RESEARCH ARTICLE

Simultaneous Structural and Optical Control of Tungsten Oxide (WO₃) Nanoparticles through Cobalt Doping for Super Conducting Applications

V. Hariharan^{1,2*}, B. Gnanavel³, V. Aroulmoji⁴, R. Sathiyapriya⁴, K. Prabakaran², C. Sekar⁵

¹Research and Development Centre, Bharathiar University, Coimbatore – 641 046, Tamilnadu, India ²PG & Research Department of Physics, Mahendra Arts and Science College, Kalipatti, Namakkal – 637 501 ⁴PG & Research Department of Physics, Chikkaiah Naicker College, Erode – 638 004, Tamilnadu, India ⁴Center for Research and Development, Mahendra Engineering College, Mallasamiduam, Namakkal-637 503 ⁵Department of Bioelectronics and Biosensors, Alagappa University, Karaikudi – 630 003, Tamilnadu, India

ABSTRACT: This paper present the synthesis and characterization of pure (WO₃) and doped (Co = 2 and 5 wt.%) in a facile microwave irradiation process, followed by the annealing process at 600°C in air for 6 h in order to know the suitability of the material for superconducting applications. The samples were characterized with powder X-ray diffraction; field emission scanning electron microscopy, UV-VIS diffusion reflectance spectroscopy, and photoluminescence spectroscopy along with, the corresponding magnetic behaviors of the products were analyzed through electron spin resonance spectroscopy and vibrational sample magnetometer. X-ray diffraction patterns showed both undoped and doped WO₃.H₂O crystallized with orthorhombic phase. The annealing effect showed that doped WO₃ (Co pprox 2 wt.%) formed with orthorhombic phase and the remaining products were found to be monoclinic phase (pure and Co pprox5 wt.%) indicating the role of dopant in determining the crystalline phase of the end products. The effect of doping on crystalline perfection of the samples was also monitored using power X-ray analysis. FE-SEM micrographs suggested that the dopants are able to influence the growth rate and morphology of the prepared nanopowders. UV-VIS-DRS spectroscopy was employed to determine the optical band gap of these samples and the results revealed the incorporation of dopant (Co ion) in the intermediate energy level in determining the optical band gap. Blue emissions were verified using PL at room temperature for the annealed samples when exited with 390 nm wavelength. The room temperature PL spectra reveal the distortions in WO42- tetrahedron structure due to microwave irradiation on the samples. The hysteresis loops curve through vibrational sample magnetometer for annealed samples suggest that the cobalt doped samples revealed the suitability of the samples for super conducting applications, In addition with the above the coexistence of dia and ferromagnetism also observed in cobalt doped samples suggests the role of dopant in fixing the magnetic behaviour of the resultant samples.

KEYWORDS: Tungsten oxide, Microwave irradiation, Cobalt doping, Nanoparticles

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1. INTRODUCTION

Nanosized materials have attracted great attention as a result of exhibiting unique surface to volume ratio. In particular, high surface area materials have been of great interest in a wide range of applications such as catalysis, chemical and biosensors, fuel cell electrodes and so forth [1]. As a well known inorganic oxide, WO₃ is a promising candidate for many applications such as electrochromic [2], photocatalytic [3], photoluminescent [4] and as a gas sensor device [5] due to their existence of various structural polymorphs and easily tunable oxygen content of the end product by varying the growth atmosphere. In fact, the optical and electrical properties of this compound strongly depend on size and morphology of the corresponding end product. Accordingly, the recent scenarios for many practical applications are mainly based on morphology and size distribution of the nanoparticles.

This can be done by varying the synthesis procedure and growth atmosphere which influence the morphology and size distribution of the nanoparticles.

On the other hand, dopants have offered relatively better morphology and high surface to volume ratio of the nanoscale materials. To date, following methods have been adopted to synthesis pure and doped WO₃ in the form of powders; vapor deposition [6], hydrothermal route [7], sol-gel [8], acidification method [9], electrospinning method [10], electrodeposition method [11] etc. However, the above mentioned techniques are more time consuming and cost effective. Great efforts are being taken to explore new synthesis methods to control the morphology and size distributions to satisfy certain applications. Recently, most of the works focused on the preparation of doped nanocrystalline WO₃ following their successful applications. Zhu et al. have prepared Cu-doped

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WO3 materials with photonic structures using combined sol-gel templating and calcinations method for the detection of various volatile organic gases. They suggested that the photonic crystal of Cu-doped WO₃ replica sensor has a much higher response as well as selectivity when compared to that of pure one due to their different morphologies [12]. Cheng et.al fabricated Zn-doped WO₃ thin films and found the enhanced behavior of Zn doped WO_3 with a suitable amount in the case of photocurrent and photo-activity [13]. Zamani et al. have synthesized Crdoped mesoporous WO₃ nanomaterial by chemical route for the detection of amines and tetra methyl amines. Finally they summarized the product showed low sensitivity to NH3 and TMA was detected more efficiently [14]. Xia et al. have prepared pure and Au-doped WO_3 nanopowders by a colloidal chemical method. They concluded that proper Au loading on WO₃ is suitable for the detection of NO_2 at relatively low temperature [15]. Kalidindi et al. fabricated Ti-doped WO₃ films on Si (100) wafers using sputtering technique and found that the electrical conductivity of Ti-doped samples at room temperature is more than that of pure sample [16].

