

Synthesis of Nanocrystalline ZnWO₄ via Molten Salt Route and Its Photoluminescence

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ZnWO₄ nanocrystalline powder has been synthesized by the molten salt route using KNO₃/NaNO₃ mixture as reaction media. Pure ZnWO₄ phase was obtained at 250 °C for 2 h without any intermediate phase. Particle size and morphology of the powder were studied by transmission electron microscopy (TEM). The luminescent properties of the final powder as functions of the reaction temperature and time have been studied.

Molten salt synthesis (MSS) method is one of the simplest techniques to prepare pure, stoichiometric oxide powder.¹ In this method, low-melting, water-soluble salt, or salt mixture is used as the reaction media, which provide an alternative to aqueous chemistry by offering the possibility to change the solubility and/or the reactivity of the reactants.² Up to now, various materials have been prepared by the MSS method, including mullite,³ alumina,^{1,4} calcium hydroxyapatite,⁵ niobates,⁶ titanates,⁷ and tungstate.⁸

Zinc tungstate (ZnWO₄) is an important material for its promising application in microwave amplification,⁹ X-ray scintillators¹⁰ and optical hole burning lattice (OHB) material.¹¹ Therefore, ZnWO₄ nanocrystalline powders with high quality are required for the application. Traditionally, ZnWO₄ powders are synthesized by solid-state reaction of powdered ZnO and WO₃.¹² As the reactions are generally controlled by slow diffusion mechanisms, high temperature and long time must be used for the reaction to go to completion (almost above 1000 °C for 24 h). Moreover, the reaction product is often strongly aggregated, and the size of the product is between micron and millimeter.¹³ Thus, wet chemical methods have been developed to reduce the formation temperature of ZnWO₄ and improve the phase purity of the prepared powder. Wen et al.¹⁴ have prepared and researched the photoluminescent properties of ZnWO₄ and Eu³⁺-doped ZnWO₄ micropowder by hydrothermal reaction route. Chen et al.¹⁵ have prepared nanocrystalline ZnWO₄ with different morphologies and sizes via hydrothermal route. Ryu et al.¹⁶ have synthesized ZnWO₄ nanocrystalline powder by the polymerized complex method. Besides these researches, to our knowledge, no other studies have ever been reported for the synthesis of ZnWO₄ powder.

In this paper, we reported synthesis of nanocrystalline ZnWO₄ via molten salt route using KNO₃/NaNO₃ mixture as reaction media. The variation of the properties of the final powder has been studied as functions of the reaction temperature and time.

Na₂WO₄ and Zn(NO₃)₂ of analytic reagent grade were used as the starting materials. Appropriate amounts of Na₂WO₄ and Zn(NO₃)₂ were dissolved in distilled water to form aqueous solutions with 1 mol/L concentration, respectively. The Na₂WO₄ solution was thoroughly stirred at room temperature, and then

the Zn(NO₃)₂ solution was slowly added while continuously stirring. The white precipitate was washed several times using distilled water and absolute ethanol, then air-dried at 80 °C overnight. After grinding with an agate mortar and pestle to pass through a 200-mesh sieve, the precipitate (precursor) was mixed with KNO₃/NaNO₃ by grinding the mixture for 30 min. The weight ratio of KNO₃/NaNO₃ (molar ratio = 1:1, melting point: 228 °C) mixture to the precursor was fixed to 20:1. The above mixture was placed in an alumina crucible and heated at various temperatures. The resulting products were dipped into distilled water to dissolve KNO₃/NaNO₃. The precipitate was filtered, washed with distilled water and absolute ethanol for several times, then dried in vacuum at 60 °C for characterization. The phase compositions of the powder were identified using X-ray diffractometry (Model D/MAX-2550V, Rigaku Co., Tokyo, Japan). The morphologies of the powder were examined using transmission electron microscopy (Model 200, JEOL, Tokyo, Japan). The FTIR spectra were obtained by using a UV-3101 Fourier transform infrared spectrophotometer. The room temperature luminescent spectra were measured on a luminescence spectrometer (Model LS55, Perkin-Elmer, U.S.A.).

