

Exploration of structural, optical, and magnetic properties of Cr doped MnWO₄ nano flakes

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Abstract:

The structural, optical, and magnetic properties of pristine and Chromium (Cr) doped Manganese Tungstate (MnWO₄) nanoflakes prepared by precipitation process are investigated and reported. The tetragonal structure of pure and Cr doped MnWO₄ compounds is shown by X-Ray Diffraction (XRD) studies. The Scherrer equation was used to compute the crystallite size of the flakes. Fourier Transform Infrared (FTIR) spectroscopy was used to analyze the appearance of metal oxide vibrations (Pb, W, O, and Cr). The creation of a double taper-like structure in MnWO₄ and the morphological alterations generated by Cr ions in the doped lead tungstate samples are confirmed by electron microscope pictures. Magnetization investigations show that the paramagnetic character of the pure compound and carrier generated exchange interactions, resulting in an anti-ferromagnetic phase transition in Cr doped MnWO₄ samples with greater concentrations. According to the findings, the tunability of magnetism in the MnWO₄ system at room temperature in relation to dopant concentration leads to the material being used to fabricate magneto-optical and electrical devices.

Key words: MnWO₄, chemical precipitation, Nano flakes, optical bandgap, Magnetism

1. Introduction

Manganese oxide-based compounds have grown in popularity, and their catalytic activity is comparable to that of Platinum group metals [PGM] based versions. Furthermore, Mn is the earth's crust's 12th most prevalent element. According to a recent assessment, the inherent applicability of Mn-based oxygen cathodes, as well as minor tweaks to their individual forms, structures, and exposed facets, play a critical influence in catalytic output [1,2,3]. Tuning the morphology of manganese oxide was a hot topic of research [4] exploring the function of altering precursor ratios to create morphologies from tremella to nanobelts, On the other hand, changing the solvent composition to obtain nanoparticles, nanorods, and nanoflakes.

MnWO₄ is a remarkable multiferroic oxide with a spiral spin structure that induces ferroelectricity [5]. One of the benefits of studying MnWO₄ is that it only has one type of magnetic ion (Mn²⁺), whereas, other multiferroic oxides typically contain many magnetic ions, making investigation of their magnetic characteristics more difficult. We have the electromagnetic coupling behavior thanks to the single magnetic ion advantage, and we can perform straightforward evaluations of magnetic field dependency and SOC effects. MnWO₄ has a wolframite crystal structure, which includes WO₆ octahedra. [6,7]. It has many anti ferromagnetic states such as (first phase appears below TN3 ≈ 13.5 K. Successive magnetic phase transitions occur at TN2 ≈ 12.5 K and TN1 ≈ 6.5–8 K, forming 3 different antiferromagnetically ordered phases: AF1 (T ≤ TN1), AF2 (TN1 ≤ T ≤ TN2), and AF3 (TN2 ≤ T ≤ TN3) [14, 15]. Neutron scattering investigations have identified AF1 as having a collinear up-up-down-down spin structure, AF2 as having a non-collinear spiral spin structure, and AF3 as having a sinusoidal collinear spin structure [8,9]. At AF2, spontaneous electric polarization occurs, implying that the non-collinear spiral structure is the source of MnWO₄'s induced ferroelectricity.

The optical and magnetic characteristics of MnWO₄ are the subject of this study. Under the Néel temperature of 13.5 K, the magnetic structure of MnWO₄ is reported to be frustrated. As a result of this dissatisfaction, a number of unusual magnetic structures arise. The structure is an antiferromagnet with an up-up-down–down structure along an axis at low temperatures. Above 8 K, the magnetic ordering transforms into a helical spin density wave with a long period. The spiral magnetic structure is expected to produce a polarization perpendicular to the

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spin rotation axis and an incommensurate wave vector, according to the theory presented by Mostovoy [10]. As a result of that MnWO_4 has a spiral magnetic structure and is expected to be ferroelectric and antiferromagnetic.