With this basis, bear in mind the role of dopants in nanocrystalline WO_3 . H_2O and WO_3 , we have been able to synthesis cobalt doped WO_3 . H_2O nanopowders with different W/CO (0.02 and 0.05) ratios using simple, efficient straight forward microwave irradiation method. The procedure reported here, to the best of our knowledge, is the first demonstration in the synthesis of cobalt doped WO_3 . H_2O nanopowders. In the microwave irradiation method, time required for the synthesis was

around 10 min only and the reaction process was also very simple.

2. EXPERIMENTAL DETAILS

 $W_{1-x}Co_xO_3$ (x \approx 0, 0.02 and 0.05) nanopowders were prepared by microwave irradiation method at room temperature [17]. The followed experimental procedure is described as below: Analytical grade of 4.98g of tungstic acid (H₂WO₄) was dissolved in 20 mL of sodium hydroxide (NaOH) with one molar ratio. The resultant solution was stirred for 20 min. This resulted in yellow colored hydrated sodium tungstate solution due to proton exchange protocol process [18]. Subsequently, 2 wt.% and 5 wt.% of cobalt hexa chloride (CoCl₂.6H₂O) was mixed along with the total amount of tungstic acid which dissolved into 20 mL of deionized water. Both the solution was mixed slowly together and the final solution was stirred again 20 min. The pH of the solution was found to be neutral (\approx 7.0) and it was adjusted up to 1 by adding few drops of HCl because it can act as a precipitating agent and also medium for the product to have desired morphology [19]. In addition with that above solution 5 ml double distilled water (i.e. 50 vol. % of precursor solution) was added with the above solution in order to respond to microwave quickly. In the sequence, the final mixture was transferred into a microwave oven (2.45GHz and maximum power of 900 W). The conditions into microwave oven were kept into 180 W for 10 min. After microwave treatment the yellow precipitate was finally collected. The obtained powders were annealed in a tubular furnace at 600°C for 6 h in air in order to remove the sub products and to improve the crystallanity.



Fig. 1 Schematic illustration of synthesis of cobalt doped WO₃.H₂O in microwave atmosphere

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3. RESULTS AND DISCUSSION 3.1. Powder XRD Analysis

Fig. 2a shows the powder XRD spectra of resultant pure and cobalt doped WO₃.H₂O nanopowders. From the fig.2, it is confirmed the formation of WO₃.H₂O with high crystalline nature under orthorhombic structure in accordance with JCPDS card no: 43-0679. There is a small shift in smaller Bragg angle side for Co-doped (≈ 0.02) sample indicating the incorporation of Co ion in WO₃.H₂O crystalline lattice site and it is due to the less atomic radius of Co ion (1.16 pm) compared to that of tungsten ion (1.5 pm). Additionally, in the case of Co-doped (≈ 0.05) sample it retains its original current phase due to the fact that: i) the complete replacement of tungsten ion by cobalt ion because of its considerable atomic radius ii) can be the initial concentration for the formation of cobalt based secondary phase. Fig. 2b shows the variation of crystallite size using Debye scherrer's formula as a function of cobalt concentration along (020) and (111) planes. The re attainment of crystallite site for cobalt (≈ 0.05) sample nearly to the value of pure sample along (020) plane clearly resembled the incorporation of Co ion in WO4²⁻ (020) tetrahedron structure not in water molecule site (111) which is another confirmation for the attainment of original parent phase nature.



