**International Journal of Research in Engineering and Applied Sciences(IJREAS)**
Available online at http://euroasiapub.org/journals.php
Vol. 7 Issue 1, January-2017, pp. 118~127
ISSN (O): 2249-3905, ISSN(P) : 2349-6525 | Impact Factor: 6.573 | Thomson Reuters Researcher ID: L-5236-2015

# Characterization of Nanostructured Mno Synthesized by Modified Combustion Technique

**J.S Sherin[1],**
*Department of Physics, Karunya University, Coimbatore 641114, India*

**M. Haris[2],**
*Department of Physics, Karunya University, Coimbatore 641114, India*

**D. Shiney Manoj[3]**
*Department of Physics, Christian College Kattakada, University of Kerala, Thiruvananthapuram 695572, Kerala, India*

**J.K. Thomas[4]**
*Department of Physics, Electronic Materials Research Laboratory, Mar Ivanios college, University of Kerala, Thiruvananthapuram 695015, Kerala, India*

## ABSTRACT

We have studied the magnetic properties of MnO synthetized by auto igniting modified combustion technique and its suitability for various applications are reported. The structure and phase purity of the sample analysed by X-ray diffraction, the particle size from the transmission electron microscopy and scanning electron microscopy is 45nm and specifies spherical shape for MnO nanoparticles. The optical properties of the nano MnO are studied using UV-visible absorption spectroscopy which showed that the material is a wide band gap semiconductor with band gap of 3.15 eV. The sample points out maximum absorbance in visible-near infrared region. The photoluminescence spectra indicate intense emission in blue region. Magnetic measurements indicate that the blocking temperature of the MnO structures is 22.4K for $H_c$ = 100 Oe. The magnetization and coercivity of the nanocrystal under FC condition is found to be 0.5709 emu/g and 50.21 G. It is shown that MnO nanoparticles exhibits weak ferromagnetic behaviour due to uncompensated surface spins at low temperature.

**KEY WORDS**
MnO, Nanoparticles, Facile Combustion, Characterization

## INTRODUCTION

The Science of Nanomaterials is substantiating to be one of the most attractive and promising fields for technological development in this century (Shikao and Wang, 2001). In the scientific literature several terms related to Nanoscience can be found, of which it is worth highlighting nanoparticles, nanocrystals, nanofibers, nanotubes and nano-composites. In fact, all these are related to nanostructured materials, which have well-defined structural features. The physical and chemical properties of materials at the nanometer scale (usually set in the range of 1–100 nm) are of immense interest and increasing importance for future technological applications (Afanasiev, 2007). Nanostructured materials often exhibit different properties when compared to other materials (Patil and Mimani, 2001).

Manganese oxides are one of the most versatile cost effective magnetic materials for general use in both low and high frequency devices because of their high resistivity, low dielectric losses and good chemical stability (Angstrong and Bruce (1996), Seo *et al.* (2004). The magnetic properties of manganese oxides strongly dependent on their chemical composition, density and grain size (Ghosh *et al.* 2006). In particular, MnO (*Manganosite*) is known to be an efficient electrode material for the preparation of Li-Mn-O electrodes for rechargeable lithium batteries and for soft magnetic materials, such as magnetic ferrite, which is applicable as magnetic cores in transformers for power supplies Zhang *et al.* (2004), Yang *et al.* (2006) and Na *et al.* (2005). The literatures contain various proposals for the synthesis of MnO nanomaterials using vapour deposition sol-gel, template direction, hydrothermal electro deposition or thermal decomposition method

In this paper we report the synthesis of manganese oxide nanoparticles by facile combustion method as it is simple and cost effective technique. Here the study is aimed to examine the possibility of the synthesized nanopowder as a magnetic material.

## EXPERIMENTAL PROCEDURE

### Preparation of the sample

Manganese oxide nanocrystals were synthesized by a simple auto-igniting combustion method. In this method, aqueous solution containing ions of Mn was prepared by dissolving stoichiometric amount of high purity $MnCl_2 . 4H_2O$ (99.5%, Aldrich) in double distilled water in a beaker. Citric acid (99%, Aldrich) was then added to the solution containing Mn ions. Amount of citric acid and the reducing agents for maximum release of energy during combustion. Oxidant/ fuel ratio of the system was adjusted by adding nitric acid and ammonium hydroxide and the ratio was at unity. The solution containing precursor mixture was heated using a hot plate at 250°C in a ventilated fume hood. The solution boils on heating and undergoes dehydration accompanied by foam. The foam then ignites itself on persistent heating giving voluminous and fluffy black product on combustion. The combustion was calcinated about 610° for 1 hr. The final powder was collected and subsequently characterized as single phase nanocrystals of MnO. The calcined powder was again ground well for 2 h in the ball mill with acetone as the wetting medium. The specimen was again dried well and 5% polyvinyl alcohol was added as a binder and again ground well and dried. The powder was then pressed in the form of a cylindrical pellet at a pressure of 150MPa using

