



Raman and photoluminescence spectroscopy of zinc tungstate powders

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ARTICLE INFO

Article history:

Received 1 October 2008

Received in revised form

15 May 2009

Accepted 19 May 2009

Available online 27 May 2009

PACS:

63.20.-e

78.55.Hx

78.30.-j

81.07.Wx

Keywords:

ZnWO₄

Raman spectroscopy

Photoluminescence

Nanopowder

ABSTRACT

ZnWO₄ powders, synthesized using co-precipitation technique and annealed in air at different temperatures in the range of 80–800 °C, were studied by Raman and photoluminescence spectroscopy. ZnWO₄ single crystal was used for comparison. The interpretation of the observed variations of the Raman spectra and intrinsic photoluminescence band upon annealing is suggested.

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1. Introduction

Zinc tungstate ZnWO₄ is an attractive material, having many useful applications in scintillators [1–3], optical fibers [4], Raman laser converters [5], photocatalysts [6], high-temperature solid lubricant [7,8] and phase-change optical recording [9].

ZnWO₄ has monoclinic wolframite-type structure with the space group P2/c and two formula units per primitive cell [10,11]. The distorted ZnO₆ and WO₆ octahedra are joined by edges into infinite zigzag chains, consisting of octahedral units of the same type and running parallel to *c*-axis. Each such chain is interconnected through the octahedra apexes to four other chains, composed of octahedra of another type [10,11]. The distortion of the WO₆ octahedra has been studied using W L₃-edge X-ray absorption spectroscopy [12]. It was found that six oxygen atoms are well separated into two groups, composed of four nearest atoms, located at the mean W–O distance about 1.83 Å, and two oxygen atoms making longer bonds of about 2.12 Å [12].

The lattice dynamics of single-crystal ZnWO₄ has been probed by Raman scattering, and the observed Raman lines have been interpreted based on the group-theoretical analysis [13,14]. Due to peculiarity of chemical bonding in ZnWO₄, the lattice interactions

can be approximately divided into internal vibrations of the [WO₆] octahedral groups and the external vibrations, in which the octahedral groups vibrate as units. Recently it was proposed, based on the results of high-temperature Raman spectroscopy, that these octahedral groups transfer into [WO₄] tetrahedral groups in the molten state [15,16].

The luminescent properties of single-crystal ZnWO₄ have been widely studied in the past [2,17–20]. It is believed that intrinsic luminescence band, observed at room temperature at about 2.5 eV, is determined by a charge transfer between oxygen and tungsten ions in the [WO₆]⁶⁻ molecular complex [2,17,21,22].

In this work, we present the results of Raman scattering and photoluminescence studies of ZnWO₄ powders, synthesized using co-precipitation technique and annealed in air at different temperatures in the range of 80–800 °C.

2. Experimental

ZnWO₄ powders were synthesized using co-precipitation technique by mixing two aqueous solutions of Na₂WO₄ · 2H₂O and ZnSO₄ · 7H₂O salts in bi-distilled water. The solution pH value was equal to 8. The tungstate sediment was subsequently washed, filtrated and after drying, annealed in air for 4 h at different temperatures in the range of 80–800 °C. All thus obtained powders were white colored. ZnWO₄ single crystal was used for comparison.

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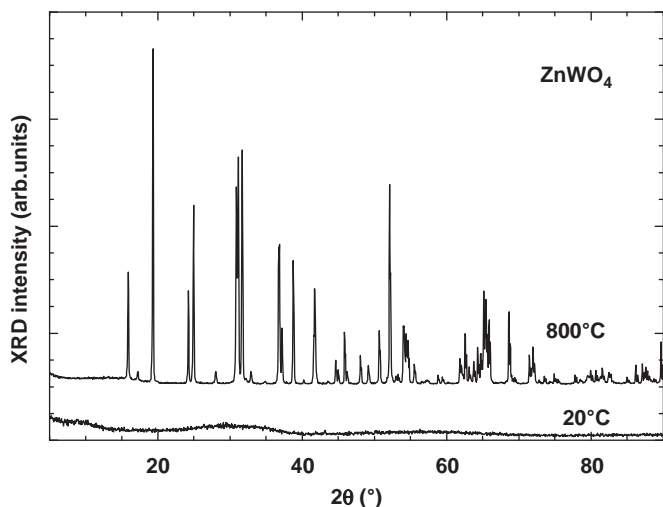


Fig. 1. X-ray diffraction patterns of as-prepared (20°C) and annealed at 800°C ZnWO₄ powders.

