

Luminescence mechanism of ZnWO₄ nanopowder synthesized by microwave-assisted heating

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Abstract. The luminescence investigations on the calcinated zinc tungstate nanopowder (ZnWO₄ NP) synthesized by microwave-assisted synthesis are presented using photoluminescence (PL) and time-resolved photoluminescence (TRPL) analyses. The X-ray diffraction (XRD) patterns exhibit that the significant wolframite structure of ZnWO₄ NP can be detected at calcination temperatures above 300 °C. The 12 K PL and TRPL results demonstrated that the deformation of WO₆ octahedra is responsible for the low-energy side of PL spectra and dominate the red-shifted PL spectra with increasing calcination temperatures.

Introduction

Zinc tungstate (ZnWO₄) belongs to the tungstate crystals AWO₄ with A = Zn, Cd, etc. [1,2] and it is a wolframite-structure material with monoclinic space group P2/C and typical lattice parameter $a = 4.74 \text{ \AA}$, $b = 5.7 \text{ \AA}$, $c = 4.95 \text{ \AA}$, $\beta = 90.1^\circ$ [2]. It consists of Zn cations and WO₄ tungstate groups in the anionic positions. Each tungsten atom has six oxygen atoms in the nearest surroundings forming distorted octahedral tungstate groups WO₆⁶⁻.

ZnWO₄ has been a promising material for photocatalyst [3,4], microwave dielectric ceramics [5], photo-stimulated photoluminescent [6,7] due to its optical and catalytic properties as well as possibility of preparation in nanostructures [7]. The optical properties of single-crystal ZnWO₄ have been intensively studied in the past [1,2,8]. It has been reported that the intrinsic luminescence band, observed at room temperature at about 2.5 eV, can be attributed to a charge transfer between oxygen and tungsten ion in the [WO₆]⁶⁻ molecular complex [1,8]. However, as few reports has been presented on the luminescence properties of nanostructured ZnWO₄ with calcination treatment.

In this work, ZnWO₄ NP were prepared by microwave-assisted synthesis. The as-synthesized samples were further calcined in air at different temperatures in the range of 300–900 °C. The PL and time-resolved PL spectra were carried out to discuss the luminescent mechanism of ZnWO₄ NP.

Experimental

ZnWO₄ NP were synthesized by heating a mixture of NaWO₄·2H₂O and ZnSO₄·7H₂O in deionized water (DI water) using microwave technology. The detailed synthesis process has been discussed elsewhere. The as-synthesized ZnWO₄ NP were further calcined in air at several temperatures of 300 °C, 450 °C, 600 °C, 750 °C and 900 °C for 2 hours. The XRD spectrometer (Shimadzu XRD-6000) with a CuK α line of 1.5405 Å was used to study the crystal phases in the as-synthesized and calcined ZnWO₄ NP. The PL and TRPL were measured at 12 K by using a diode laser with an excitation wavelength of 377 nm (PicoQuant). The diode laser produces light pulses with 50 ps duration and a repetition rate of 1 MHz. PL measurement was setup using a spectrometer (Zolix omni- λ 500) with a

grating of 1200 grooves/mm, and detected using a photomultiplier tube (PMT). TRPL was performed using the technique of time-correlated single-photon counting (TCSPC). The luminescence decay was detected with a high-speed PMT, followed by a computer plug-in TimeHarp counting card, which was triggered with a signal from the diode laser.

Results and discussion

Figure 1 presents the XRD spectra of the as-synthesized and calcined ZnWO₄ NP. The XRD patterns of the as-synthesized ZnWO₄ sample (Fig. 1(a)) exhibits unresolved diffraction features, indicating that the as-synthesized ZnWO₄ samples are amorphous. From Figs. 1(b)~(e), it is observed that several significant XRD peaks can be clarified after calcination. According to the JCPDS card No. 73-0554, the pronounced diffraction signals can be identified to the (100), (011), (111), and (021) peaks, which means that the calcined ZnWO₄ NP has a monoclinic sanmartinite structure [1,4].

