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SYNTHESIS AND CHARACTERIZATION OF NOVEL NANOCRYSTALLINE ZIRCONIUM (IV) TUNGSTATE SEMICONDUCTOR

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Nanocrystalline zirconium (IV) tungstate is prepared by chemical coprecipitation method using ethylene diamine tetra acetic acid as the templating agent. Elemental composition is determined by EDS. The characteristic bonding position is identified using FTIR.XRD is used to find the theoritical value of size and phase identification using JCPDS. Morphology is examined using SEM and HRTEM. UV absorption at 260 *nm corresponds to an energy gap of* 4.48 *eV, characteristic of semiconducting nanoparticles.*

Keywords: *ZIRCONIUM (IV) TUNGSTATE, SEMICONDUCTOR, BAND GAP, EDS, HRTEM, ZIRCONIA, TUNGSTEN OXIDE*

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1. INTRODUCTION

Metal oxide semiconductor nanomaterials are usable as semiconducting gas sensors because they have many advantage such as small diamensions, low cost, low power consumption, on-line operation and high compatibility with microelectronic processing. These include SnO_2, WO_3, ZrO_2, WO_3, etc. These materials have non-stoichiometric structures, so free electrons orginating from oxygen vacancies contribute to electronic conductivity [1]. Tungsten oxide is an n-type semiconductor with energy gap in the range of 5.59 - 5.7 eV. Therefore, it is suitable for applications such as electrochromic, optochromic and gasochromic coatings for smart windows, information display and various sensors [2]. Many researchers have studied the sensor, magnetic and electric properties of WO_3 prepared by heat treatment, arc discharge, sol gel etc with different morphology and structure. These materals are studied in different forms such as nanowires, nanorods, dopped with transition metal, etc [3, 4, 5, 6] which are either in the isolated form or in mixed oxide form. These mixed oxide forms are non-stoichiometric forms with varying metal concentration.

In the present work, nanoform of zirconium (IV) tungstate is prepared in the stoichiometric form by chemical coprecipitation method. The material is well characterized using EDS, XRD, FTIR, SEM and HRTEM. UV spectrum is used to find the optical band gap.

2. EXPERIMENTAL

2.1 Preparation of zirconium (IV) tungstate in the nanoform

The nanoform of zirconium (IV) tungstate is synthesized by chemical coprecipitation method. In this, equimolar aqueous solutions of zirconium oxychloride and sodium tungstate in the volume ratio 1:2 is added to ethylene diamine tetra acetic acid template at a pH ~ 1.5 with constant stirring using a magnetic stirrer. The precipitate of zirconium (IV) tungstate is separated by filtration and washed with distilled water. It is then converted to the hydrogen form by immersing in 1M HCl.

2.2 Characterization of the material

EDS spectrum of the material was taken using JOEL Model JED-2300. X-ray diffractogram ($2\theta = 10 - 90°$) was obtained on XPERT-PRO powder diffractometer with Cu-Kα radiation. The FTIR spectrum was recorded using KBr wafer on the Thermo Nicolet FTIR model AVATAR 370 DTGS.SEM was taken from BJOEL Model JSM-6390LV.PHILIPS Model CM 200 was used to take the HRTEM. The absorption spectra were recorded at room temperature using SHIMADSU UV-2550 UV Visible spectrophoto-meter.

2.3 Results and Discussion

EDS spectrum shows the presence of zirconium and tungsten in the stichiometric proportion. The empirical formula calculated is $Zr_2W_3O_{13}$. The EDS spectrum is shown in figure 1. The X-ray diffractions of the nanoparticles of zirconium (IV) tungstate consist (figure 2) of cubic phases of ZrW_2O_8, agreeing with the JCPDS file No.89-6670 with small amount of isolated cubic zirconia (JCPDS file No.89-9069) and hexagonal tungsten oxide (JCPDS file No.82-2459).

