Research Article

Effect of Electron Beam Irradiation on Optical Properties of Manganese Tungstate Nanoparticles

K. P. Priyanka, 1 N. Aloysius Sabu, 1 Anu Tresa Sunny, 2 P. A. Sheena, 3 and Thomas Varghese 1

1 Department of Physics, Nanoscience Research Centre (NSRC), Nirmala College, Muvattupuzha, Kerala 686 661, India
2 School of Chemical Sciences, M.G. University, Kottayam 686560, India
3 M.E.S. Asmabi College, P. Vemballur, Kerala 680671, India

Correspondence should be addressed to Thomas Varghese; nanoncm@gmail.com

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Manganese tungstate (MnWO₄) nanoparticles were synthesized at room temperature by chemical precipitation method. The effect of high energy electron beam (EB) irradiation on the optical properties of MnWO₄ nanoparticles was investigated. The absorption spectra, photoluminescence intensity, and Raman bands of the irradiated samples were modified, which has been attributed to defects and particle size variation. The present investigation found that the beam irradiation is a new and efficient method to enhance the optical absorption performance and photoactivity of MnWO₄ nanoparticles.

1. Introduction

Nanostructured tungstate materials have aroused much interest because of their luminescence behaviour, structural properties, and potential applications. MnWO₄ has bulk electrical conductivity, relatively low melting point, novel magnetic property, and photocatalytic property [1, 2]. The optical and luminescence properties of MnWO₄ have received great attention as they are widely used as scintillating detectors in high-energy particle physics, rare-event searches, and medical diagnosis [3]. The electrical conductivity of MnWO₄ is also sensitive to changes in humidity, thereby making it useful as a humidity sensor with potential applications like meteorology, medicine, food production, agriculture, and industrial and domestic environment [4, 5]. There are a number of processes used to synthesize nanocrystalline MnWO₄, such as microwave-assisted synthesis [1], surfactant-assisted complexation-precipitation method [2], melt solution process [6], solvothermal route [7], aqueous salt metathesis reaction [8], sol-gel technique [4, 9], ambient template synthesis [10], and solid state metathetic approach [11].

In the present work, manganese tungstate nanoparticles are synthesized by careful control of the reaction kinetics of aqueous precipitation. As-prepared MnWO₄ nanoparticles are characterized by X-ray diffraction [XRD], transmission electron microscopy [TEM], UV-Visible absorption spectroscopy, photoluminescence [PL] spectroscopy and Raman spectroscopy. In addition, the optical properties of the pure and EB irradiated samples of MnWO₄ nanoparticles were evaluated in context of the band gap.

2. Experimental Details

Manganese chloride (MnCl₂·4H₂O) (99.8%, Sigma Aldrich) and sodium tungstate (Na₂WO₄·2H₂O) (99.9%, Alfa Aesar) were used without further purification for the synthesis of MnWO₄. Distilled water was used in all synthesis procedures.

2.1. Preparation of the Samples. The synthesis procedures for the preparation of MnWO₄ nanoparticles used in this work has been described elsewhere [12]. Nanocrystalline manganese tungstate samples were prepared by reacting aqueous solutions of manganese chloride and sodium tungstate (0.1 M each) at room temperature, keeping the pH = 7. The precipitate formed was centrifuged, filtered, washed with distilled water a number of times, and dried in an oven to get
Figure 1: The scheme of preparation of MnWO₄ nanoparticles by chemical precipitation method.

2. Results and Discussion

Figure 2 shows the powder X-ray diffraction patterns of pure and EB irradiated samples of MnWO₄ nanoparticles. From TEM photographs of the pure nanocrystalline MnWO₄ powder samples were taken using a Tecnai 30 G2 Stwin (model), FEI make 300 KV High Resolution Transmission Electron Microscope (HRTEM).