The wolframite-type structure of metal tungstate (A=bivalent ions like Fe, Mn, Co, Ni, and Zn) crystallizes. Wolframite crystal structure has distorted WO_6 motifs share oxygen atoms at the edges to form zigzag chains along the c axis, and bi-valent TM ions fill in the octahedrons by corner sharing O with WO_6 clusters to form zigzag chains. Due to edge sharing, the two forms of zigzag chains alternately stack along an axis. Metal tungstate materials have piqued the curiosity of scientists in a variety of domains, including photonics and photo electronics [11,12]. Manganese tungstate's optical (phonon) characteristics, electronic structure, [13] conductivity [14], magnetic properties [15] were extensively studied.

Hence in the present work, the pure and Cr doped MnWO_4 is synthesized by precipitation process and their structural, optical and magnetic properties are studied.

2. Experimental**2.1 Starting materials**

Analytical grade of (>99.0 % pure) Manganese acetate, Sodium tungstate tri hydrate, Chromium nitrate hexa hydrate was supplied by M/s. Alfa Acer (Germany) and Fluka Chemie AG, Buchs, Switzerland.

2.2 Synthesis of MnWO_4 by precipitation process

Chemical precipitation was used to make nanocrystalline MnWO_4 powders. In appropriate amounts of DI water, stoichiometric amounts of Mn acetate and sodium tungstate were dissolved separately. Dropwise, using a burette, sodium tungstate solution was added to Mn acetate solution. The solution was agitated continuously for 5 hours, after which the precipitate was aged for 24 hours before being washed with DI, Ethanol, and Acetone using centrifugation. Following that, the precipitate was dispersed in acetone and ultrasonicated for 15 minutes. The product was then allowed to dry for 24 hours at room temperature. The powders were then crushed and stored at 120°C for 12 hours. Finally, the final product was calcined for 4 hours at 500 degrees Celsius to obtain nanocrystalline MnWO_4 molecules. This de-agglomeration phase was repeated once more, and the powder was then dried for roughly an hour under an infrared (IR) lamp [16].

2.3 Synthesis of MnWO₄ doped with Chromium

Using a similar chemical precipitation approach, Cr doped with MnWO₄ was synthesized. This process was quite similar to the one used to make MnWO₄. However, Mn acetate solution was mixed with a stoichiometric ration of Cr nitrate solution. The dopant concentration (Cr) was chosen to correspond to that of the dopants (Cr-5%, Cr-10%, Cr-15% and Cr-20%)

2.4 Characterizations

Phase identification done by powder x-ray diffraction through PAN Analytical (Model: X'Pert PRO) diffractometer generating Cu-Ka1 radiation of wavelength 1.5406 Å. Fourier Transform Infra-Red (FTIR) spectra are recorded using Shimadzu spectrograph (Model: 8700) over a range between 4,000 and 400 cm⁻¹ at a scan rate of 20 cm⁻¹ per second. Raman spectra are recorded in the range 50–1,000 cm⁻¹ using a confocal micro-Raman microscope (Renishaw inVia Reflex) with 0.6 mW power of Ar ion laser source and excitation wavelength of 488 nm. Surface morphology and elemental composition is analyzed using High Resolution Scanning Electron Microscope (HR-SEM) instrument of FEI Quanta FEG 200 and Energy Dispersive X-ray Analysis (EDAX) thermo Nicolet respectively, Room temperature M–H curve parameters measurements are carried out using Vibrating Sample Magnetometer (Lakeshore VSM 7410)

3. RESULTS AND DISCUSSION

3.1 PHASE IDENTIFICATION AND ANALYSIS

Figure 1(a&b) shows the XRD of MnWO₄ samples and Cr doped MnWO₄ (Cr-5%, 10%, 15% and 20%) samples. The tetragonal structure of MnWO₄ compound with space group P 2/c (JCPDS card no:13-0434; a= 4.82900 b=5.75900; c=4.99800; a/b=0.83851; c/b=0.86786) is indexed to all detected diffraction peaks and relative intensities. As the dopant concentration increased, the peak broadened, indicating that the Cr ion interacts with the host lattice. The computed average crystallite size of the produced compounds is around 15 nm, with a modest drop in crystallite size as the Cr content increases. This could be related to ionic radius differences and microstructural variability. The Scherrer formula, as shown in equation 2, is used to find the average crystallite size.