X-ray powder diffraction (XRD) patterns were recorded at 20°C using Bragg–Brentano powder diffractometer ($\theta/2\theta$ scans) with a graphite monochromator in the diffracted beam for elimination of sample fluorescence. Conventional tube with copper anode (Cu $K\alpha$ radiation) was used as X-ray source. The measurements were performed at room temperature in the angle range $2\theta = 5\text{--}90^\circ$ with the step $\Delta(2\theta) = 0.05^\circ$. The XRD data (Fig. 1) show that as-prepared ZnWO₄ powder is X-ray amorphous, whereas it becomes well crystalline upon annealing at 800°C, in agreement with Refs. [6,23,24].

The photoluminescence spectra and decay kinetics were measured using pulsed YAG:Nd laser excitation (4.66 eV, 8 ns) at 20°C. Photoluminescence registration was carried out by photomultiplier tube HAMAMATSU H8259 and photon counting board fastComTec Communication Technology module P7888-1E, having the time resolution 2 ns. The photoluminescence kinetics for each sample were collected at three energies, corresponding to the intrinsic luminescence band maximum and two band edges. The three kinetics were close, therefore only data, taken at the band maximum, will be presented due to their better statistics.

Raman spectra were collected at 20°C using a confocal microscope with spectrometer “Nanofinder-S” (SOLAR TII, Ltd.) [25]. The measurements were performed through Nikon Plan Fluor 40× (NA = 0.75) optical objective. The Raman spectra were excited by a He–Cd laser (441.6 nm, 50 mW cw power) and dispersed by 1800 grooves/mm diffraction grating, having a resolution of about 2.5 cm⁻¹ and mounted in the 520 mm focal length monochromator. The Peltier-cooled back-thinned CCD camera (ProScan HS-101H, 1024 × 58 pixels) was used as a detector. The elastic laser light component was eliminated by the edge filter (Omega, 441.6AELP-GP).

3. Results and discussion

The Raman spectra of ZnWO₄ powders change significantly depending on the annealing temperature (Fig. 2). According to their overall shape, one can distinguish three annealing ranges: below 400°C, at 400–450°C and above 450°C. It is convenient to start a discussion from the results for high-temperature annealing region.

Group theory analysis for wolframite-type ZnWO₄ predicts 36 lattice modes, of which 18 even vibrations ($8A_g + 10B_g$) are Raman

