

## Investigations on Synthesis, Structural, Morphological and Dielectric Properties of Manganese Oxides Nanoparticles

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### Abstract

Manganese oxides ( $\text{MnO}_2$ ) nanoparticles were synthesized using a co-precipitation technique. The as prepared nanopowder was used for further characterization. The size, structure and morphology of  $\text{MnO}_2$  nanoparticles were characterized by X-ray diffraction (XRD) and SEM. The crystallite size of the synthesized  $\text{MnO}_2$  nanoparticles was obtained from X-ray diffraction study using Debye-Scherrer formula and it was found to be 22 nm. The surface morphology of prepared  $\text{MnO}_2$  nanoparticles was analyzed by scanning electron microscope. The optical properties were analyzed using UV-studies. Dielectric studies were carried out for the pelletized sample of  $\text{MnO}_2$  nanoparticles. The dielectric properties of  $\text{MnO}_2$  nanoparticles were studied in the different frequency range of 50Hz- 5MHz at different temperatures. The frequency dependence of the dielectric constant and dielectric loss is found to decrease with an increase in the frequency at different temperatures.

**Keywords:**  $\text{MnO}_2$  nanoparticles; XRD; SEM; Dielectric constant and dielectric loss

### Introduction

Nano-sized materials are new substances quickly developed and generally measured as 1 to 100 nm size in one dimension. At a nanometer scale, the surface area increases hastily as particle size decreases, as a result, the electromagnetic, thermal, optical, and mechanical properties of nanomaterials modify. In recent years, manganese oxides ( $\text{MnO}_2$ ) have concerned considerable research interest due to their characteristic physical and chemical properties and broad applications such as ion exchange, molecular adsorption, energy storage, catalysis, biosensor [1-3]. Manganese oxides have established application in catalysis, ion exchange reactions, as cathode materials for rechargeable batteries and as distinguish agents for magnetic resonance imaging (MRI). The manganese oxide nanoparticles were used to improve the mechanical and thermal properties of polymers and to enhance the ionic conductivity of polymer electrolytes [4-6]. Manganese oxides take place in a variety of oxidation states and chemical and structural forms. Due to their distinctive properties and wide applications, the synthesis of manganese oxide nanoparticles has been investigated in order to put their chemical composition, structure, size and morphology under control [7,8]. Several novel and effective routes have been devoted to prepare manganese oxides nanomaterials with various shapes and excellent properties, such as hydrothermal method [9-12], sol-gel synthesis [13], wet chemical route [14,15], pulsed laser deposition method [16], and precursor technique [17]. Co-precipitation method offers advantages like, simple and rapid preparative method, easy control of particle size and composition can be made in this method and also, there are various possibilities to modify the particle surface state and overall homogeneity. In the present study,  $\text{MnO}_2$  nanoparticles were synthesized by co-precipitation method. Present work reports synthesis of  $\text{MnO}_2$  nanoparticles and its characterization by XRD, SEM, UV-analysis and Dielectric studies.

### Materials and Method

$\text{MnO}_2$  nanoparticles were prepared co-precipitation method by using the manganese (II) sulphate and manganese oxalate in the method reported in literature [18]. The salts were dissolved in de-ionized water and stirred well by magnetic stirrer for 30 min at a constant temperature 50°C. Sodium hydroxide solution was added drop wise

into the solution. The solution stirring was continued then heated at 60°C for 1hr in a closed vessel. Ethanol was added to the brown coloured solution obtained, and the total volume of the solution was adjusted to 100 ml. Precipitates were dried for overnight at 100°C. Then the precipitates was kept in muffle furnace at 500°C for 3 hrs. The XRD pattern of the  $\text{MnO}_2$  nanoparticles was recorded by using a powder X-ray diffractometer (Schimadzu model: XRD 6000 using  $\text{CuK}\alpha$  ( $\lambda=0.154$  nm) radiation, with a diffraction angle between 0° to 80°. The crystallite size was determined from the broadenings of corresponding X-ray spectral peaks by using Debye Scherrer's formula. Scanning Electron Microscopy (SEM) studies were carried out on JEOL, JSM-67001. The optical absorption spectrum of the  $\text{MnO}_2$  nanoparticles has been taken by using the VARIAN CARY MODEL 5000 spectrophotometer in the wavelength range of 200-600 nm. The dielectric properties of the  $\text{MnO}_2$  nanoparticles were analyzed using a HIOKI 3532-50 LCR HITESTER over the frequency range 50 Hz-5 MHz.