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3.1)$$

Where, K = shape factor, β = Full width half maximum,

λ = wavelength of Cu radiation (1.5418 Å), θ = Bragg angle (degree) [17].

The calculated crystallite sizes are in the sub-micron range 48 nm for pure MnWO₄ and then crystallite size is decreasing upon dopant concentration (Cr-5%= 42nm, Cr-10%=38nm, Cr-15% = 40). Then there is slight increase in crystal size (46nm). This is because of the ionic radii difference of the elements (Mn, W, Cr and O). Hence, the XRD confirms the formation of single-phase compounds, even addition of dopant does not induce structural or phase change in the host lattice.

3.2 FTIR Studies.

Pure and Cr doped MnWO₄ compounds' FTIR spectra are shown (Fig. 2a and 2b). The band detected at 3410 cm⁻¹ is suggestive of vibration of the O–H bond of the surface hydration, according to the spectra. The deformation (H–O–H) vibration of surface hydroxyl group is represented by the band at 1568 cm⁻¹. The stretching vibrations (symmetric and asymmetric) of the W–O bond. The absorption peaks at 880 cm⁻¹ and 808 cm⁻¹, respectively. The asymmetrical stretching vibrations of the W–O bond in the (W₂O₄) are shown by the strong band at 808 cm⁻¹, whereas the presence of stretching vibrations of the Mn–O bond is indicated by the strong band at 586 cm⁻¹. The existence of stretching vibrations in the Mn–O–Mn bond caused the band to appear at 454 cm⁻¹ [16-17].

3.3 Raman analysis.

The Raman modes at 880, 698, 545, 380, 330, 258, 202, and 127 cm⁻¹ are detected for MnWO₄ compounds (Fig.3), which are produced through different ways of absorption of different translational levels [6]. The significant symmetric stretching of the WO₂ group in the MnWO₄ caused a very strong band to form in the 880 cm⁻¹ mode. The presence of mild (asymmetric and symmetric) stretching vibration modes of the W–O–W bond is shown by the bands at 698 cm⁻¹ [18]. Stretching vibration of Mn–O is responsible for the peak at 545 cm⁻¹. The occurrence of symmetric stretching of W–O–W is indicated by the band at 380 cm⁻¹. The 330 cm⁻¹ band confirms W–O–W scissoring. The bending mode of [WO₆] is shown by a faint band at 202

cm^{-1} . The tungsten translational mode is represented by the bands at 127 cm^{-1} [18-19]. As a result, the fluctuation in raman intensity implies that the lattice vibrations have been perturbed by the local perturbation.

3.4. Surface morphology and Elemental analysis.

Figure (4a, b, and c) shows HRSEM images of pure, Cr-5% and Cr-15%. The size of the particle is reduced and the particles are agglomerated together before forming a flake-like morphology. The size reduction is due to the first distortion created around the Cr atom inside the Mn-W-O lattice [17, 20]. This could be due to the fact that particulate systems tend to agglomerate or develop into larger particles to reduce their surface free energy. EDAX analysis is used to confirm the existence of dopants in a MnWO_4 lattice. Only the elements Mn, W, and O are present in the pure sample, according to the spectra. The presence of additional Cr peaks and the absence of other contaminants are plainly seen in the doped sample.

3.5. Optical studies.

Figure 5 shows the UV-visible optical absorption spectra of pure and Cr doped materials. A high optical absorption peak was discovered about 260 nm, as seen in the image. The transition between the 2p oxygen state and the 3d Mn state determines the optical absorbance of MnWO_4 . There is a minimal fluctuation in the absorbance intensity when Cr ions are added to the host lattice, which increases as the function of dopant concentration grows. This means that Cr doping in MnWO_4 causes significant lattice disruption. Various factors, such as oxygen shortage, surface roughness, and impurity centres, are likely to influence optical absorbance. When Cr-5 percent is injected into the lattice, the absorption values climb to their maximum, as seen in the figure. This could be owing to the dopant-induced charge carriers. Furthermore, as the amount of Cr increases, the position of the optical absorption spectra shifts towards the lower wavelength. The Burstein–Moss effect [20] could explain the observed minor blue shift. With an increase in charge carriers, the Fermi level blends into the conduction band, and the optical band gap widens [21].