hydraulic press. The pellets were then sintered in a controlled heating schedule of 4° C/min up to 600° C and soaked for 1h to expel polyvinyl alcohol. This was followed by heating the samples at a rate of 5 °C / min up to the optimized sintering temperature with a soaking time of 3h. The samples were then furnace cooled to room temperature.

**Characterization of the sample**.

The structural characterization of the resultant products was done by XPERT-PRO diffractometri using $CuK_{\alpha}$ radiation source for XRD. The morphological study was done by JEOL/EOJSM- 6390 scanning electron microscope (SEM) operated at 5 kV, JEOL/JEM 2100 transmission electron microscope (TEM) operated at 200 KV. The optical studies were done using Shimadzu UV-Vis 2400 pc spectrophotometer (UV -Vis) and Shimadzu RF 5301 PC spectrophotometer in the range 300-550nm. The magnetic studies were done using a Quantum design Vibrating Sample Magnetometer between 1 KOe and 15 KOe at15 K. ZFC and FC measurements were carried out at 100 Oe and the blocking temperature was determined.

## RESULTS AND DISCUSSION

Figure 1 shows XRD pattern of as prepared MnO nanocrystals at different pH obtained directly after combustion. All the combustion synthesized powders was single phase. No diffraction peak that could be related to impurity or secondary phase was observed in the XRD pattern. From the figure, it is noticed that the intensity of XRD peaks of MnO nanocrystal with pH=7 is highly increased. The XRD pattern represents the cubic FCC structure with Fm 3m space group of MnO as per JCPDS (07-230) standards. The sharp intense peak of MnO confirms the high purity and good crystalline nature. The lattice parameter 'a' calculated were also in accordance with the reported value.

The average grain size of the samples were estimated with the help of Debye Scherrer equation

$$D = \frac{0.9\lambda}{\beta \ Cos \ \theta} \quad \text{---------- (1)}$$

Where, λ is the wavelength ($Cu\ K_{\alpha}$), β is the full width at half maximum of the [200] MnO peak and θ is the diffraction angle. The grain size calculated from equation 1 varies from 34 nm to 44 nm as the pH varies from 5.5 to 7.5. The FWHM of the peaks were proportional to crystallite size which indicates better quality with respect to crystallite size of MnO.

The calculated results show significant in lattice strain associated with the crystallite size. The graph between average lattice strain and particular size is shown in fig 2. The variation in the grain size, average lattice strain corresponding to different pH values were tabulated in table 3.1.

Representative SEM and TEM images of the manganese oxide nanocrystals are displayed in fig 3 clearly proves that the obtained samples are composed of well-defined nanoparticles with a high degree of agglomeration. The size of MnO nanocrystals is more uniform with spherical shape. Comparison of the average crystallite size calculated from XRD with average size extracted from TEM images reveals that the nanoparticles are composed of single crystals of the nanometric size region.

Fig 4a shows the UV-Vis. Absorption spectra of the MnO nanocrystal with a sharp excitonic

absorption peak around 423nm in the blue region may due to the interband transition of $Mn^{2+}$ en fm the inner sheel to the uppermost shell as the time passes and also due to quantum confine effect. The optical band gap of MnO nanocrystal is calculated using the Tauc's relation and is shown in fig 4b. Allowed direct band gap of MnO nanocrystals is calculated to be 3.45eV which is almost in agreement with theoretical value ~ 3.42eV. The PL spectra of MnO were recorded in the range of 250-800nm is shown in fig 4c. The sample was excited at 290nm laser wavelength, a peak at 325nm was observed in the emission spectrum. This peak is due to the electronic band to band transition which is in good agreement with tauc's plot of absorption spectrum. The result indicates that MnO has blue fluorescence emission. The band gap was calculated using the formula is about 3.45eV.