### Results and Discussion

#### X-ray diffraction analysis

In an X-ray tube, the high voltage maintained across the electrodes draws electrons toward a metal target (the anode). X-rays are produced at the point of impact, and radiate in all directions. X-ray diffraction pattern of the as prepared  $\text{MnO}_2$  nanoparticles is shown in Figure 1. From the XRD pattern, it is clear from the broadening of diffraction peaks of that the particles crystallize at nanoscale range. The average particle size was calculated using Debye-Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

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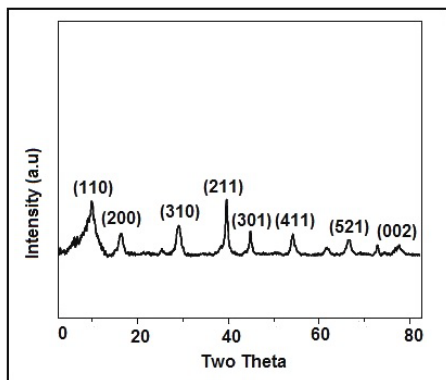


Figure 1: Powder XRD patterns of MnO<sub>2</sub> nanoparticles.

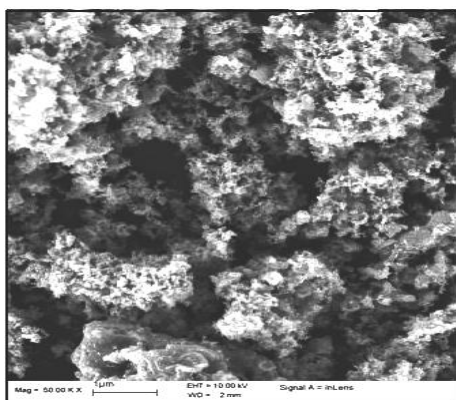


Figure 2: The SEM image of MnO<sub>2</sub> nanoparticles.

By Knowing the wavelength ( $\lambda$ ) full width at half maximum (FWHM) of the peaks  $\beta$  and the diffracting angle  $\theta$ , Particle size (D) was calculated. The calculated average particle size of MnO<sub>2</sub> nanoparticles was found to be around 22 nm.

### SEM analysis

Scanning electron microscopy (SEM) was employed to analyze the morphology and the growth features of the aggregates of the as prepared MnO<sub>2</sub> nanoparticles. SEM images of as synthesized MnO<sub>2</sub> nanoparticles are shown in Figure 2. From the image, it is clear that the particles were highly agglomerated in nature. Due to aggregating or overlapping of smaller particles there are some larger particles. The SEM pictures clearly show randomly distributed grains with smaller size.

### UV-visible absorption spectrum

Ultraviolet spectrometer consists of a light source, reference and samples beams, a monochromator and a detector. The ultraviolet spectrum for a compound is obtained by exposing a sample of the compound to ultraviolet light from a light source. Optical absorption measurement was carried out on nanoparticles. Figure 3 shows the variation of the optical absorbance with the wavelength of the nanoparticles. The optical absorption coefficient has been calculated in the wavelength range of 200-600 nm. The absorption edge has been obtained at a shorter wavelength. The absorption edges are seen

to be shifted slightly towards lower wave number (blue shift). This shift indicates an increase in the band gap, which can be attributed to a decrease in particle size. The value of the absorption edge of nanoparticles is 340 nm, blue shift was observed due to the quantum confinement effects.

