DC electrical conductivity of nanocrystalline Mn$_3$O$_4$
synthesized through a novel sol-gel route

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Abstract. Manganese oxides have generated considerable interest in recent years due to their electronic and magnetic properties with potential industrial applications. Among manganese oxides, Mn$_3$O$_4$ is one of the stable oxides with normal spinel structure and it has variety of important applications. In the present work nanocrystalline Hausmannite, Mn$_3$O$_4$ with phase purity and average crystallite size of 8 nm was synthesized through a novel sol-gel route at a temperature of 0-5°C. The samples were annealed at different temperatures to understand the thermal stability and the structural characterization was done using techniques such as X-ray powder diffraction (XRD), Transmission Electron Microscopy (TEM) and Fourier Transform Infrared Spectroscopy (FTIR). The UV visible absorption spectra of the samples show that there are two types of transitions corresponding to Mn$^{2+}$ ions and Mn$^{3+}$ ions. The dc electrical conductivity of the samples increases in comparison with that of bulk.

1. Introduction
Manganese oxides have generated considerable interest in recent years due to their electronic and magnetic properties with potential industrial applications[1]. Manganese (Mn) is a transition metal having multiple valencies +2, +3, +4, +5, +6, +7 etc and hence it forms a number of oxide systems such as MnO, MnO$_2$, Mn$_2$O$_3$, Mn$_3$O$_5$, MnO$_3$, Mn$_2$O$_7$ and many nonstoichiometric phases beside Mn$_3$O$_4$. Among these Mn$_3$O$_4$ is one of the stable oxides with normal spinel structure [2]. Herein, we report the synthesis of nanocrystalline Mn$_3$O$_4$ at a temperature of 0-5°C through a sol-gel route and studies on the characterization techniques such as X-ray powder diffraction, Transmission Electron Microscopy(TEM), Surface Area Electron Diffraction(SAED), UV visible absorption spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR) and temperature dependent dc electrical conductivity.

2. Experimental Methods
Nanocrystalline Mn$_3$O$_4$ sample was synthesized by a novel sol-gel route, using manganese acetate and lithium hydroxide as the starting materials and ethanol as the reacting medium. The reaction was carried out in the temperature range 0 to 5°C. The reaction yielded highly dispersed nanocrystalline samples in one step[3]. The sample obtained was washed several times with ethanol and water and finally dried at 40°C in a hot air oven (Sample Code Mn40). In order to investigate the stability of the sample against temperature the as prepared sample was annealed at different temperatures, viz.100°C (Sample code Mn 100), 300°C (Sample code Mn 300) and 400°C (Sample code Mn 400) for two hours
each. The X-ray diffraction (XRD) patterns of the samples were recorded using a Philips XPERT-PRO power diffractometer employing Cu $K_\alpha$ (1.540560 Å) radiation in the 2θ range 0° to 80° with a step size of 0.05°. The TEM and SAED patterns were recorded using PHILIPS CM 200 transmission electron microscope, to measure the particle size, surface morphology and crystalline nature. The room temperature UV Visible absorption spectra of the samples were recorded using a SHIMADZU UV-2550 double beam UV visible spectrophotometer in the range 200-800nm. Infrared transmission spectrum of the sample was recorded using Perkin Elmer Fourier Transform Infrared (FTIR) spectrometer for the frequency range 200-4000 cm$^{-1}$. The dc electrical conductivity of the samples in the temperature range 313-423K was measured with an interval of 10K using KEITHLEY 2400 Source meter have an accuracy of ±.01.

3. Results and Discussion

3.1. XRD Analysis

Figure 1 shows the XRD patterns of all the samples. The broadened nature of the XRD peaks indicates the nanocrystalline nature of the samples. The interplanar spacing ($d_{hkl}$) and relative intensity ($I/I_0$) values are in agreement with JCPDS-ICDD Pattern number 80-0382 for tetragonal haumannite Mn$_3$O$_4$. The full width at half maxima of the peaks was estimated by a nonlinear curve fitting routine using a Pseudo-Voigt function. The average crystallite size of the samples was estimated using Scherrer equation. The crystalline size of the sample Mn 40 is 8 nm. The crystallite size of the samples Mn 100, Mn 200, Mn 300 and Mn 400 are shown in table 1. Thus annealing of the as prepared Mn$_3$O$_4$ sample in air in the temperature range 100–400°C does not lead to any phase change and there is considerable grain growth on annealing. But there is no appreciable change in size of the sample as the temperature increases from 100 to 200°C.

![Figure 1. XRD Patterns of all the Samples](image1)

![Figure 2. (a) TEM (b) Lognormal fit and (c) SAED pattern of the sample Mn 40](image2)

3.2. TEM Analysis

The TEM image of the sample Mn 40 is shown in figure 2. The particle size distribution was obtained by fitting a lognormal profile on the data obtained from TEM and is shown in the inset of figure 2. The average particle size obtained from the XRD pattern for all samples is in agreement with the particle size distribution obtained from TEM, which is shown in table1. The inset of figure 2 also shows SAED pattern of the sample Mn 40. SAED pattern shows multiple intense rings which reveal the crystalline nature of the nanocrystals.
### 3.3 Analysis of UV Visible Absorption Spectrum

Figure 3 shows the UV Visible absorption spectra of the samples recorded in the range 200-800nm. The spectra show several absorption peaks which was obtained by curve fitting. The absorption peaks were observed at 220, 260, 325 and 500 nm and the edges were located at 325 and 500 nm. The bands at lower wavelength region are attributed to the allowed $O^{2-}\rightarrow Mn^{2+}$ and $O^{2-}\rightarrow Mn^{3+}$ charge transfer transitions and that at higher wavelength region may be related to d-d crystal field transitions [4,5]. The optical band gap energy ($E_g$) of the sample was calculated using the equation $(\alpha h\nu)^n = A(h\nu - E_g)$ where $\alpha$ is absorption coefficient, and $A$ is a constant. The values of band gap energy of $Mn_3O_4$ with an average crystallite size was calculated by assuming the direct transition ie, $n=2$ because the optical absorption in $Mn_3O_4$ is direct allowed. The exact values of the band gap energies were obtained by extrapolating the straight line portions of the $(\alpha h\nu)^2$ versus $h\nu$ graph which is shown in table 2. The band gap energies for sample $Mn\ 40$ are 3.07 and 2.72 eV[6].