The magnetic properties of the MnO nanocrystals with different magnetic field at 50 Oe, 100 Oe and 150 Oe are presented in the figure 5a. The magnetization of the nanocrystals under the FC condition is found to be 21.5 K (50 Oe), 22.5K (100 Oe) and 22.8K (150 Oe). The blocking temperature, $T_B$, is defined as the temperature corresponding to the peak point of the ZFC curve and is a small length scale phenomenon, where the energy required to change the direction of the magnetic moment of a particle is comparable to the ambient thermal energy. From fig, $T_B$ is found to have a value in the range of ~ 21.5 - 22.8 K. The curve behaviour indicates a ferromagnetic to paramagnetic phase transition at 22.5 K. The above magnetic measurement shows that the MnO nanocrystal with diameters less than 45nm show ferromagnetic behaviour instead of antiferromagnetic at low temperatures in consistent with previous reports. The anomalous ferromagnetic behaviour might related to not only the size effect but also the surface spin effect. For certain, the nanoclusters in the MnO nanocrystal have a very high surface to volume ratio, and the surface atoms possess reduced co-ordination of surface spins, which eventually induces a change in the magnetic order throughout the nanoclusters as the surface spin overpowers the body effects.

The temperature – dependent magnetization properties of MnO nanocrystals was investigated in the range of 5K – 20K with an applied magnetic field of -15 KOe to 15 KOe. The curve shows conclusively that MnO nanocrystals exhibit ferromagnetic behaviour at low temperatures. The hysterisis loop at temperatures 5K, 10 K, 15 K and 20 K are 10.5 G, 12.6 G, 25.6 G and 57.1 G respectively and remanence value of 1.05 emu/g, 1.85 emu/g, 5.24 emu/g and 10.59 emu/g which are the typical phenomena for a ferromagnetic material. These results are consistent with superparamagnetic theory which predicts a non-zero value of $H_c$ at temperature lower than $T_B$ (22.5 K). The MnO nanocrystals synthesized in the present study have a greater magnetization than the larger nanoparticles.

## CONCLUSION

Nanocrystalline semiconducting MnO was synthesized through a modified combustion process. The X-ray diffraction studies showed that the nanopowder was single phased with cubic structure. The SEM image of the sintered sample indicates that the material achieved high densification and particles are spherically agglomerated. TEM analysis confirms that the nanocrystalline nature of the sample has a mean size of 45nm. The UV-VIS spectra analysis revealed that the material is a wide band semiconductor of band gap 3.1eV along with good transmittance in the visible region which makes it suitable for transparent conducting oxide films

for window layers on solar cells, warming coatings, and antireflection coatings. The magnetic properties of MnO nanoparticles were investigated by measuring the magnetization in both zero-field cooled and field cooled modes under 100 Oe and150 Oe showed the superparamagnetic behaviour. The transition temperature for MnO is found to be 22.8 K, above which the material is ferromagnetic. The hysteresis loop studies on MnO are the typical phenomena for ferromagnetic material which predicts a non-zero value of $H_c$ at temperature lower than $T_c$. The sample possesses excellent optical and magnetic behaviour which makes this material a promising candidate for electrochromic devices and magnetic materials.

## ACKNOWLEDGEMENTS

The authors acknowledge The Electronic materials research laboratory (EMRL), Mar Ivanios College, Thiruvananthapuram; Central Instrumentation Facility, Karunya University, Coimbatore and Central Instrumentation Centre, Pondicherry Central University, Pondicherry for the facilities provided by them. And special thanks to Rev. Dr. J. W. Prakash, Principal of Bishop Jesudasan Junior College, Etturnagaram, Telangana for his continuous encouragement, prayer and support.

## CONFICT OF INTEREST AND ETHICAL STATEMENT

The authors declared that they have no conflict of interest and we are affirming that, the work described has not been published before; that it is not under consideration for publication anywhere else; that its publication has been approved by all co-authors, as well as by the responsible authorities explicitly at the institute where the work has been carried out.