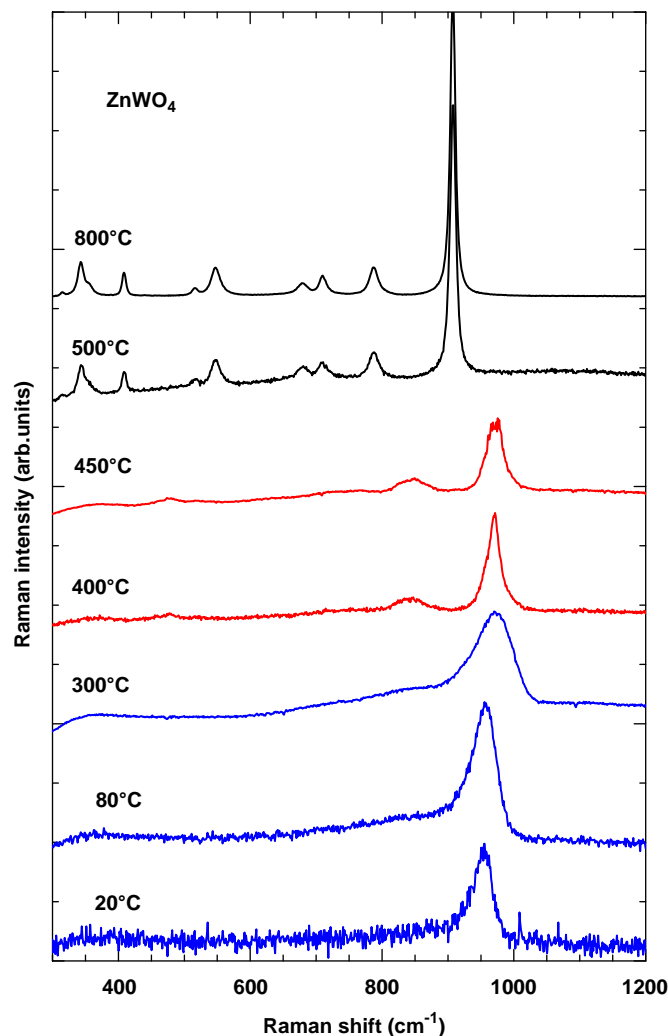


Fig. 2. (Color online) Raman scattering spectra in ZnWO₄ powders annealed at different temperatures. Measurements were performed at 20°C.

active. Eleven of them are expected [13,14] in the frequency range accessible in our experiment due to the cut-off by the edge filter around 270 cm⁻¹. In fact, all expected lines (907, 787, 709, 679, 547, 516, 409, 355, 343, 315 and 276 cm⁻¹) are observed in the Raman signal for powder annealed at 800°C. Note that the highest frequency line at 907 cm⁻¹, corresponding to the stretching W–O mode, has a linewidth about 9 cm⁻¹. At low annealing temperature (500°C), the Raman lines of wolframite-type ZnWO₄ are broadened due to a reduction and a dispersion of the crystallites size but still can be detected.

For the annealing in the range of 400–450°C, the Raman spectrum changes dramatically and is composed of five broad lines: 320–420, 430–560, 670–800, 800–900 cm⁻¹ and the intense line at 971 cm⁻¹ with the linewidth 20–30 cm⁻¹. This result cannot be due to homogeneous or inhomogeneous broadening, but should be caused by some relaxation of ZnWO₄ particles structure upon their size reduction. Note that heating of polycrystalline ZnWO₄ up to 1227°C (below melting temperature) leads to homogeneous Raman line broadening and only slightly affects the lines position [15,16].

The Raman spectra of samples, annealed at temperatures below 400°C, are close enough to that from previous group, but further significant lines broadening occurs. The signals consist of one main line at 950–960 cm⁻¹ with a linewidth equal to

50–70 cm^{-1} and a broad line with low intensity at 700–900 cm^{-1} . There is also some evidence of a weak broad line spreading from 300 to 500 cm^{-1} . It is interesting that these Raman signals are close to that observed for ZnWO_4 melt in Refs. [15,16], where the origin of lines has been attributed to the internal vibrational modes of isolated $[\text{WO}_4]^{2-}$ complexes.

Our interpretation of the observed Raman signals shape does not support the appearance of tetrahedral $[\text{WO}_4]$ groups in as-prepared or annealed at low-temperature ZnWO_4 powders. We believe that due to a small particle size, being in the nanoscale range, the large surface-to-bulk ratio leads to the strong relaxation of the particle structure. Additionally, the surface tungsten–oxygen bonds could play an important role. It is known that the sharp Raman line around 950 cm^{-1} is observed in crystalline tungsten hydrates and is attributed to the short double terminal $\text{W}=\text{O}$ bonds [26]. Besides, similar but broad line is observed in ground pure WO_3 powder and has been attributed to the $\text{W}^{6+}-\text{O}^-$ or $\text{W}^{6+}-\text{OH}$ surface terminating bonds in Ref. [27]. Further support for the octahedral coordination of tungsten is provided by photoluminescence results given below.

The photoluminescence spectra of ZnWO_4 powders (Fig. 3) consist of a broad band, peaked at about 2.5 eV. The band position and the bandwidth dependence on the annealing temperature are shown in Fig. 4. The photoluminescence kinetics, measured at the band maximum, in the time interval up to 25 μs , are shown in Fig. 5. As in the case of Raman spectra, one can distinguish three temperature ranges: below 400 °C, at 400–450 °C and above 450 °C.

When annealing above 450 °C, the photoluminescence spectra of ZnWO_4 powders are close to that of single crystal with a maximum at about 2.51 eV at room temperature [28] and a bandwidth of about 0.52 eV. The kinetics can be fitted as a sum of three exponents, and decay time values are in good agreement with that in Ref. [28], where high laser power was used.