The optical energy band gap of MnWO_4 compounds (Fig. 6) was calculated using a Tauc plot and found to be 2.6 eV. The band gap increased slightly as the dopant concentration increased (2.67 eV, 2.73 eV and 2.8 eV). This could be owing to the quantum confinement

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effect, in which the addition of a dopant reduces the crystallite size while increasing its bandgap.

3.6. Magnetic studies.

Figure 7 shows the M-H curves of pure and Cr doped MnWO_4 compounds at room temperature. The anti-ferromagnetic signature is readily visible in all of the produced compounds based on magnetization experiments. In general, metal tungstates are paramagnetic, but all of the compounds produced in this study are antiferromagnetic; it has already been shown that MnWO_4 compounds containing the magnetic cation Mn^{2+} are antiferromagnetic materials [20,21&22]. In general, the magnetic properties of compounds are influenced by vacancy, defects, and surface shape. There may be an interaction between Cr's 3d spin states, Mn's 3d states, and W's 4f state when the amount of Cr in the host lattice grows. The interaction of Cr with the Mn-W-O lattice plays a bigger influence in magnetic properties. Similarly, the presence of Cr ions causes oxygen vacancies, which function as double electron donors, potentially altering the magnetic properties of the material.

4. Conclusions

A simple chemical precipitation approach was used to successfully synthesize pure and Cr doped MnWO_4 compounds. XRD was used to establish the phase identification and monoclinic structure of the produced compounds. FTIR and Raman spectra were used to investigate metal oxide vibrations and local structural disorder characteristics. HRSEM revealed poly-dispersed and agglomeration particles. The band gap corresponding to the significant optical absorption around 260 nm was computed. Magnetic tests at room temperature revealed that all of the produced compounds have an antiferromagnetic signature

Reference

- 1]. Vincent Hardy, Christophe Payen, Françoise Damay, Lynda Meddar, Michaël Josse and Gilles Andre, Phase transitions and magnetic structures in $\text{MnW}_{1-x}\text{MoxO}_4$ compounds ($x \leq 0.2$) J. Phys.: Condens. Matter 28 (2016), 336003.
- [2]. V Felea, P Lemmens, S Yasin, S Zherlitsyn, K Y Choi, C T Lin and C Payen, J. Phys.: Condens. Matter 23 (2011), 216001.

- [3]. Feihui Li, Xia yang, Xub, Jialei, Huo, Wei Wang, A simple synthesis of MnWO_4 nanoparticles as a novel energy storage material, *Materials Chemistry and Physics*, Vol. 167, (2015), pp.22-27.
- [4]. O Heyer, N Hollmann, I Klassen, S Jodlauk, L Bohaty, P Becker, J A Mydosh, T Lorenz and D Khomskii, A new multiferroic material: MnWO_4 , *J. Phys.: Condens. Matter* 18 (2006) L471–L475
- [5]. S Muthamizh, R Suresh, K Giribabu, R Manigandan, S Praveen Kumar, S Munusamy, V Narayanan MnWO_4 nanocapsules: synthesis, characterization and its electrochemical sensing property, *J. Alloys and Compounds* 619 (2015) 601–609.
- [6]. Lynda Meddar, Michael Josse, Philippe Deniard, Carole La, Gilles Andre, Francoise Damay, Vaclav Petricek, Stephane Jobic, Myung-Hwan Whangbo, Mario Maglione, and Christophe Payen, *Chem. Mater.* 21 (2009), 5203–5214.
- [7] L. Zhang, C. Lu, Y. Wang, Y. Cheng, “Hydrothermal synthesis and characterization of MnWO_4 nanoplates and their ionic conductivity” *Mater. Chem. Phys.* 103 (2007) 433.
- [8] W. Tong, L. Li, W. Hu, T. Yan, X. Guan, G. Li, J. “Systematic Control of Monoclinic CdWO_4 Nanophase for Optimum Photocatalytic Activity”, *Phys. Chem. C* 114 (2010) 15298.
- [9] S.J. Chen, X.T. Chen, Z. Xue, J.H. Zhou, J. Li, J.M. Hong, X.Z. You, “Morphology control of MnWO_4 nanocrystals by a solvothermal route” *J. Mater. Chem.* 13 (2003) 1132.
- [10] S. Lei, K. Tang, Z. Fang, Y. Huang, H. Zheng, “Synthesis of MnWO_4 nanofibers by a surfactant-assisted complexation–precipitation approach and control of morphology” *Nanotechnology* 16 (2005) 2407.
- [11] W.B. Hu, X.L. Nie, Y.Zh. Mi, “Controlled synthesis and structure characterization of nanostructured MnWO_4 ”, *Mater. Charact.* 61 (2010) 85.
- [12] Y. Xing, S. Song, J. Feng, Y. Lei, M. Li, H. Zhang, “Microemulsion-mediated solvothermal synthesis and photoluminescent property of 3D flowerlike MnWO_4 micro/nanocomposite structure, *Solid State Sci.* 10 (2008) 1299.

