



## Influence of pH values on synthesis of nanocrystalline ZnWO<sub>4</sub> powders

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### ABSTRACT

*In this paper, the effects of two factors including pH of the reaction mixture and temperature in heat treatment involved in synthesis of ZnWO<sub>4</sub> nanoparticles are represented. ZnWO<sub>4</sub> nanocrystallites were obtained from zinc nitrate and sodium tungstate. The different conditions of pH and calcination temperature were provided in order to scrutinize their impact on the structural and morphological changes. The obtained powders were characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). Nanocrystalline ZnWO<sub>4</sub> powder synthesized at pH = 9 and calcined at 600°C showed an excitation band at 295 nm and a broad emission band at 477 nm.*

**Keywords:** ZnWO<sub>4</sub>; Nanocrystalline powders; X-ray diffraction; Scanning Electron Microscopy;

### INTRODUCTION

Nanosized oxide particles or mixed oxides particles are gaining increasing technical importance for classic areas of application such as catalysts, passive electronic components, or ceramic materials. Numerous approaches have been explored for the preparation of spherical nanosized particles including various methods [1,2].

Metal tungstates (AWO<sub>4</sub>, A = Co, Mn, Fe, Ni, Mg, Zn) have attracted much interest since they can be used as scintillating medium and in electro-optic applications [3]. ZnWO<sub>4</sub> has been suggested as a possible new material for MASER (microwave amplification by stimulated emission of radiation), scintillator and OHB (optical hole burning) lattice material [4-7]. The present investigation is based on the synthesis of nanocrystalline ZnWO<sub>4</sub> powders by polymerization followed by the combustion of organic agents added to the mixture of zinc nitrate and sodium tungstate at different experimental conditions. The precursors and synthesized powders were evaluated in term of the crystallization process, thermal decomposition and morphology. The effects of pH and the temperature were investigated for analyzing their impact on structure and morphology of nanocrystalline ZnWO<sub>4</sub> powders. The possible reasons of the structural and morphological changes in ZnWO<sub>4</sub> nanoparticles have been tentatively explained on the basis of the literature and experimental results.

### EXPERIMENTAL SECTION

Zinc nitrate and sodium tungstate were used as the metal sources. In the calculated ratio, sodium tungstate was added to the aqueous solution of metal nitrate; prepared in deionized water. To investigate the effect of pH, three values 7.5 8.0 and 9.0 were chosen. Sodium hydroxide solution was then added in different volume to obtain the three solutions of different pH. The equal volume of di-sodium salt of ethylenediaminetetraacetic acid (EDTA)

solution was added to the solutions with pH = 7.5, 8 and 9 followed by the addition of equal volume of 50% glycerol. The reaction mixtures were then stirred for 3 h at 75°C. The resultant solutions were dried in an oven. So obtained dry mass was calcined at 650°C to get oxide powders. To illustrate the effect of calcination temperature, dry mass obtained from the solution of pH = 9 was calcined at 550, 600 and 650°C keeping other factors constant.

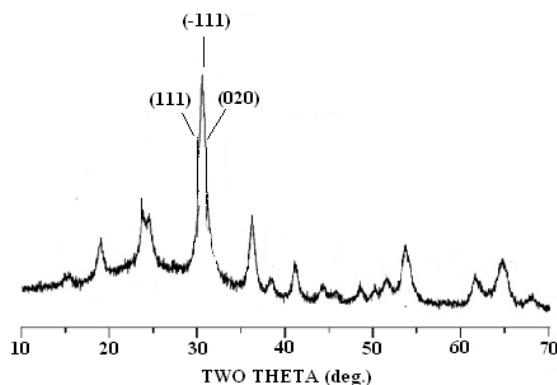
**Table 1 Reaction conditions in synthesis of ZnWO<sub>4</sub> powders and particle size.**

Sample code	pH of reaction mixture	Calcination temperature (°C)	Average particle size (nm)
GJ-I	7.5	600	22.45
GJ-II	8	600	20.37
GJ-III	9	600	15.56
GJ-III(A)	9	550	19.75
GJ-III(B)	9	650	18.65

The phases in the powders after calcination were identified by X-ray diffraction (XRD). The average crystallite size of the calcined powders was calculated using the X-ray diffraction line broadening method through Scherrer's relationship [8]. The microstructure and surface morphology of the nanocrystalline powders were observed by scanning electron microscopy (SEM). The excitation and emission spectra of the samples were carried out on Fluorimeter with a Xe-arc lamp (450 W) as the source of excitation.

## RESULTS AND DISCUSSION

The XRD patterns of the sample GJ-III is shown in Fig. 1. All of the peaks detected in XRD patterns are indexed to ZnWO<sub>4</sub> (JCPDS: 15-0774). The XRD patterns show that there are no characteristic peaks of other impurity phases besides the samples of ZnWO<sub>4</sub>. The influence of pH variation was studied. It is well known that, EDTA is a multi-dentate ligand with strong affinity towards metal ions. It forms a complex with metal ions at higher pH. At pH = 7, the coordination between metal ions and EDTA is suppressed. Therefore, the pH of reaction mixture was adjusted to desired range by addition of a base. In the present investigation, it was observed that with increase in pH of the reaction mixture from 7.5 to 9, the intensity as well as width of the peaks increases. Therefore, the particle size tends to decrease from 22.45 to 17.56 nm (Table 1). Thus, it is quite clear that at pH = 9, better coordination is possible between metal ion and EDTA which and for the formation of ZnWO<sub>4</sub> nanoparticles.