For ZnWO_4 powders annealed in the intermediate temperature range (400–450 °C), the photoluminescence band maximum shifts to the lower energy, and the bandwidth is larger (~ 0.55 eV) than that for the powders annealed above 450 °C, and for single crystal. The photoluminescence kinetics are faster and more complex, so that they cannot be fitted with three exponents.

In the temperature range below 400 °C, the photoluminescence spectra maximum shifts further to lower energies, but some

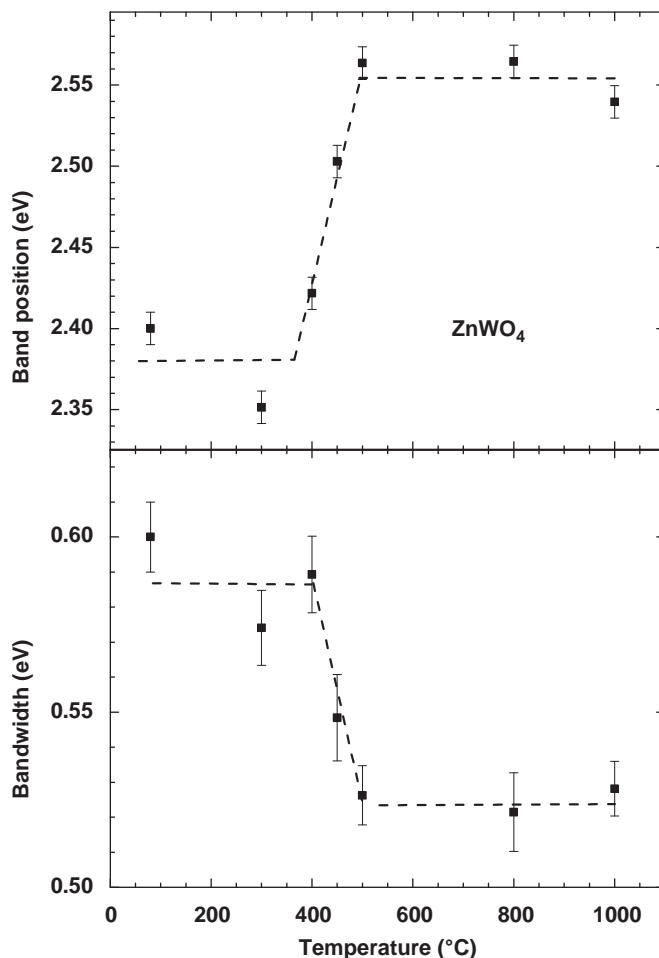


Fig. 4. Photoluminescence band maxima position (top plot) and the bandwidth (bottom plot) in ZnWO_4 powders annealed at different temperatures. The point $T = 1000^\circ\text{C}$ corresponds to the single crystal. The dashed lines are guides for eye.

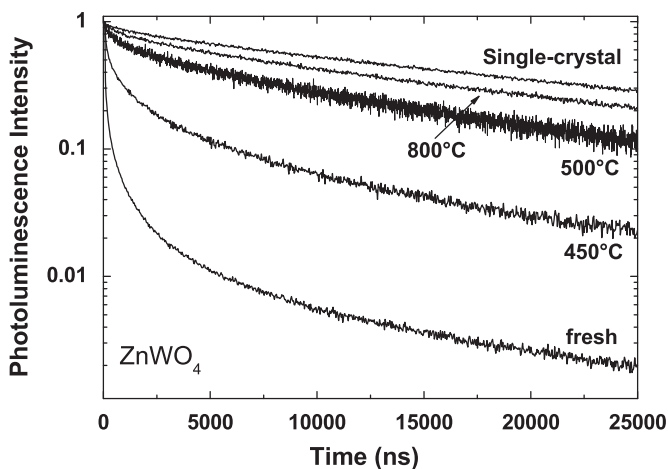


Fig. 5. Photoluminescence kinetics, measured at the intrinsic band maximum, in ZnWO_4 powders annealed at different temperatures.

spread in the band maximum position is observed. The bandwidth is larger (~ 0.60 eV) and kinetics even faster.

