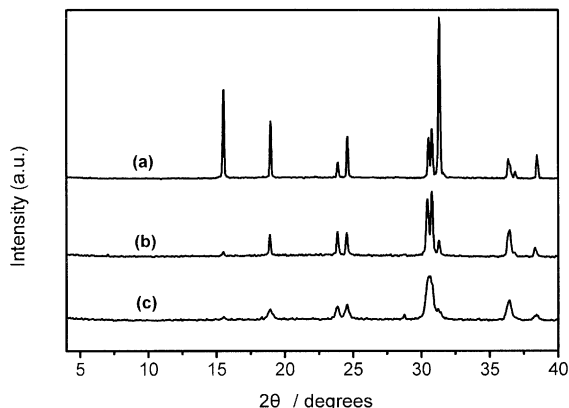


Fig. 2. Powder X-ray diffraction patterns for ZnWO_4 with different morphologies: (a) flake-like (b) hexagonal prism and (c) cubic.

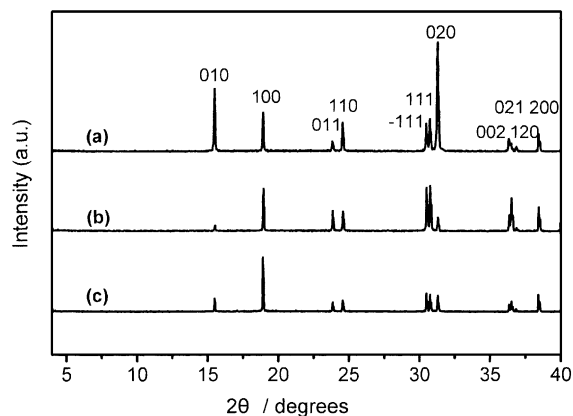


Fig. 3. Powder X-ray diffraction patterns for ZnWO_4 with different sizes: (a) 453 K, 7 days, $\text{H}_2\text{O}/\text{Zn}(\text{OAc})_2 = 50$; (b) 453 K, 4 days, $\text{H}_2\text{O}/\text{Zn}(\text{OAc})_2 = 50$; and (c) 443 K, 10 days, $\text{H}_2\text{O}/\text{Zn}(\text{OAc})_2 = 50$.

The crystallization time is longer than 10 days if the crystallization temperature is below 453 K. When the crystallization temperature is kept at 433 K, a crystallization period longer than 30 days is needed. The initial reactants and pH value of the reaction system are also important for the formation of the ZnWO_4 crystals. The crystallinity of the product increases with the pH value, while the particle size decreases. A pH value lower than 7.0 prolongs the crystallization time significantly. At first, upon fixing the crystallization temperature, the particle size of the crystals increases with the crystallization time. However, further increasing the reaction time leads to decrease of particle size again. It is interesting to note that the morphologies of the hydrothermally synthesized zinc tungstate change with the amount of water added in the reaction mixture. A molar ratio of $\text{H}_2\text{O}/\text{Zn}(\text{OAc})_2 = 50$ results in cubic crystals (Fig. 1a), whereas when the molar ratio is increased to 100, the shape of the crystals is either hexagonal prism or octahedron (Fig. 1b). Further increase of the molar ratio favors the formation of flake-like crystals (Fig. 1c).

3.2. XRD patterns

The powder X-ray diffraction patterns for different morphologies of ZnWO_4 are shown in Fig. 2. All the peaks in the patterns are indexed on the basis of the crystallographic data of the known structure of ZnWO_4 (JCPDS code 15-0774), suggesting that the

as-synthesized samples are phase pure. In the XRD pattern of the flake-like ZnWO_4 crystals, the peak intensities of the (010) and (020) reflections are higher than those of other peaks (Fig. 2a) whereas the (100), (-111) and (111) reflections are rather distinct and the (010) peak is very low in intensity for the hexagonal prism ZnWO_4 crystals (Fig. 2b). For the cubic ZnWO_4 crystals, the peaks of (100) and (200) reflections are higher than the others (Fig. 2c). The intensity fluctuation for the diffraction peaks is obviously a reflection of preferred orientation for different morphologies.