### Dielectric studies

The dielectric constant was measured as a function of the frequency at different temperatures as shown in Figure 4, while the corresponding dielectric losses are depicted in Figure 5. Figure 4 shows the plot of the dielectric constant versus applied frequency. It is observed that the dielectric constant decreases with increasing frequency and then attains almost a constant value in the high frequency region. This also shows that the value of the dielectric constant increases with an increase in the temperatures. The involvement of the decrease in the dielectric constant due to electronic polarization is quite less. Dipolar polarization is also predictable to decrease with temperature as it is inversely proportional to temperature. The contribution to polarizability of the space charge depends on the purity of the nanoparticles. At low temperature and high frequency, we may take it as small. However, it is significant in the low frequency region. As the temperature increases, the contribution of the space charge effect towards polarization may have a tendency to increase [19].

The dielectric loss considered as a function of frequency at different temperatures is shown in Figure 5. These curves suggest that the

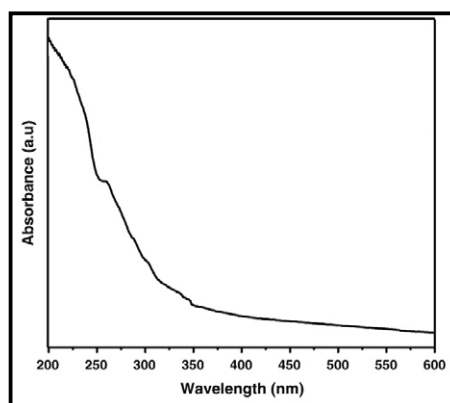


Figure 3: Optical absorption spectrum of MnO<sub>2</sub> nanoparticles.

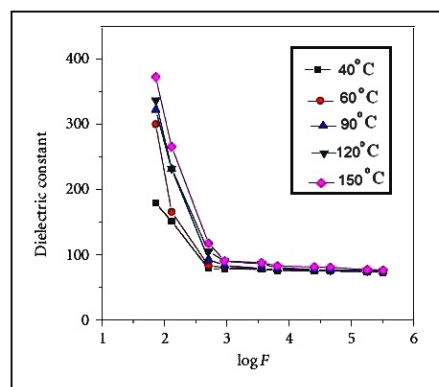


Figure 4: Variation of dielectric constant with frequency.

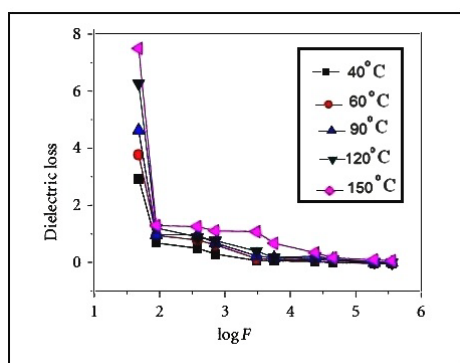


Figure 5: Variation of dielectric loss with frequency.

dielectric loss is strongly dependent on the frequency of the applied field, similar to that of the dielectric constant. The dielectric loss decreases with an increase in the frequency at almost all temperatures. In the low frequency region, high energy loss is observed, which may be due to the dielectric polarization, space charge and rotation direction polarization occurring in the low frequency range [20].

## Conclusion

MnO<sub>2</sub> nanoparticles were synthesized by using co-precipitation method. The X-ray diffraction (XRD), scanning electron microscopy (SEM), was used to characterize the structure and morphology of the MnO<sub>2</sub> nanoparticles. X-ray diffraction analysis reveals that the crystallite size of the MnO<sub>2</sub> nanoparticles was found to be 22 nm. The morphology of the MnO<sub>2</sub> nanoparticles was characterized using scanning electron microscopy (SEM). The optical properties were studied by the UV-Visible absorption spectrum. The dielectric constant and dielectric loss of the material decreases with increasing the frequency. In higher frequencies, dielectric constant and dielectric loss are almost constant compared to the lower frequency values.

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