The behavior of photoluminescence spectra from ZnWO_4 powders allows to draw several conclusions. First, we did not observe in our powders the quantum size effect, leading to a blue

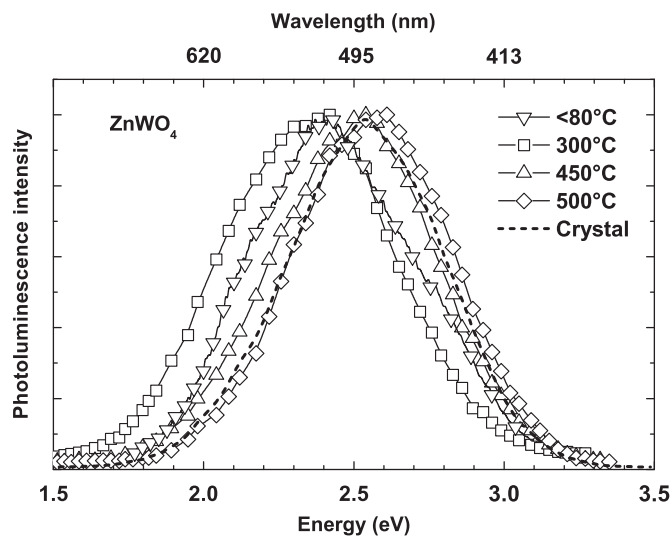


Fig. 3. Photoluminescence of ZnWO_4 powders annealed at different temperatures. The spectra intensities are normalized at the band maximum. Measurements were performed at 20 °C.

shift of the luminescence band, which one may expect for a nanosized material [29]. Our result agrees well with that for ZnWO₄ thin films [30] and nanoparticles [31], having a size of 28–56 nm. The absence of the quantum size effect can be explained by the origin of the luminescence. It is due to electronic transitions of the charge transfer type between oxygen and tungstate states in the [WO₆]⁶⁻ molecular complexes [2,17,21], which exist in our ZnWO₄ powders independently from the particle size.

Some variation in the band position, observed in Fig. 3, can be related to a change in the distortion of the [WO₆]⁶⁻ complexes, caused by a change of the particle size. At low annealing temperatures (below 400 °C), the average size of the ZnWO₄ particles is small (below ~20 nm), as follows from diffraction experiments [23,24], and, thus, the number of [WO₆] groups located at the particle surface, whose atoms relax more than of those located in the bulk, increases.

The position of the luminescence band allows also to exclude another scenario, in which the relaxation proceeds so strong that it is able to promote a transformation of octahedral [WO₆] groups into tetrahedra [WO₄]. However, in this case, one expects a blue shift of the luminescence band maximum to ~2.95 eV, which is typically observed in scheelites, for example, CaWO₄ [32].

Significant changes of the luminescence kinetics may be also related to the deformation of [WO₆]⁶⁻ complexes. It has been shown [11,22,33] that in single crystal and polycrystalline ZnWO₄, the luminescence kinetics can be approximated by three exponents. Corresponding decay times can be associated with three types of self-trapped excitons (STE) [22]. In our samples produced at low annealing temperatures, kinetics are faster and cannot be adequately described by three exponential decay functions. This fact can be explained by the presence of a large number of defects, appearing in small ZnWO₄ particles of different size and able to trap excitons with different lifetimes. For high annealing temperatures, the larger particles with less amount of defects are responsible for that the distribution of lifetimes becomes narrower.

4. Conclusions

The temperature dependence of the Raman scattering indicates a dramatic variation of the vibrational properties in ZnWO₄ powders, synthesized by co-precipitation method and annealed in air at different temperatures in the range of 80–800 °C. In particular, a strong variation of the Raman line at 900–950 cm⁻¹, corresponding to the stretching W–O frequency, is observed.

Photoluminescence band shift to longer wavelengths, comparing to single crystal, is also observed for powders annealed at temperatures below 450 °C, whereas the band position for ZnWO₄ powders annealed at higher temperatures is identical to that in single crystal. The annealing temperature has also strong influence on the bandwidth of the photoluminescence band and decay kinetics.

The observed effects are attributed to the change in a distortion of the [WO₆]⁶⁻ molecular complexes, occurring upon a decrease of the ZnWO₄ particles size. While Raman spectra show some evidence for tetrahedral coordination of tungsten atoms in small particles, the analysis of the intrinsic photoluminescence band excludes this possibility.

Acknowledgments

This work was partially supported by Latvian Government Research Grant nos. 05.1717, 09.1211 and Latvian National Research Program in Materials Science.

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