The powder X-ray diffraction patterns for ZnWO_4 with different particle sizes are shown in Fig. 3. From the half-peak width of the XRD patterns, it can be seen that the particle size of (c) is very small, while (a) has the largest size among the samples obtained. The variation of particle sizes of ZnWO_4 is realized by changing the reaction temperature and time as discussed in the previous section.

3.3. Photoluminescence spectra

It is well known that the blue emission band of ZnWO_4 is due to the intrinsic tungstate emission. This is because there exist WO_6 octahedral structures in the matrix, playing the role of luminescence centers. The nature of the optical transitions of tungstates is still unclear, but it is assumed that a charge-transfer transition takes place during emission. This optical transition involved in the luminescence of W–O

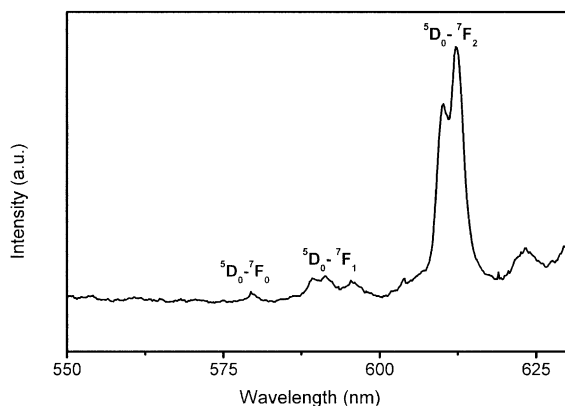


Fig. 4. Emission spectrum of Eu^{3+} in the hydrothermally obtained Eu^{3+} -doped ZnWO_4 at room temperature: $\text{Eu}^{3+}/\text{WO}_4^{2-} = 2.9 \times 10^{-2}$, excitation at 303 nm.

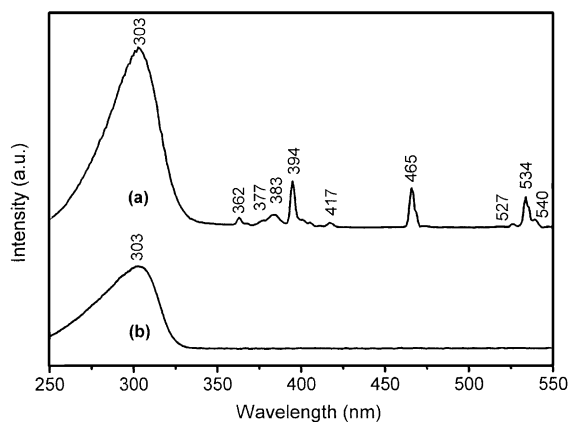


Fig. 5. Excitation spectra of Eu^{3+} -doped and pure ZnWO_4 at room temperature: (a) Eu^{3+} -doped ZnWO_4 , emission at 612 nm and (b) pure ZnWO_4 , emission at 470 nm.

groups might be due to charge transfer between the O 2p orbitals and the empty d orbitals of the central W ion [12]. The blue emission band of ZnWO_4 is bell-shaped without fine vibrational structure. The luminescence properties of zinc tungstate synthesized by hydrothermal method are essentially the same as the ZnWO_4 synthesized by traditional solid state method.

The emission spectrum of the Eu^{3+} ion in ZnWO_4 is presented in Fig. 4. The electronic dipole transition $^5\text{D}_0-^7\text{F}_0$ at about 579 nm is clearly observable and contains only one weak line. There are three lines