The absorption spectra of the pure and irradiated samples in the range of 200–800 nm were recorded using a double beam UV-Visible Spectrophotometer (UV 2600 model, Shimadzu). For measurement, the nanoparticles were pressed into a thick pellet and placed at the entrance port of the integrating sphere using a sample holder. Calibration of the absorbance scale was done using standard reference materials.

Photoluminescence spectroscopy is an effective way to investigate the electronic structure and optical characteristics of nanomaterials. This analytical technique reveals information such as surface defects and oxygen vacancies as well as the separation and recombination of photo-induced charge carriers [13]. PL spectra of the pure and EB irradiated samples of MnWO₄ were measured at room temperature by a Fluoromax3 Spectrophotometer.

Raman spectroscopy is a powerful tool for the investigation of the structural properties of nanoparticles because the variations in Raman spectra with decreases in particle size can be easily detected. Raman spectra of the pure and irradiated samples of MnWO₄ were obtained at room temperature using a Bruker FRA 106/S Raman spectrometer with excitation line of 785 nm.
XRD patterns, the average particle size of the as-prepared and irradiated samples has been estimated using Debye-Scherrer equation. Average crystallite sizes obtained for samples S1, S2, and S3 are 26 nm, 23.4 nm, and 24.5 nm, respectively. The average crystallite size of sample S2 was decreased from 26 nm to 23.4 nm due to EB irradiation (5 kGy). However, the size of sample S3 was decreased only up to 24.5 nm after a dose of 10 kGy irradiation. The principal "d" values taken from the JCPDS file no. 80-0135 for MnWO₄ are in close agreement with the observed "d" values. The XRD results showed that crystallite size and percentage of crystallinity decreased after irradiation. It confirms amorphization of the sample due to irradiation which is responsible for the change in optical properties. The results show that average particle size decreases with the EB irradiation dose and suggest the possible control of the size and the density of the MnWO₄ nanoparticles by EB irradiation.

All XRD patterns of MnWO₄ samples correspond to a wolframite-type monoclinic structure, which is in agreement with the respective Inorganic Crystal Structure Database (ICSD) no. 67907. Unit cell parameters were $a = 0.4787$ nm, $b = 0.5809$ nm, $c = 0.4999$ nm, and $\beta = 91.19^\circ$ for sample S1, $a = 0.4843$ nm, $b = 0.5869$ nm, $c = 0.5035$ nm, and $\beta = 91.23^\circ$ for sample S2, and $a = 0.4823$ nm, $b = 0.5826$ nm, $c = 0.5021$ nm, and $\beta = 91.22^\circ$ for sample S3. All samples showed lattice parameters slightly larger than the calculated and experimental values of the bulk samples reported in the literature [14, 15]. This deviation might occur due to small particle size of the samples [16].

TEM was used to further examine the particle size, crystallinity, and morphology of MnWO₄ samples. TEM bright field images of MnWO₄ nanoparticles (calcined at 450°C) are shown in Figure 3. It can be noted from the TEM image (Figure 3) that the particles are agglomerated and exhibit bar-like shape. Selected area electron diffraction (SAED) is shown in the inset of Figure 3, which clearly indicates that the MnWO₄ nanoparticles were highly crystalline in nature. As can be seen from the TEM image, the average particle size is about 26 nm, which is in agreement with the crystallite size obtained from XRD data.

Figure 4 shows the UV-Visible absorbance spectra of pure and irradiated samples of MnWO₄ nanoparticles. From the results, it can be observed that the absorption peak of samples S2 and S3 shifts towards the shorter wavelength region. This blue shift in the absorption peak is the first-hand signature of significant size reduction of the nanoparticles resulting from EB irradiation. The blue shift in the absorption peak of sample S3 is less as compared to sample S2. It indicates that the size and size distribution of the particle increase beyond a certain EB irradiation dose level.