Ryu et al.¹⁶ have reported synthesis of ZnWO₄ nanocrystalline powder by the polymerized complex method. In their study, the powder was amorphous at 300 °C without any crystallized phases, pure phase ZnWO₄ could only be obtained at 600 °C for 3 h. In our study, the temperature could be reduced to 250 °C. Figure 1 shows the XRD patterns of the prepared powder at 250 °C for 2 h, 250 °C for 16 h, and 350 °C for 8 h, respectively. All of the three XRD patterns could be indexed to the pure phase of monoclinic sanmartinite without any intermediate phase and were in good agreement with the standard data (JCPDS No. 15-0774). It is obvious that higher temperature and longer time result in higher intensity of the XRD pattern, which suggested that elevating heating temperature and prolonging heating time would favor the crystallization and evolution of ZnWO₄ nanocrystalline powder.¹⁷

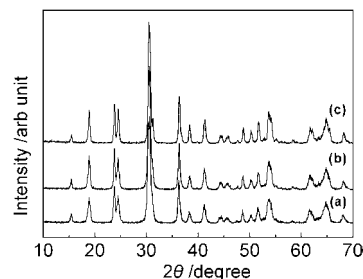


Figure 1. XRD patterns of the prepared powder at different conditions: (a) 250 °C, 8 h, (b) 250 °C, 16 h, (c) 350 °C, 8 h.

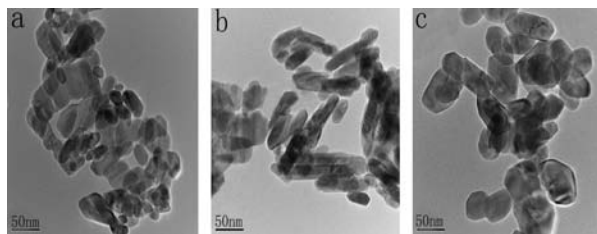


Figure 2. TEM morphologies of ZnWO_4 nanocrystalline powder synthesized at (a) 250 °C for 8 h, (b) 250 °C for 16 h, and (c) 350 °C for 8 h.

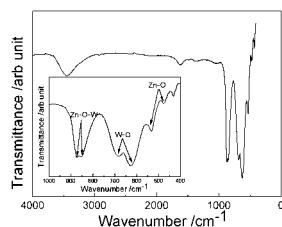


Figure 3. FTIR spectra of ZnWO_4 nanocrystalline powder synthesized at 350 °C for 8 h.

Figure 2 show the TEM morphologies of ZnWO_4 nanocrystalline powder synthesized at different conditions. The powders obtained at 250 °C for 8 h show comixed morphology with nearly spherical and elongated forms. The morphologies of particles prepared at 250 °C for 16 h were aggregation of elongated forms. The particles at 350 °C for 8 h have relatively more homogeneous morphology with a narrow size distribution. The size of the powder is 50–70 nm.

The FTIR spectra of nanocrystalline ZnWO_4 is shown in Figure 3 in the region between 4000 and 400 cm^{-1} . The peaks at 3450 and 1620 cm^{-1} are assigned to the stretching vibrations of OH groups and bending vibrations of adsorbed molecular water, respectively. Lattice vibration bands between 400 and 900 cm^{-1} prove the presence of ZnWO_4 . The adsorption peaks of curves are assigned as follows: 473 and 532 cm^{-1} to the bending and stretching vibrations of Zn–O bond; 633 and 710 cm^{-1} to the bending and stretching vibrations of W–O bond; 834 and 877 cm^{-1} to the bending and stretching vibrations of Zn–O–W bond.

The luminescent properties of the final powder as functions of the reaction temperature and time have been studied. Figures 4a and 4b show room temperature PL spectrum of the ZnWO_4 nanocrystalline powder synthesized at different temperature for different times by molten salt method. With the excited wavelength at 293 nm, the broad blue-green emission peaks appear at nearly 470 nm, which agree with ZnWO_4 particles prepared by hydrothermal route.¹⁷ Moreover, with increasing reaction temperature and time, the samples exhibit a stronger luminescence, which might be ascribed to the improvement in crystallization. According to reports,^{14,15,18} blue emission band of ZnWO_4 results from intrinsic tungstate emission, and WO_6 octahedral structures in the matrix are luminescence centers. Though the nature of the optical transitions of tungstate is still unclear, it is assumed that a charge-transfer transition takes place

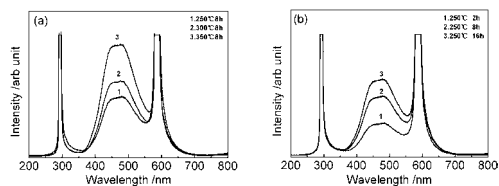


Figure 4. PL spectra of ZnWO_4 nanocrystalline powder synthesized (a) at different temperature for 8 h and (b) at 250 °C for different times (Excitation at 293 nm).

during emission. This optical transition involved in the luminescence of W–O groups might be due to charge transfer between the O2p orbital and the empty d orbital of the central W^{6+} ion. The blue emission band of ZnWO_4 is bell-shaped without fine vibrational structure.

In conclusion, pure ZnWO_4 nanocrystalline powders have been synthesized by the molten salt route using $\text{KNO}_3/\text{NaNO}_3$ mixture as reaction media at a relatively low temperature for the first time. High reaction temperature and long reaction time benefit the degree of the crystallization, which affect the morphology and PL intensity of the powder.

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