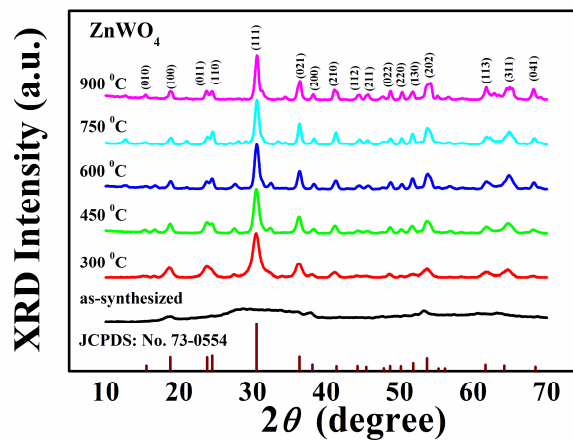


Fig. 1. X-ray diffraction patterns of as-synthesized and calcined at different temperature ZnWO₄ NP.

Figures 2(a)~(e) show the PL spectra recorded at 12 K of ZnWO₄ NP with different calcination temperatures and all spectra exhibit an asymmetric and broad luminescence shape. As shown in Fig. 2(a), the broad-band emission of ZnWO₄ NP calcined at 300 °C is centered at about 2.55 eV, which has been attributed to the radiation transitions between tungsten and oxygen states in regular octahedral WO₆ groups [1,8]. It is observed that the peak position of PL spectrum shifts to lower energy with increasing calcination temperatures, which implies that the radiative transition at low-energy side would dominate the emission spectrum of ZnWO₄ NP after calcination treatment.

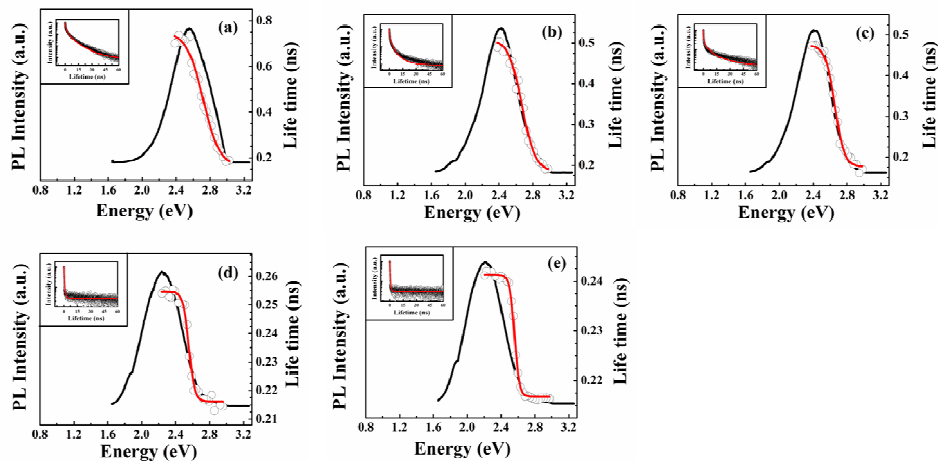


Fig. 2. 12 K PL spectrum of ZnWO₄ NP with calcination temperature at (a) 300 °C, (b) 450 °C, (c) 600 °C, (d) 750 °C and (e) 900 °C. The open circles display the emission-energy dependence of lifetime τ . The solid line displays the fitting curve obtained using Eq (2). The inset shows the PL decay profiles of ZnWO₄ NP monitored at the peak position.

To further analyze the luminescence mechanisms in ZnWO₄ NP, the dynamic behavior of luminescence were carried out by time-resolved PL technique. The inset in Figs. 2(a)~(e) display the luminescence decay profile monitored at the PL peak and the PL decay curve can be fitted by the stretch-exponential function [9]

$$I(t) = I_0 \exp\left[-(t/\tau)^\beta\right] \quad (1)$$

where τ is the decay lifetime and β is a dispersion factor, which takes a value of $0 < \beta < 1$. The red solid curve described from Eq. (1), shown in the insets of Fig. 2, can well fit the experimental data and to obtain the value of τ . It presents that the life time becomes faster with increasing calcination temperature.