The optical band gap values obtained from the absorption graphs for samples S1, S2, and S3 were 2.43 eV, 2.58 eV, and 2.51 eV, respectively. It is seen that the band gap of MnWO₄ nanoparticles shifted from 2.43 to 2.58 eV as particle size reduced from 26 to 23.4 nm and from 2.43 to 2.51 eV as
size reduced from 26 to 24.5 nm. This increase in the band gap might occur due to surface band bending with size reduction of the nanoparticles resulting from EB irradiation [16]. An additional advantage of size reduction is that the large surface area to volume ratio makes possible timely utilization of photo-generated carriers in interfacial processes [17]. Moreover, beam irradiation appeared to improve the optical absorption performance of MnWO4 nanoparticles. In addition, both pure and irradiated samples are useful for photocatalytic activities because their band gap energy values are comparable to the energy of visible or UV light photons. 

Table 1 compares present experimental band gap values of MnWO4 with experimental and calculated values reported in the literature [14, 18, 19]. The present experimental values are higher as compared to literature values, which can be attributed to the reduction in particle size of the samples.

Photoluminescence studies provide information relating to different energy states available between valence band and conduction band responsible for radiative recombina- tion. Luminescence spectrum of MnWO4 nanoparticles with 293 nm excitation is shown in Figure 5. The PL emission spectra of the nonirradiated sample show emission bands at 423, 447, 460, 485, and 529 nm. These emission bands are attributed to the transition from the 1A1 ground state to the high vibration level of 1T2 and from the low vibration level of 1T2 to the 1A1 ground state within the tetragonal WO42− groups [20, 21].

The pure and irradiated samples of MnWO4 could exhibit obvious PL signal with similar curve shapes (Figure 5). The PL spectra of irradiated samples were shown to have larger intensities relative to nonirradiated sample, which was thought to arise from defects and particle size variation [22]. Intermediate energy levels are formed with favourable characteristics due to EB irradiation, which are necessary for recombination process (electron/hole), responsible for the improvement of the PL emission at room temperature. During the excitation process, medium range defects in the monoclinic lattice caused by distortion of octahedral [WO6] clusters are responsible for the PL emission. Initially, some electrons from lower intermediate energy levels (oxygen—2p levels) near the valence band absorb the photon energy (hv) at this wavelength (λ = 293 nm) and these energetic electrons are promoted to higher intermediate energy levels (tungsten—5d levels) located near the conduction band [21]. The energies generating from the deexcitation process are converted to photons (hv'). Several photons originating from the participation of different energy states during the electronic transitions are responsible for the intense PL emission.

| Present work | Experimental | Theoretical |
|--------------|--------------|-------------|
| 2.43 (S1)    | 2.5 [18, 19] | 1.83 [14]   |
| 2.58 (S2)    | 2.37 [14]    |             |
| 2.51 (S3)    |              |             |

There was a small blue shift for PL spectra of the EB irradiated samples S2 and S3 (Figure 5). The blue shift of band gap with size reduction could be due to surface band bending with surface structural modifications [16]. It can also be seen that PL spectra of the irradiated samples S2 and S3 were broadened. This broadening of MnWO4 nanoparticles might originate from the surface band bending and lattice expansion with particle size reduction caused by the EB irradiation [16].

It can be seen in Figure 5 that the PL intensity increases initially up to 5 kGy dose and then falls off at higher doses of irradiation. The initial increase is attributed to the increase in the trap states that give raise to the luminescence. The increase in PL intensity for an irradiated sample is attributed to the recombination of self-trapped excitons, which is a combined effect of defect centers generated by oxygen vacancies, small particle size, and increased absorption over the UV and visible range [21, 22]. The increase in PL intensity is also an indication of higher photocatalytic activity.

When the EB irradiation dose rate is increased above a certain dose level, the particles agglomerate, thereby reducing the number of fluorophores. This possibly leads to a reduction in the fluorescence intensity (sample S3, Figure 5). Further increase in the irradiation dose appears to have less effect on the trap states but slowly changes the size of the particle, thereby causing a shift in the fluorescence edge to longer wavelength side.