Fig. 2: (a) Representative XRD patterns of pure and Co-doped WO₃.H₂O (b) Variation of crystallite size (nm) as a function of cobalt concentration of WO₃.H₂O



Fig. 3: The representations show how a cobalt ion incorporating in the unit cell of WO₃.H₂O (orthorhombic) crystalline atmosphere along (002) plane



Fig. 4: The representations show how a cobalt ion incorporating in the unit cell of WO₃ (Monoclinic) crystalline atmosphere along (002) plane

3.2. Microstructural Analysis (FE-SEM)

To understand the detailed morphological characteristics, FE-SEM was employed for the resultant as prepared and annealed nanopowders of pure and Co \approx 5 wt.% doped tungsten oxides that lie on a aluminium substrates are shown in Fig. 5. Figs. 5a and c show the FE-SEM images of pure and doped (Co \approx 5 wt.%) WO₃.H₂O nanopowders. Fig. 6a indicates the formation of platelet like morphology which overlapping on one another in the order of 0.1-0.29 µm in longer axis and 0.1-0.22 µm in shorter axis; moreover the white appearance in FE-SEM is due to charging phenomenon. Close examination on this image revealed that plates lying parallel to the surface of the

substrate and normal to surface are rare that clearly indicating the growth along **b** axis corresponding to (020) plane. In addition with that above phenomenon edge effects were also arised due to charge transfer between 'W' and 'O' ions present in the plates that has been marked in the corresponding fig. 2a. Conversely, particles prepared using cobalt (\approx 5 wt.%) as dopant suggested the decrease in particles size may be attributed to the faster nucleation process under the same conditions resulting decrease in particle size which is in agreement with the powder XRD analysis.

Figs. 6c and d show the micrographs of annealed pure and doped (Co \approx 5 wt.%) WO₃₋₈ nanopowders. Pure sample

revealed the formation of large quantity of particles with agglomerate and poly disperse nature that appears sheet like morphology of the order of 0.23-0.37 μm in lateral axis and 0.047-0.066 µm in longitudinal axis. As it can be seen from the fig. 6c, the agglomeration is due to fast and rapid collision between the particles during the recrystallization process from $WO_3.H_2O$ to $WO_{3-\delta}$ through annealing. On the other hand fig. 6d shows the formation of cubic like particles with the dimensions of the order of 0.188-0.37 μ m range for cobalt (Co \approx 5 wt. %) doped sample. The attainment of highly uniform nature than the pure sample illustrated the role of dopant in modifying the morphology of the end product. Moreover, it can be seen from the fig. 6d that oxygen content also play an important role in fixing the condition for morphology, because the percentage of oxygen in cobalt doped sample is more than that of pure sample. Even though it is impossible to measure the amount of oxygen present in the compounds, the variation in morphology clearly exhibits the difference in adsorption rate of oxygen from air during the annealing process since the presence of excess of holes (cobalt ion) present in the crystalline medium of WO42- tetrahedron structure.

3.3. UV-VIS Diffusion Reflectance Analysis

The observed reflectance phenomenon in UV – visible region of pure and cobalt doped as prepared and annealed samples are shown in Fig. 6. There are strong and wide reflectance peaks between 500-650 nm implies that the prepared nanoparticles can display optical conductivity in the visible region. The maximum reflectance intensities have obvious blue shifts (as prepared samples) and red shifts (annealed samples) within the spectral region 500-650 nm. The band gap energies for all the samples may be determined by using Kubelka-Munk (K-M model and its corresponding relation is given below.

$$\frac{K}{S} = \frac{\left(1 - R_{\infty}\right)^2}{2R_{\infty}} = F(R_{\infty})$$

 $F(R_{\ensuremath{\mathbb{Z}}})$ is the so called remission or Kubelka – Munk function, where

A graph is plotted between $[F(R_{\infty})h\nu]^2$ Vs $h\nu$ and the intercept value is the band gap energy Eg of the individual sample [20]. The band gap energies as a function of cobalt concentration were found to be 2.81 (W0₃H₂O), 3.12 (W_{0.98}Co_{0.02}O₃.H₂O) and 3.19 eV (W_{0.95}Co_{0.05}O₃.H₂O) respectively. On the contrary for annealed samples the band gap energies in the identical doping conditions to be 3.52, 3.19 and 3.06 eV respectively.

$$R_{\infty} = rac{R_{sample}}{R_{std.}}$$

We propose the following to explain the above controversy findings between as prepared and annealed samples from the reflectance spectra. The increase in E_g (as prepared) can be explained using Burstein-Moss (BM) [21] effect in which the lowest states in the conduction band are blocked and the allowed transitions can take place only to energies above Fermi level to unblocked valance level (between W^{6+} to Co^{2+}) due to the introduction of Co²⁺ ion in the intermediate energy state. As a consequence, the introduction of Co²⁺ in tungsten site is effective to generate oxygen vacancy by shifting the position of H₂O molecule and weakened the W-O bond inside the crystalline structure of WO₃.H₂O and hence increases the carrier density which leads to increase in optical band gap energy (Fig.6a). On the other hand, in the case of annealed samples, the decrease in band gap energies as a function of cobalt concentration is due to the fact that exchange interaction between the band electrons of d_{x2-y2} and d_{xy} orbital of tungsten to the d_{x2-y2} and d_{z2} orbital of Co²⁺ ion. It gives rise to the positive correction in the valance band and leads to narrowing the band gap (Fig. 6b).