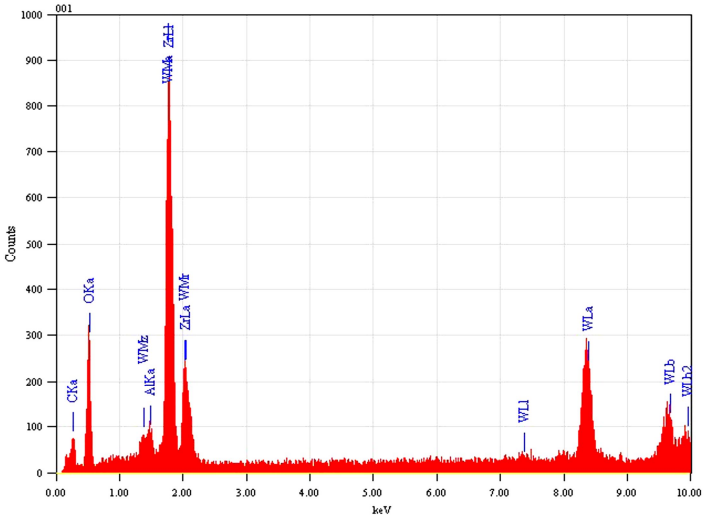

***Fig. 1** – EDS of zirconium (IV) tungstate*

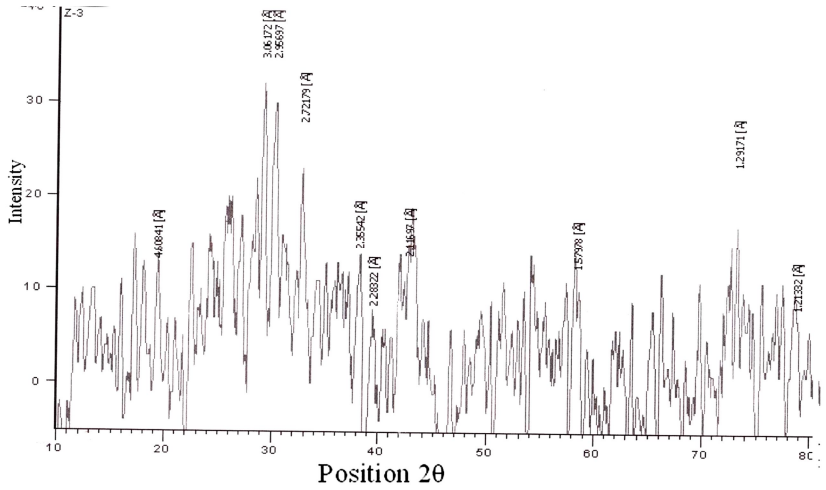

***Fig. 2** – XRD of zirconium (IV) tungstate*

FTIR spectrum (figure 3) shows bands due to water molecules/surface hydroxyl groups (~ 3415 cm^{-1}, 1637 cm^{-1}, 1380 cm^{-1}). Band in the region 837 cm is due to WO_4^2 species and at 711 cm^{-1} is due to W-O stretching vibration. Band in the region 493 cm^{-1} is due to Zr-O vibration [7, 8].

SEM and HRTEM shown in figure 4 and figure 5 are used to examine the morphology of the nanomaterial. The spherical nature of the particles is revealed from both the SEM and HRTEM. Further from HRTEM it is seen that the particles are less than 50 nm in size.

UV Spectrum shown in figure 6 gives information about excitonic or interband transition of nanocrystalline material. It shows absorption at 260 nm which corresponds to an energy gap of 4.77 eV. The fundamental absorption which corresponds to electron excitation from the valence band to the conduction band is used to determine the nature and the value of optical band gap. The relation between absoption coefficient (α) and incident photon energy ($h\nu$) is given by the Tauc relation,

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g),$$

where A is a constant, E_g is the band gap of the material, α, is the absorption coefficient and the exponent 'n' depends on the type of transition [9]. The value of band gap can be determined by plotting $(\alpha h\nu)^{1/n}$ versus $h\nu$ (figure 7) and extrapolating the straight line portion of the graph to $h\nu$ axis. The direct allowed band gap calculated is 4.48 eV. A more straight forward method of determining an approximate value of band gap regardless of band structure is by plotting the absorbance versus energy, and extrapolating to zero absorbance which in this case gives a band gap of 4.49 eV. Bulk ZrW_2O_8 is an insulating dielectric ceramic and the calculated band gap for α-phase is 2.81 eV and for γ-phase is 1.74 eV [10]. The increase in the band gap to 4.48 eV of this material is due to small size and the quantum confinement limiting. The quantum confinement effect is expected for semiconducting nanoparticles and the absorption edge will be shifted to high energy with decrease in particle size [11].