Raman spectra for MnWO4 nanoparticles of pure and irradiated samples are shown in Figure 6. All the eighteen Raman modes were observed in the range 50–1200 cm−1 at room temperature. The most intense band observed at 886 cm−1 originated from the symmetric stretching vibration of a short terminal W–O bond, while the asymmetric stretching vibration of a short terminal W–O bond appeared at 775 cm−1. Other bands are contributed by asymmetric stretching vibration modes of longer W–O bond, symmetric stretching vibrations of longer W–O bond, deformation vibration of short W–O bonds, vibration modes of Mn–O, and interchain deformation modes and lattice modes [16, 23, 24]. It can be observed that Raman peaks were slightly shifted for
the irradiated samples S2 and S3, and the shift was found large for the sample S2.

It can be seen in Figure 6 that Raman peaks of samples S2 and S3 were extremely broadened. The vibration mode for sample S2 at 886 cm$^{-1}$ broadened from 15.5 to 30.2 cm$^{-1}$, while for the sample S3, the line width broadened from 15.5 to 23.49 cm$^{-1}$. The broadened Raman bands could be due to the quantum confinement effect [18]. Besides the quantum confinement, lattice expansion may also contribute to the broadened Raman peaks. The increased lattice volume for MnWO$_4$ nanocrystals at smaller particle sizes would give the enlarged average length of W–O bonds, which may decrease the force constant of the W–O bond [25, 26]. As a result, Raman peaks of MnWO$_4$ nanoparticles became broadened as particle size reduced.

Present experimental Raman modes of MnWO$_4$ nanoparticles are presented in Table 2 along with previous experimental and calculated values [23, 27]. Present results are slightly higher than the reported values, and this variation could be caused by the nanoscale size of the samples.

The structural characterization and optical studies of MnWO$_4$ nanoparticles confirm the size reduction and structural modifications caused by the EB irradiation, which in turn result in blue shift in the absorption and PL spectra, and enhanced and broadened PL as well as Raman spectra.

| Mode | Present values | Literature values | Calculated values |
|------|----------------|-------------------|-------------------|
|      | S1  | S2  | S3  | [23, 27] |   |       |
| B$^g$ | 90  | 79  | 82  | 89     | 95 |
| A$^g$ | 130 | 119 | 123 | 129    | 129|
| B$^g$ | 162 | 151 | 154 | 160    | 165|
| B$^g$ | 168 | 157 | 161 | 166    | 171|
| B$^g$ | 182 | 171 | 174 | 177    | 183|
| A$^g$ | 205 | 193 | 198 | 206    | 226|
| B$^g$ | 276 | 265 | 269 | 272    | 278|
| A$^g$ | 259 | 242 | 252 | 258    | 264|
| B$^g$ | 297 | 290 | 293 | 294    | 296|
| A$^g$ | 330 | 317 | 320 | 327    | 338|
| B$^g$ | 361 | 349 | 354 | 356    | 373|
| A$^g$ | 399 | 393 | 395 | 397    | 389|
| B$^g$ | 514 | 506 | 508 | 512    | 509|
| A$^g$ | 547 | 528 | 535 | 545    | 548|
| B$^g$ | 675 | 633 | 642 | 674    | 662|
| A$^g$ | 702 | 688 | 695 | 694    | 694|
| B$^g$ | 776 | 762 | 769 | 774    | 775|
| A$^g$ | 888 | 878 | 882 | 885    | 858|

**4. Conclusions**

MnWO$_4$ nanoparticles were synthesized by simple chemical precipitation method, and the effect of high energy EB irradiation on their optical properties was studied in order to improve the optical absorption performance and photoactivity. The EB irradiation may have resulted in size reduction, which in turn caused an increase of the optical band gap as well as photoluminescence intensity and broadening of Raman bands. Furthermore, the data obtained here would seem to show that the method of EB irradiation may be considered as efficient means to enhance the optical response and photoactivity of MnWO$_4$ nanoparticles for varied applications.

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