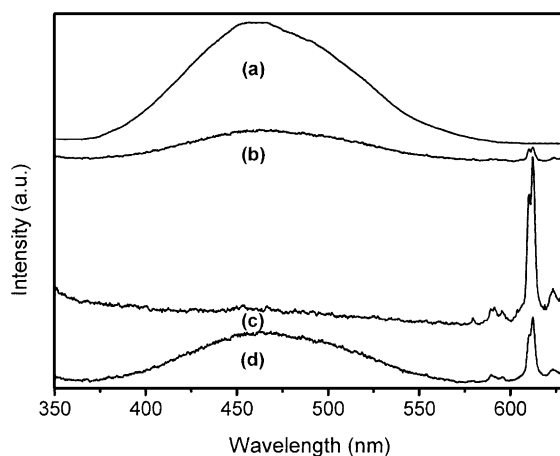


Fig. 6. Emission spectra of Eu^{3+} -doped ZnWO_4 with different doping concentrations: (a) pure ZnWO_4 ; (b) $\text{Eu}^{3+}/\text{WO}_4^{2-} = 1.7 \times 10^{-3}$; (c) $\text{Eu}^{3+}/\text{WO}_4^{2-} = 2.9 \times 10^{-2}$; (d) $\text{Eu}^{3+}/\text{WO}_4^{2-} = 9.5 \times 10^{-2}$. Excitation at 303 nm.

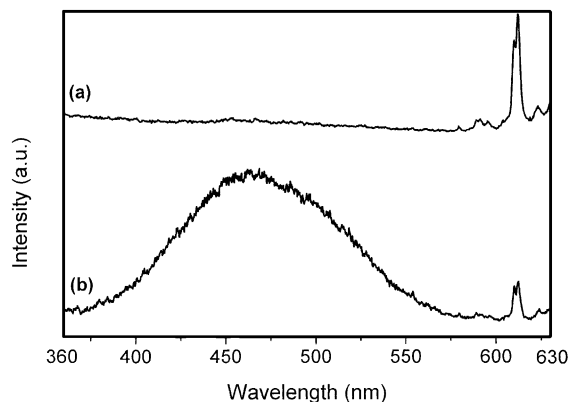


Fig. 7. Emission spectra of Eu^{3+} -doped ZnWO_4 synthesized by hydrothermal and solid state method: (a) Eu^{3+} -doped ZnWO_4 by hydrothermal method; (b) Eu^{3+} -doped ZnWO_4 by solid state method. (a) and (b): $\text{Eu}^{3+}/\text{WO}_4^{2-} = 2.9 \times 10^{-2}$, excitation at 303 nm.

(589, 592 and 596 nm) in the magnetic dipole transition ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ and five lines (604, 610, 612, 619 and 623 nm) in the electronic dipole transition ${}^5\text{D}_0\text{--}{}^7\text{F}_2$, respectively. The emission spectrum is dominated by the ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ transitions. On the basis of the emission spectrum, a crystallographic site with symmetry C_2 for the Eu^{3+} ions is deduced [13]. The tungstate emission consists of a broad band in the region 350–580 nm with a maximum at about 470 nm. Fig. 5 shows the excitation spectra of the Eu^{3+} emission ($\lambda_{\text{em}} = 612$ nm) of Eu^{3+} -doped ZnWO_4 and the tungstate emission ($\lambda_{\text{em}} = 470$ nm) of pure ZnWO_4 , respectively. It consists of the sharp lines due to the transitions within the $4f^6$ shell of the Eu^{3+} and a broad band (250–350 nm) in the UV region. The broad band in the UV region may contain the charge-transfer excitation spectrum of Eu^{3+} ion with a maximum at 253 nm [14]. Overlap between excitation spectra of tungstate groups and Eu^{3+} ions has also been observed previously for $\text{AgGd}_{0.96}\text{Eu}_{0.04}\text{W}_2\text{O}_8$ [15]. This broad band in the UV region of the excitation spectrum of the Eu^{3+} emission indicates efficient energy transfer from the tungstate group to Eu^{3+} [13]. The emission spectra for Eu^{3+} -doped ZnWO_4 with various doping concentrations are shown in Fig. 6. From Fig. 6b and c, as the amount of doped Eu^{3+} increases, the luminescence intensity of tungstate groups decreases because the tungstate groups absorb energy from UV excitation and transfer the energy to

Eu^{3+} ions. However, the luminescence intensity of tungstate groups is enhanced again when the concentration of Eu^{3+} ions increases further (Fig. 6c and d). This is probably because of the concentration quenching for the Eu^{3+} ions. Concentration quenching of Eu^{3+} emission usually occurs through energy migration within the Eu^{3+} sublattice to quenching sites [16].