Fig. 6.2 illustrates the PL spectra of pure and doped tungsten oxides (annealed) at room temperature. In this present case, the attained PL results indicated that the variation in broad intense peaks related with both structural disorder and order happened into the WO₃ octahedral group due to the distortions caused by the cobalt ion into the W-O crystal lattice which is in agreement with the XRD results. The most intense broader peak for pure WO₃ nanoparticles clearly indicating the structural disorder of the WO₃ crystalline lattice than Co ≈ 0.02 doped sample.

The reason we believed behind this is due to the faster nucleation growth could be taken place because of non uniform interaction or absorption of microwave radiation of tungsten ion present in W0₃.H₂O octahedral groups during the conversion of Na₂WO₄.2H₂O into WO₃.H₂O. Hence, it is identified that PL is a sensitive technique to check the structural disorder in the lattice and/or the presence of defects due to the foreign atom on crystalline WO₃ nanoparticles. Moreover the decrease in intensity for Co \approx 0.02 doped sample probably may occur due to the structural order (monoclinic to orthorhombic) occurred in the crystalline lattice and the approximate original parent intensity reproduced for Co \approx 0.05 cases which are in concurrence with the XRD spectra.



Figs. 5a and b. FE-SEM images of WO₃.H₂O a) Pure b) Co \approx 5 wt. % doped and Figs. 6c and d of WO₃ c) Pure d) Co \approx 5 wt. % doped





Fig. 6a Schematic illustration of the creation of oxygen vacancy due to the incorporation of coblat ion in WO4²⁻ tetrahedron structure





Fig. 6.1 K-M model for pure and cobalt doped samples (c) as prepared samples (d) annealed samples Photo luminescence analysis







Fig. 7 Room temperature hysteresis loops of WO _3- $\ensuremath{\mathbbm {O}}$ (a) pure (b) Co-2wt.% (c) Co-5wt.%

In all the samples blue emissions originated at ambient temperature may be connected with several factors, the variation in angle between O-W-O due to the existence of Co^{2+} ion in the crystalline lattice, then electronic transitions between localized energy levels between the blocked conduction band and unblocked valance band which are able to influence the final reply of PL emission in the visible region and also it may be attributed to the defects or oxygen vacancy during faster nucleation growth during the formation of WO₃.H₂O in microwave atmosphere. The blue emissions characterized by PL emission for WO₃ based nanostructures are well agreement with the literature reports [22]

3.4. Magnetic behavior (VSM)

Fig. 9 describes the hysteresis loops measured at room temperature of pure and cobalt doped WO3-12 nanopowders. The measurements were performed on annealed samples. It is well known that, stoichiometric tungsten oxide will exhibit dia magnetic behavior at room temperature. Interestingly, The present parent compound exhibits the co existence of both dia and ferromagnetic behavior [23]. It is attributed to the fact that the in homogeneity in holes density due to the lack of oxygen $(W_{17}O_{47})$ which gives rise to the unpaired electrons in holes rich region enhanced the ferromagnetic behavior in addition with the dia magnetic nature. Subsequently, it can seen from the cobalt doped samples cobalt doped samples which are having light excess of oxygen than pure sample could enhance the diamagnetic behavior at negative magnetic field due to its stoichiometric oxygen content (W0.98CO0.02O3 and W0.95CO0.05O3). These unexpected results suggest that the cobalt doped samples try to persist well into the superconducting or diamagnetic state, namely the coexistence of dia and ferromagnetism in the hole rich clusters. The enhancement of dia magnetic behavior in cobalt doped samples with respect to the relative suppression of ferro magnetic behavior indicate the role of cobalt in fixing the oxygen content and magnetic behavior of the end product.

4. CONCLUSION

Cobalt doped WO₃.H₂O has been successfully synthesized by efficient microwave irradiation method. The crystalline phase of all the as prepared samples was orthorhombic structure. In the case of annealed samples pure and Co≈0.05 doped samples were found to be monoclinc and for Co≈0.02 became orthorhombic structure. Hence, these unexpected results suggested the role of cobalt at higher concentrations in fixing the oxygen content and to tune the crystalline phase of the end product. UV-VIS-DRS studies displayed that the as prepared samples having more optical conductivity than that of the annealed samples. Moreover, it additionally recommends that the required optical conductivity can be attained by doping elements itself instead of annealing process. Photo luminescence spectra clearly indicating that the pure and Cobalt (≈ 0.05) having more luminescence property than that of Co ≈ 0.02 sample due to its structural symmetric nature which is in agreement with the powder XRD results. The interesting results from hysteresis loops

suggested that the cobalt doped samples try to persist well into the superconducting or diamagnetic state than pure sample.

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