## REFERENCES

1. Armstrong, A.R.; Bruce, P. G. Synthesis of layered $LiMnO_2$ as an electrode for rechargeable lithium batteries Nature 1996, 381, 499-500.
2. Ghosh, M.; Biswas, K.; Sundaresan, A.; Rao, C. N. R. J. Mater. MnO and NiO nanoparticles: synthesis and magnetic properties Chem. 2006. 16, 106-111.
3. Afanasiev, "Molten salt synthesis of barium molybdate and tungstate microcrystals," Materials Letters, vol. 61, no. 23-24, pp. 4622–4626, (2007).
4. Patil, K.C., Mimani, T.: Solution combustion synthesis of nanoscale oxides and their composites. Mater. Phys. Mech. 4, 134–137 (2001)
5. Seo BB, et al. (2004) Functional expression of the single subunit NADH dehydrogenase in mitochondria in vivo: a potential therapy for complex I deficiencies. Hum Gene Ther 15(9):887-95
6. Seo, W. S.; Jo, H. H.; Lee, K.; Kim, B.; Oh, S. J.; Park, J.T. Size-dependent magnetic properties of colloidal $Mn_3O_4$ and MnO nanoparticles. Angew. Chem., Int. Ed. 2004, 43, 1115-1117.
7. Shikao, S., Wang, J.: Combustion synthesis of Eu activated Y3Al5O12 phosphor nanoparticles. J. Alloys Comp. 327, 82–86 (2001)

8. Yang, L. X.; Zhu, Y. J.; Tong, H.; Wang, W. W.; Cheng, G. F. J. Low temperature synthesis of $Mn_3O_4$ polyhedral nanocrystals and magnetic study. Solid State Chem. 2006, 179, 1225-1229.
9. Zhang, Y. C.; Qiao, T.; Hu, X. Y. J. Preparation of Mn3O4 nanocrystallites by low-temperature solvothermal treatment of γ-MnOOH nano-wires. Solid State Chem. 2004, 177, 4093-4097.

## TABLE AND FIGURES

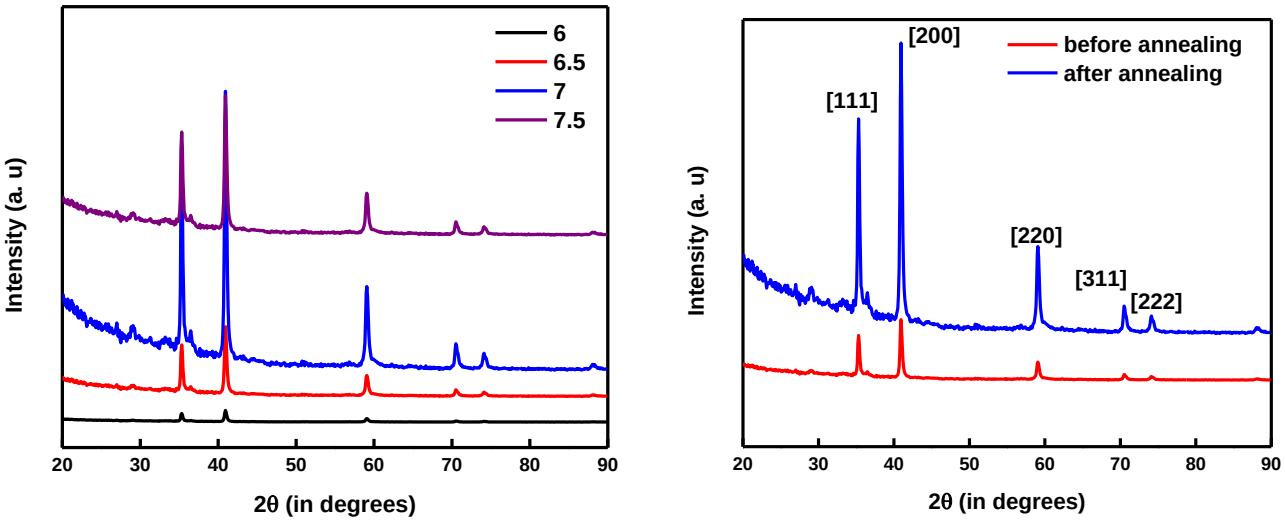


**Fig 1. XRD pattern of MnO nanoparticle with different pH and MnO nanoparticle (pH = 7) before and after annealing**

The lattice strain (ε) has been calculated using tangent formula, $\varepsilon = \frac{\beta}{4\tan\theta}$ ----(2)