**Figure 1 X-ray diffraction pattern of sample GJ-III.**

The morphology and structure of all the powders were investigated by SEM and presented here only for sample GJ-III, GJ-III(A) and GJ-III(B). The SEM image reveals that sample GJ-III shows uniform and dispersive particles with average particle size of around 16 nm, in agreement with the results calculated from Scherrer's formula in XRD. The effect of calcination temperature on morphology was also studied. The calcination temperatures, 550°C (sample GJ-III(A)) and 650°C (sample GJ-III(B)) were found to be unsuitable as the bigger particles were observed in the micrographs of these samples as compared to the powder calcined at 600°C (sample GJ-III).

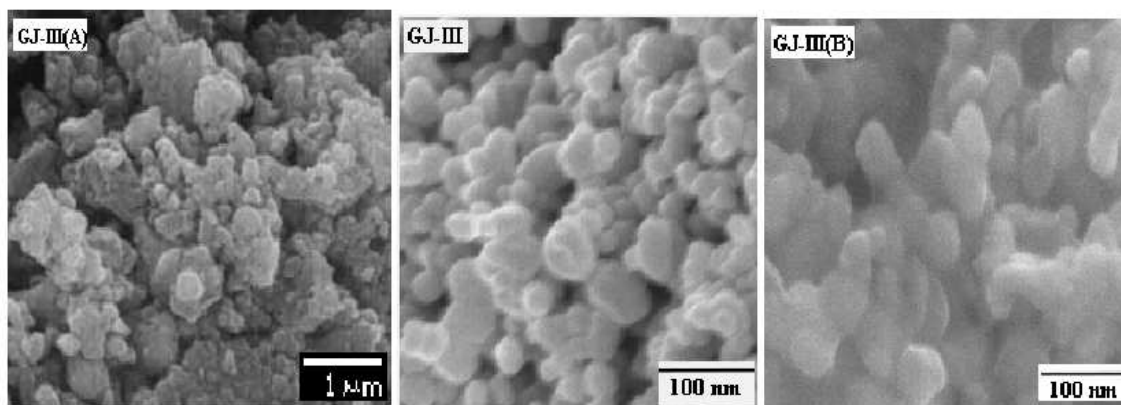


Figure 2 Scanning electron micrographs of sample GJ-III(A), GJ-III and GJ-III(B).

Based on the above results, it is clear that the factors like pH of the reaction mixture and calcination temperature greatly affect the morphology of  $\text{ZnWO}_4$  nanoparticles. As we know, the formation of a crystal can be divided into two stages of nucleation and growth. External conditions may stress tremendous effects on the size and morphology of a given crystal by participating in the nucleation and growth, in which multiple critical roles integrate to dominate the process. The mechanism for the effects of the above-mentioned four factors will be qualitatively elucidated.

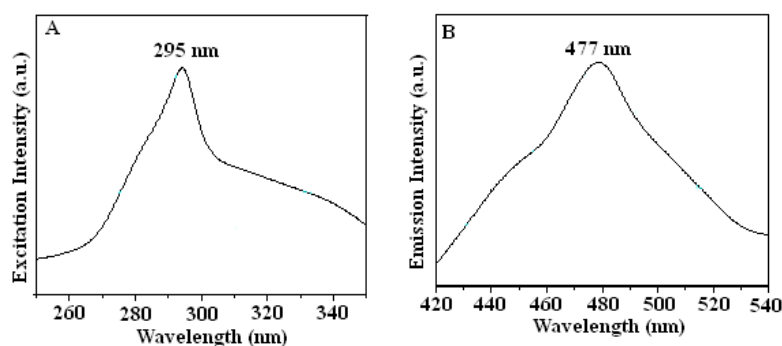


Figure 3 A) Excitation spectra (with  $E_{\text{emi.}} = 477 \text{ nm}$ ) and B) emission spectra (with  $E_{\text{exci.}} = 295 \text{ nm}$ ) of GJ-III

The excitation and emission spectra of sample GJ-III is presented in figure 3A and 3B. The excitation spectrum (Fig. 3A) reveals a strong band at 295 nm. Figure 3B shows the emission spectrum of  $\text{ZnWO}_4$  ceramic powder in the wavelength range of 420-540 nm with 295 nm excitation showing a broad blue emission at 477 nm. This is related to the presence of  $\text{WO}_6$  structures in the matrix, playing the role of luminescence centers and a charge-transfer transition between the 2p- orbitals (of oxygen ions) and the empty d-orbitals (of the central W ion) that could be causing this luminescence [9].

## CONCLUSION

Nanocrystalline  $\text{ZnWO}_4$  powders were successfully synthesized using EDTA and glycerol at various range of pH (from 7.5-9). The pH of reaction mixture played a key role in particle size determination. The average particle sizes were 16~23 nm showing tendency to increase with increase in the pH of solution. The calcination temperature also affected the crystallization and the particle size of products. With optimum reaction conditions selected, this nanocrystalline tungstate with high qualities was successfully prepared.  $\text{ZnWO}_4$  ceramic powder calcined at 600°C demonstrated a broad and intense blue emission at 477 nm, which indicates its usefulness in further development of optoelectronic devices.

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