The emission spectra of Eu^{3+} -doped ZnWO_4 synthesized by the hydrothermal and the solid state methods are shown in Fig. 7. It is found that the luminescence intensity of Eu^{3+} ions for the Eu^{3+} -doped ZnWO_4 obtained through the solid state method is lower than that through the hydrothermal route. This may be because the amount of doped Eu^{3+} ions in ZnWO_4 crystal lattice in the former is small, and as a result, the efficiency of energy transfer from tungstate group to Eu^{3+} ions is low. Therefore, we believe that the hydrothermal synthesis is a more effective way than the solid state reaction to dope Eu^{3+} ions in the lattice of ZnWO_4 .

4. Conclusions

The morphology and particle size of ZnWO_4 crystals can be controlled by adjusting the hydrothermal reaction conditions. Compared to the high-temperature (normally above 1000 K) solid state methods, the temperature of hydrothermal synthetic routes is decreased to 453 K. Significant energy transfer from WO_4^{2-} groups to Eu^{3+} ions has been observed during the photoluminescence of the Eu^{3+} -doped compounds. Thus, it was found that the hydrothermal synthesis is a more effective way than the solid state reaction to dope Eu^{3+} ions in the lattice of ZnWO_4 .

Acknowledgements

We are grateful to the National Natural Science Foundation of China for financial support.

References

- [1] F.A. Kröger, *Some Aspects of the Luminescence of Solids*, Elsevier, Amsterdam, 1948.
- [2] L.G. Van Uitert, S. Preziosi, *J. Appl. Phys.* 33 (1962) 2908.

- [3] T. Oi, K. Takagi, J. Fukazawa, *Appl. Phys. Lett.* 36 (1980) 278.
- [4] B.C. Grabmaier, *IEEE Trans. Nucl. Sci.* NS-31 (1984) 372.
- [5] Y.C. Zhu, J.G. Lu, Y.Y. Shao, H.S. Sun, J. Li, S.Y. Wang, B.I. Zheng, Z.P. Zheng, Y.D. Zhou, *Nucl. Instrum. Methods Phys. Res., Sect. A* 244 (1986) 579.
- [6] H. Wang, Y. Liu, Y.D. Zhou, G. Chen, T. Zhou, J.H. Wang, B.Q. Hu, *Acta Phys. Sin.* 38 (1989) 670.
- [7] H. Wang, F.D. Medina, D.D. Liu, Y.D. Zhou, *J. Phys.: Condens. Matter* 6 (1994) 5373.
- [8] J.C. Brice, P.A.C. Whiffin, *Br. J. Appl. Phys.* 18 (1967) 581.
- [9] A.R. Phani, M. Passacantando, L. Lozzi, S. Santucci, *J. Mater. Sci.* 35 (2000) 4879.
- [10] S.H. Feng, R.R. Xu, *Acc. Chem. Res.* 34 (2001) 239.
- [11] Th.P.J. Botden, *Philips Res. Rep.* 6 (1951) 425.
- [12] H. Wang, F.D. Medina, D.D. Liu, Y.D. Zhou, *J. Phys.: Condens. Matter* 6 (1994) 5373.
- [13] C.C. Torardi, C. Page, L.H. Brixner, *J. Solid State Chem.* 69 (1987) 171.
- [14] S. Shigeo, M.Y. William, *Phosphor Handbook*, CRC Press, Washington, DC, 1998.
- [15] F. Shi, J. Meng, Y.F. Ren, Q. Su, *J. Mater. Chem.* 7 (1997) 773.
- [16] G. Blasse, *J. Less-Common Met.* 112 (1985) 1.