### 3.4 Analysis of FTIR Spectrum

The FTIR spectrum of the sample $Mn\ 40$ is shown in the inset of figure 3. Several vibrational modes were identified by curve fitting the data in the region 400-800 cm$^{-1}$. The vibration frequencies of $Mn$-$O$ modes are 684, 637, 592, 518, 481 and 441 cm$^{-1}$[6, 7]. The peaks in the range 1084-1554 cm$^{-1}$ correspond to the vibration of O-H bonds connected with $Mn$ atoms[8]. The other peaks in the 1636-3286 cm$^{-1}$ are due to the presence of moisture in the $Mn_3O_4$ sample[8].

### 3.5 Analysis of conductivity

The dc electrical conductivity of all the samples in the temperature range 313K to 423K was measured using the source meter. The variation of conductivity with inverse temperature is shown

![Figure 3](image-url)

**Figure 3.** (A) UV Visible Absorption spectra (B) FTIR Spectrum of the Sample $Mn\ 40$

![Figure 4](image-url)

**Figure 4.** (A) Variation of conductivity with inverse temperature, (B) Arrhenius plot

### Table 1. Comparison of size from XRD and TEM and Band gap energy.

| Sample Code | Size from XRD (nm) | Standard deviation | Size from TEM (nm) | Standard Deviation | Band Gap Energy |
|-------------|-------------------|--------------------|-------------------|--------------------|-----------------|
| Mn 40       | 8.66              | 1.229              | 8.07              | 1.110              | 3.07            |
| Mn 100      | 11.26             | 2.286              | 8.30              | 2.078              | 3.05            |
| Mn 200      | 10.67             | 0.805              | 8.43              | 1.498              | 2.92            |
| Mn 300      | 13.08             | 1.436              | 11.09             | 1.591              | 2.42            |
| Mn 400      | 13.66             | 1.66               | 15.09             | 2.607              | 2.06            |

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in figure 4. The conductivity of the sample Mn 40 increases from a value \((3.68 \pm 0.03) \times 10^{-8}\) ohm\(^{-1}\) m\(^{-1}\) at 313K to \((2.04 \pm 0.001) \times 10^{-5}\) ohm\(^{-1}\) m\(^{-1}\) at 423K. The conductivity of all other samples increases with increase in temperature which are listed in the table 2. The electrical transport in Mn\(_3\)O\(_4\) is due to the thermally activated polaronic hopping of electron from Mn\(^{3+}\) ions in the tetrahedral site to Mn\(^{2+}\) ions in the octahedral sites. This is due to interaction of autolocalized holes with lattice vibrations\[^9\]. The inset of figure 4 shows the variation of \(\ln \sigma/d\sigma\) with inverse temperature \((1/T)\). It is in good agreement with Arrhenius law. The activation energy of the sample Mn 40 is 0.69eV which is smaller than the reported value of 1.35eV of bulk Mn\(_3\)O\(_4\) phase\[^10\]. It is found that the activation energy of the samples decreases with increase in crystallite size which is listed in table 2.

### Table 2. Variation of conductivity with crystallite size and temperature.

| Sample Code | Conductivity (\(\sigma\)) (ohm\(^{-1}\)m\(^{-1}\)) | Activation Energy (eV) |
|-------------|----------------------------------|----------------------|
|             | 313 K | 423 K |            |            |
| Mn 40       | \((3.68 \pm 0.037) \times 10^{-8}\) | \((2.044 \pm 0.001) \times 10^{-5}\) | 0.69 |
| Mn 100      | \((2.036 \pm 0.025) \times 10^{-8}\) | \((1.093 \pm 0.001) \times 10^{-5}\) | 0.69 |
| Mn 200      | \((6.810 \pm 0.006) \times 10^{-6}\) | \((6.061 \pm 0.005) \times 10^{-4}\) | 0.45 |
| Mn 300      | \((2.412 \pm 0.002) \times 10^{-3}\) | \((7.082 \pm 0.008) \times 10^{-2}\) | 0.34 |
| Mn 400      | \((6.426 \pm 0.005) \times 10^{-3}\) | \((13.772 \pm 0.11) \times 10^{-2}\) | 0.32 |

4. Conclusion
Nanocrystalline Mn\(_3\)O\(_4\) with an average crystallite size of 8-15nm was synthesized through a sol gel route. The phase purity of the sample was confirmed from the X-ray diffraction analysis. The as prepared sample exhibited grain growth on annealing while no phase transition was observed till 400°C. The optical band gap estimated from UV-Visible absorption exhibits quantum size effect. The Mn-O vibrational modes of the sample were identified through the FTIR spectroscopy. The activation energy of the samples was found to decrease with increase in crystallite size, which shows that the electrical conductivity of the nanocrystals increases in comparison to that of bulk.

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