Enhancement of electrical properties of manganese tungstate nanoparticles by beam irradiation

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Abstract. MnWO₄ nanoparticles were synthesized using simple chemical precipitation method. The dielectric properties of irradiated and non-irradiated samples of monoclinic manganese tungstate nanoparticles have been studied as a function of frequency. It is found that electric properties such as dielectric constant, loss tangent and a.c. conductivity of the irradiated sample were much larger as compared to the non-irradiated sample, which has been attributed to defects and reduction in particle size caused by the beam irradiation. The present investigation observed that the electron beam irradiation is an efficient technique to modify the electrical properties of MnWO₄ nanoparticles.

1. Introduction

Nanostructured tungstate materials have aroused much interest because of their luminescence behaviour, structural properties and potential applications. The electrical conductivity of MnWO₄ is sensitive to changes in humidity, thereby making it useful as a humidity sensor with potential applications like meteorology, medicine, food production, agriculture, industrial and domestic environment [1-5]. 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 [5], aqueous salt metathesis reaction [7], sol-gel technique [4,8], ambient template synthesis [9] and solid state metathetic approach [10].

In the present work, we report a systematic study of the dielectric properties and a.c. conductivity of pure and electron beam (EB) irradiated samples of MnWO₄ nanoparticles.

2. Experimental details
Manganese chloride (MnCl₂·4H₂O) (99.8%, Sigma Aldrich) and sodium tungstate (Na₂WO₄·2H₂O) (99.9%, Alfa Aesar) were used for the synthesis of nanocrystalline MnWO₄. 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 fine powders of manganese tungstate. The obtained powder samples were calcined for 3 hours in a furnace at 450°C in an aerobic atmosphere. The samples were irradiated at a dose rate of 5 kGy with an electron beam of 8 MeV energy obtained from a variable energy Microtron at Mangalore University, India. S1 is pure sample of MnWO₄ and S2 is the irradiated samples with a dose rate of 5 kGy.

The structural characteristics of the pure and irradiated samples have been studied by X-ray powder diffraction (XRD) using Bruker D8 Advance X-ray diffractometer (λ=1.5406 Å). The crystallite size was estimated from the Scherrer’s equation [8]. The dielectric properties of pellet samples sintered at 500°C are measured at room temperature using a four probe LCR meter (Wayne Kerr H-6500 model) in conjunction with a portable furnace and temperature controller (±1K). The dielectric constant (ε’) and a.c. conductivity (σac) were calculated by using equation (1) and (2),

\[ \varepsilon' = \frac{cd}{\varepsilon_0 a}, \]  
\[ \sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta, \]  

where \( a \) is face area, \( c \) capacitance of the pellet in pF, \( d \) thickness of pellet, \( \varepsilon_0 \) permittivity of vacuum, \( \omega \) angular frequency and \( \tan \delta \) loss tangent.

3. Results and discussion
Figure 1 displays the powder X-ray diffraction (XRD) pattern of pure sample (S1) and EB irradiated sample (S2). Average crystallite size obtained for samples S1 and S2 are 21 nm and 17.4 nm respectively. The principal ‘d’ values taken from the
JCPDS file No. 80-0135 for MnWO$_4$ were 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 electrical properties.

Figure 1. XRD spectra of samples S1 and S2.

Figure 2 shows the variation of dielectric constant with frequency at room temperature. It can be seen that the real part of dielectric constant $\varepsilon'$ for both the samples S1 and S2 have high values at low frequencies, which decreases rapidly as frequency increases and attains a constant value at higher frequencies. It has been found that the $\varepsilon'$ values are shifted upward for the irradiated sample (S2). The value of $\varepsilon'$ for S1 is 110 at 100Hz while its value for S2 is 215.6. The $\varepsilon'$ values for S1 and S2 at 10 MHz are 10.7 and 17.2 respectively. The increase in the dielectric constant of the irradiated samples can be attributed to size reduction of the nanoparticles caused by the EB irradiation [11]. When the particle size reduces, the volume percentage of interface boundaries and the amount of defects that cause various kinds of polarizations might increase, which in turn increases dielectric constant.

The variation of tan $\delta$ with frequency of samples is shown in figure 3 (a). The loss in MnWO$_4$ can be explained by the electronic hopping model [12]. In the high frequency region, tan $\delta$ becomes almost constant because the electron exchange interaction (hopping) between the Mn$^{+2}$ and Mn$^{+3}$ cannot follow the alternatives of the applied electric field beyond a critical frequency. The figure 3 shows that tan $\delta$ of irradiated sample S2 has high values for all frequencies as compared to pure sample S1. The value of tan $\delta$ for S1 is 9.2 at 100 Hz while its value for S2 is 13.7. The tan $\delta$ values for S1 and S2 at 10 MHz are 0.3 and 0.7 respectively. The increase of loss
tangent could be due to particle size reduction, defects and imperfections caused by EB irradiation.

![Figure 2. The variation of dielectric constant with frequency.](image)

The variation of a.c. conductivity as a function of frequency is shown in figure 3 (b). At low frequencies, $\sigma_{ac}$ has a small value which increases at higher frequencies. The conduction in manganese tungstate is due to the hopping and ionic conduction of Mn$^+$ ions. When the grain size of the sample is reduced the hopping distance increases which in turn increases the conductivity. The values are shifted upwards for the irradiated sample S2, which might occur due to size reduction caused by the irradiation. The value of $\sigma_{ac}$ for S1 is $0.48\times10^{-5}$ S/m at 100 Hz while its value for S2 is $1.57\times10^{-5}$ S/m. The $\sigma_{ac}$ values for S1 and S2 at 10 MHz are $3.45\times10^{-5}$ S/m and $6.23\times10^{-5}$ S/m respectively. Thus, electron beam irradiation is found to be an efficient method for the enhancement of the electrical properties of MnWO$_4$ nanoparticles.

![Figure 3. Variation of (a) loss tangent, and (b) a.c. conductivity with frequency.](image)
4. Conclusions

The dielectric properties of pure and EB irradiated samples have been investigated as a function of frequency. At lower frequency regime, $\varepsilon^\prime$ and $\tan \delta$ have higher values while they reach steady lower values at higher frequencies. However, the a.c. conductivity increases with the increase of frequency, which confirms small polaron hopping. It has been found that $\varepsilon^\prime$, $\tan \delta$ and $\sigma_{ac}$ values are much larger for the EB irradiated sample. This enhancement of electrical properties might occur due to defects and reduction in particle size caused by the beam irradiation. It is suggested that, the MnWO$_4$ nanoparticles modified with the EB irradiation can be used as a good dielectric material for varied applications.

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