- [13] Y.X. Zhou, Q. Zhang, J.Y. Gong, S.H. Yu, “Surfactant-Assisted Hydrothermal Synthesis and Magnetic Properties of Urchin-like MnWO_4 Microspheres” *J. Phys. Chem. C* 112 (2008) 112.
- [14] S. Thongtem, S. Wannapop, T. Thongtem, “Characterization of MnWO_4 with flower-like clusters produced using spray pyrolysis” *Trans. Nonferrous Met. Soc. China* 19, (2009) s100.
- [15]. Lynda Meddar, Michael Josse, Mario Maglione, Amandine Guiet, Carole La, Philippe Deniard, Rodolphe Decourt, Changhoon Lee, Chuan Tian, Stephane Jobic, Myung-Hwan Whangbo and Christophe Payen, *In. Chem. Mater.* 24 (2012), 353–360.
- [16]. Shingo Toyoda, Manfred Fiebig, Lea Forster, Taka-hisa Arima, Yoshinori Tokura & Naoki Ogawa, “Writing of strain-controlled multiferroic ribbons into MnWO_4 , *Nature Communications*, Vol.12, pp 6199 (2021)
- [17]. Ptak, M; Maczka, M; Hermanowicz, K; Pikul, A; Hanuza, J, Temperature-dependent Raman and IR studies of multiferroic MnWO_4 doped with Ni^{2+} ions” *Spectrochimica Acta Part A* 86 (2012) 85–92.
- [18]. Wenming Tong, Liping Li, Wanbiao Hu, Tingjiang Yan, Xiangfeng Guan, and Guangshe Li, “Kinetic Control of MnWO_4 Nanoparticles for Tailored Structural Properties” *J. Solid State Chem.* 184 (2011) 2446–2457.
- [19]. Mirosław Mączka, Maciej Ptak, Adam Pikul, Leszek Kępiński, Paweł E. Tomaszewski, Jerzy Hanuza “Phonon and magnetic properties of nanocrystalline MnWO_4 prepared by hydrothermal method” *Vibrational Spectroscopy* 58 (2012) 163–168.
- [20] Mehdi Rahimi Nasrabadi¹, Mohammad Eghbali Arani, “The effect of sugars on the morphology of MnWO_4 nanoparticles, and evaluating the product as photocatalysts” *J Mater Sci: Mater Electron* 28, (2017), 15239–15245.
- [21] Pascaline Patureau, Michael Josse, Remi Dessapt, Jean-Yves Mevellec, Florence Porcher, Mario Maglione, Philippe Deniard and Christophe Payen, “Effect of Nonmagnetic Substituents Mg and Zn on the Phase Competition in the Multiferroic Antiferromagnet MnWO_4 ” *Inorg. Chem.* 54 (2015), 10623–10631.

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[22] Yu-Xue Zhou, Qiao Zhang, Jun-Yan Gong, and Shu-Hong Yu, “Fast Production of Self-Assembled Hierarchical α -Fe₂O₃ Nanoarchitectures” J. Phys. Chem. C, 112 (2008), 13383–13389.