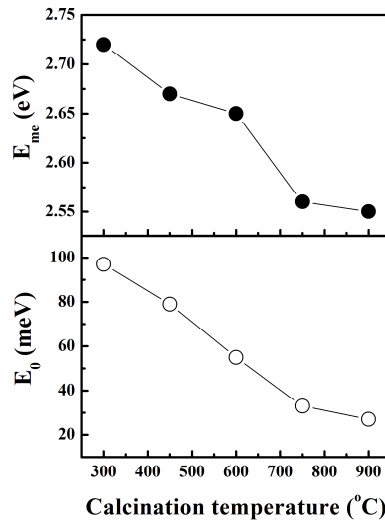


Fig. 3. Dependence of (a) E_{me} and (b) E_0 at 12 K on the calcination temperature. The solid line is given only to indicate the data trend.

So far some reports for understanding the mechanisms of the PL shape and lifetime [1,7,8], a reasonable model for the radiative transition within the $(WO_6)^{6-}$ molecular complex in ZnWO₄ material can be interpreted [8]. Mikhailik et al. have attributed the luminescence band at 2.5 eV to that the carriers transition starts from two ${}^3T_{1u}$ levels to ${}^1A_{1g}$ level of $(WO_6)^{6-}$ molecular complex and the spin-forbidden transitions are partly allowed by spin-orbit coupling that entail a long decay time of luminescence. Additionally, the distorted octahedral WO_6 would cause lowering of the site symmetry to result in allowing the parity forbidden transition from the lower-lying T_{1g} -level level, hence the deformation of WO_6 octahedra can be the probable scenario to explain the domination of low-energy emission and the acceleration of the luminescence kinetics presented in the PL and TRPL results.

The calculated PL lifetime as a function of emission energy is further plotted as open circles in Fig. 2, showing that the luminescence decay is faster on the high energy side than the low energy side of PL. The decrease in the lifetime with increasing emission energy has been understood as the characteristic of a localization effect and attributed to the localized carriers transfer process to lower energy states [10,11]. The decay rate of localized carriers is expressed as the radiative recombination rate plus the rate of transfer to lower energy sites, which results in the observed lifetime decreasing as the emission energy increases. The relationship between lifetime and emission energy can be expressed by [10,11]

$$\tau(E) = \frac{\tau_{rad}}{1 + \exp\left[(E - E_{me})/E_0\right]} \quad (2)$$

where τ_{rad} is the radiative recombination lifetime, and E_0 is the characteristic energy for the depth of the localized states. E_{me} is a definite energy for the decay time that equals the transfer time, which is similar mobility edge. The solid line in Fig. 2 indicates the best fit according to Eq. (2), and the obtained values of E_{me} and E_0 are summarized and shown in Fig. 3.

The value of E_{me} decreases linearly from 2.72 eV to 2.55 eV as the calcination temperature from 300 °C to 900 °C. In addition, the obtained E_0 for the ZnWO₄ NP calcined at 300 °C is 97 meV and that decreases to 27 meV for the ZnWO₄ NP calcined at 900 °C. This decrease indicates a reduction in the degree of carrier localization formed by the complex transition levels in the calcined ZnWO₄ NP. According to the above mentioned model, the E_{me} of 2.55 eV for the ZnWO₄ NP calcined at 900 ° is in connection with the $^3T_{1u}$ levels. The E_0 is assumed to be formed with the $^3T_{1u}$ levels and the larger value of E_0 can lead to the carrier recombination upon the $^3T_{1u} \rightarrow ^1A_{1g}$ transitions. On the other hand, the smaller value of E_0 at higher calcination temperature allows the carriers to first transfer from $^3T_{1u}$ level to the lower-lying T_{1g} -level and then to $^1A_{1g}$ level, reflecting the red-shifted PL spectra.

Summary

We have successfully synthesized the ZnWO₄ NP by microwave-assisted heating and investigated its luminescence properties by TRPL measurements. The XRD and PL spectra present that the crystallization and emission properties of the ZnWO₄ NP are affected by the calcination temperature. PL and TRPL results suggest that the distorted octahedral WO₆ is responsible for the low-energy part of emission spectrum. The decrease in emission band as a function of calcination temperature can be assigned to the increased performance of the distorted WO₆ octahedra. However, the further proof for the distorted WO₆ octahedra in the calcined ZnWO₄ NP has to investigate in the future. We suggest that the calcination treatment can be suggested as a considerable technique to control emission properties of ZnWO₄ materials.

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