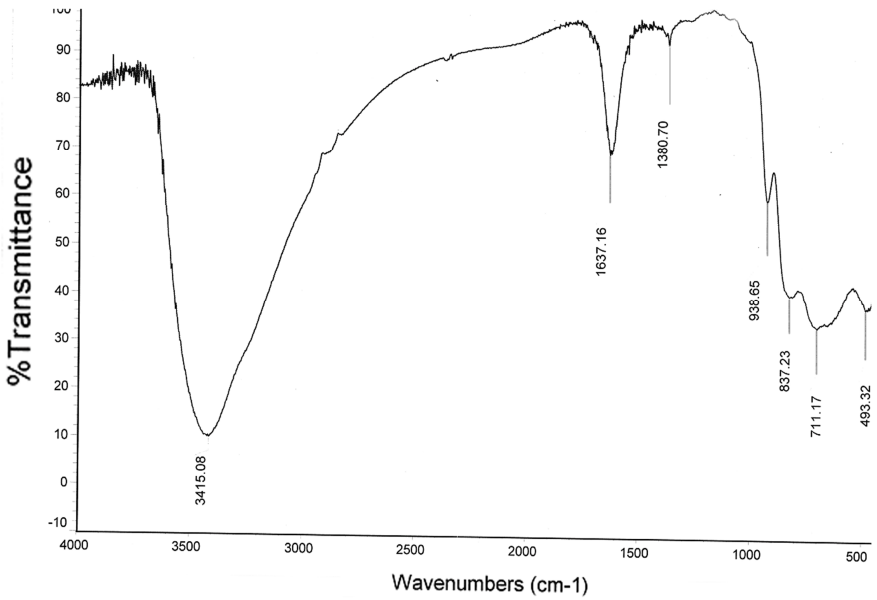

Fig. 3 – *FTIR of zirconium (IV) tungstate*

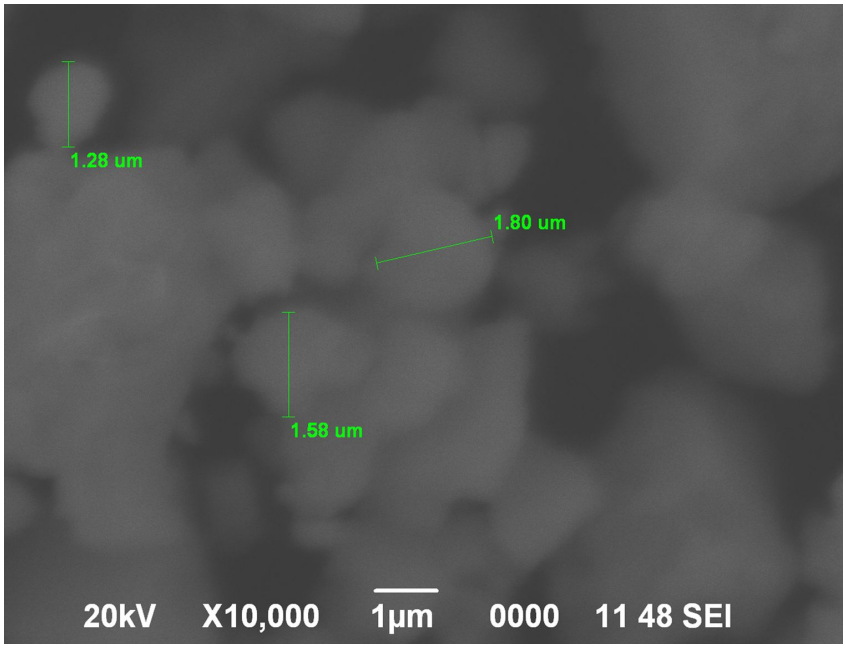

Fig. 4 – *SEM of zirconium (IV) tungstate*

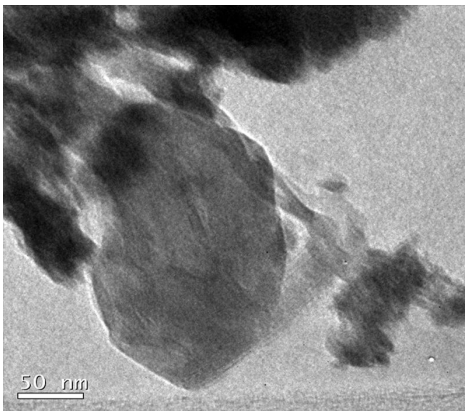

Fig. 5 – HRTEM of zirconium (IV) tungstate

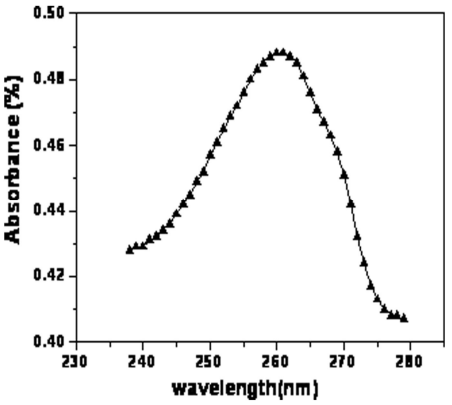

Fig. 6 – UV of zirconium (IV) tungstate

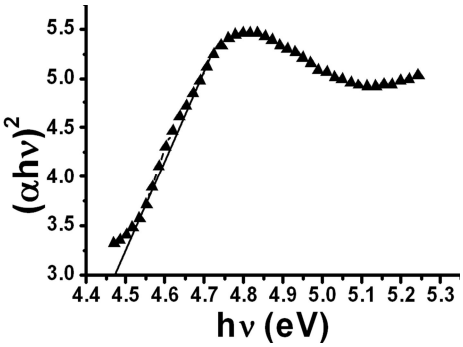

Fig. 7 – Plot of $(\alpha h\nu)^2$ versus hν

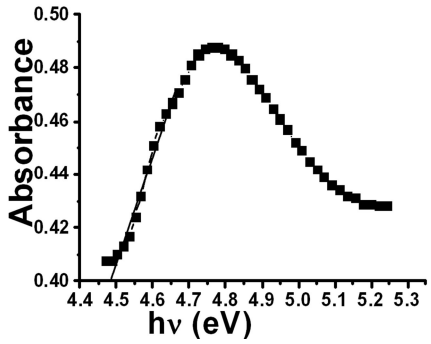

Fig. 8 – Absorbance versus energy spectrum

A band gap of 4.48 eV for nanocrystalline zirconium tungstate is due to ligand to metal charge transfer transition. The band gap also depends on the zirconia and tungstate content in the sample [12]. Also the energy gap is sensitive to particle size in 1 - 10 nm range for many semiconductors including zirconia and WO_3. In this size range, a large fraction of atoms residing at the surface alters the cluster electronic properties and hence the band gap value. Thus materials of desired band gap can be designed by changing the stoichiometry of Zr to W and thereby varying the particle size.

3. CONCLUSIONS

Zirconium (IV) tungstate is prepared in the nanoform by chemical coprecipitation method with high purity and homogeneity. XRD confirms the crystalline nature of the material. HRTEM and SEM reveal the spherical nature of the particles. Particle size is found to be < 50 nm from HRTEM. The energy gap determined by Tauc relation is 4.48 eV suggesting that it is a n-type semiconductor suitable for device applications which use metal oxide semiconductor such as gas sensors, UV sensors, etc.

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