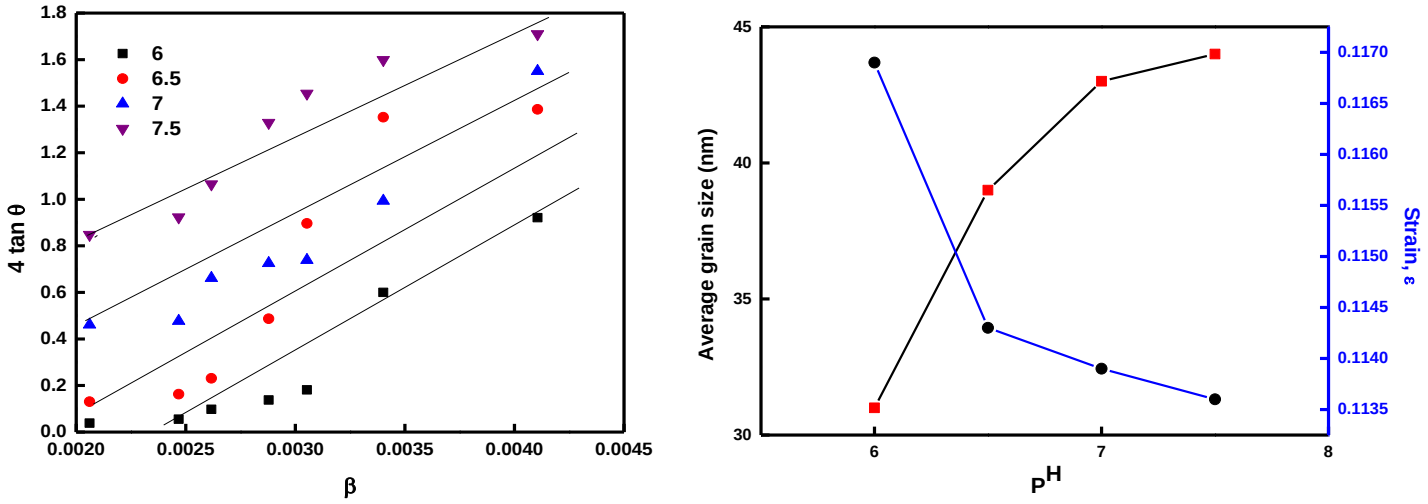


**Fig 2. W-H plot and average strain vs particle size of MnO nanoparticle at different pH.**

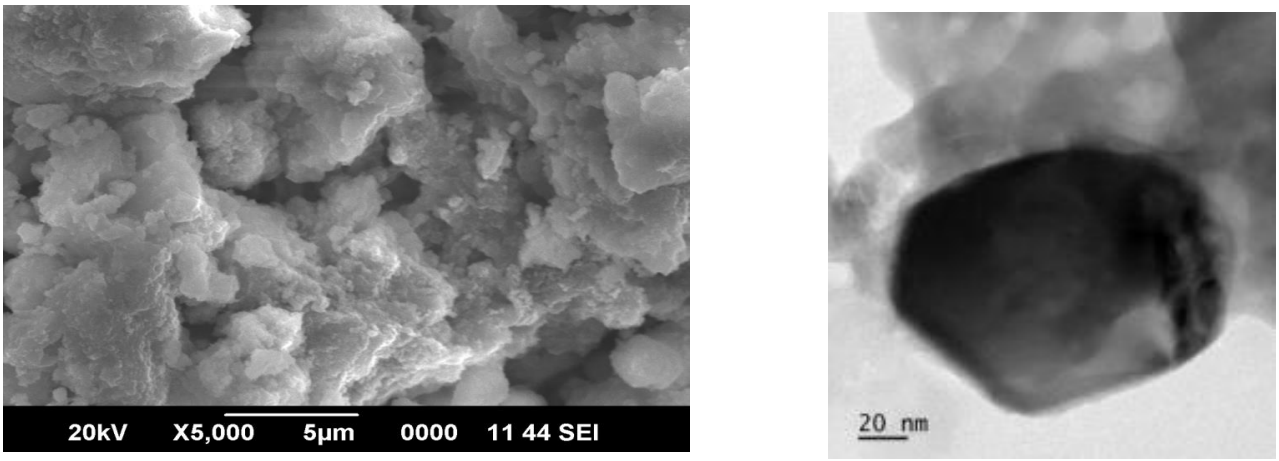


**Fig. 3. SEM and TEM micrograph of MnO nanoparticle**

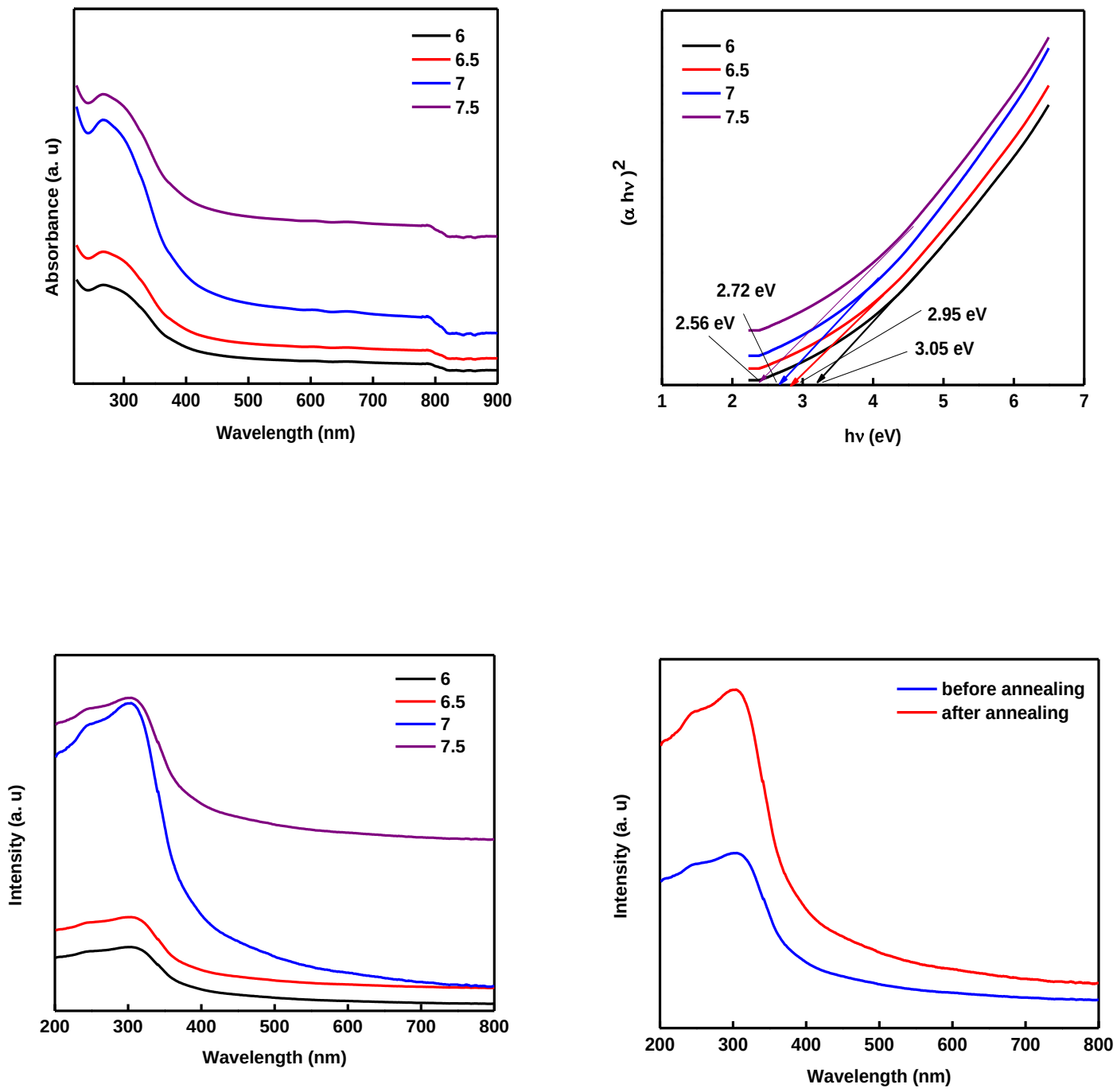


**Fig 4. UV –Vis spectra and Tauc's plot and PL spectra at different pH and at pH = 7 of MnO nanoparticle**

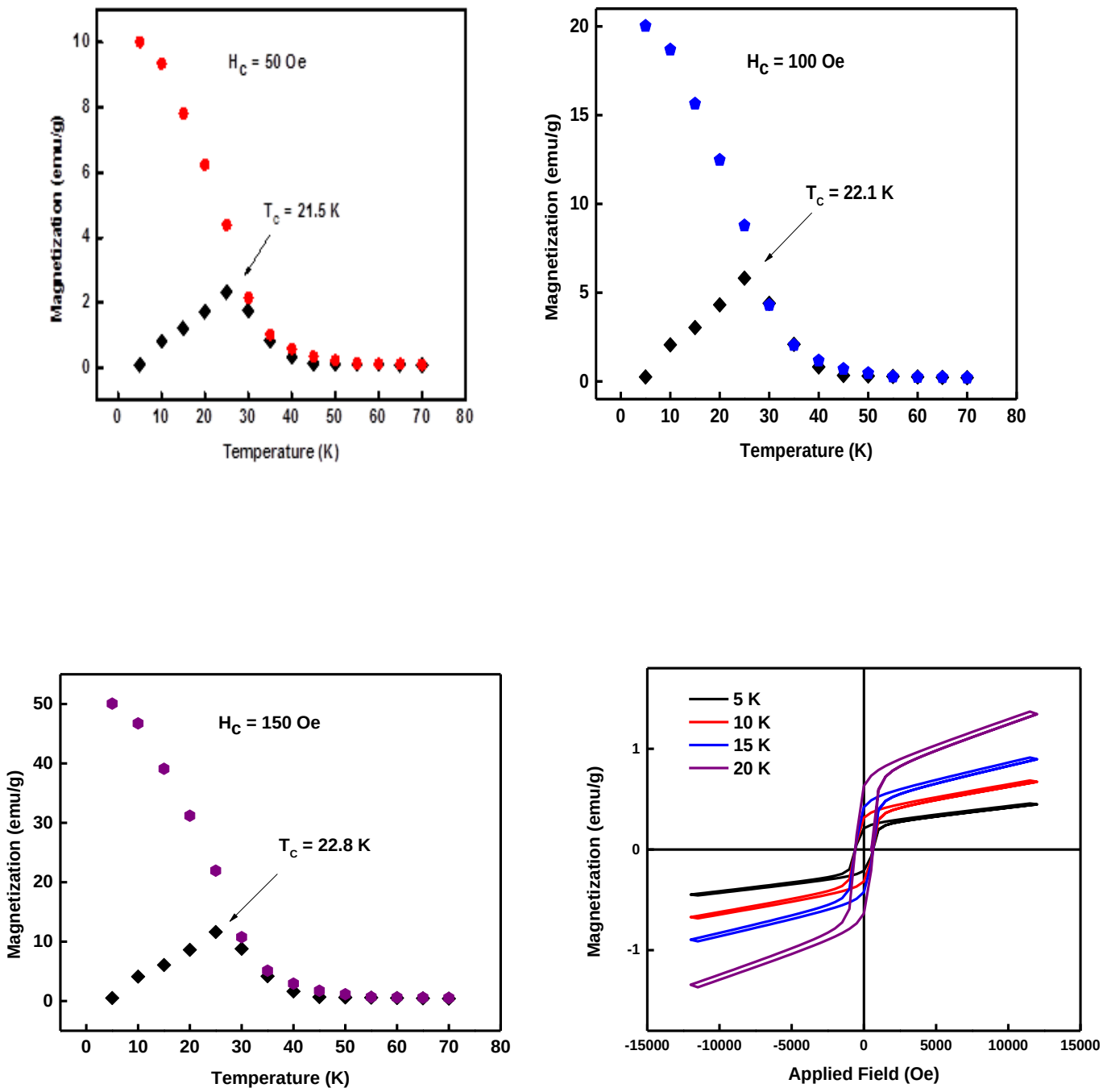


**Fig 5. ZFC-FC curve of MnO nanoparticles at 50 Oe, 100 Oe and 150 Oe and hysteresis curve**

| $p^H$ | Lattice parameter (Å) | | Average grain size, D (nm) | Strain, ε | | Dislocation density, δ ($/m^2$) |
|---|---|---|---|---|---|---|
| | Standard | Calculated | | Calculated | Graph | |
| 6 | 4.445 | 5.05 | 31 | 0.1169 | 0.1164 | $9.98 \times 10^{14}$ |
| 6.5 | 4.445 | 4.92 | 39 | 0.1143 | 0.1148 | $6.57 \times 10^{14}$ |
| 7 | 4.445 | 4.44 | 43 | 0.1139 | 0.1138 | $5.41 \times 10^{14}$ |
| 7.5 | 4.445 | 4.19 | 44 | 0.1136 | 0.1131 | $5.16 \times 10^{14}$ |

**Table 3.1 Lattice parameters, unit cell volume and average grain size values estimated from the XRD pattern of MnO nano-powder.**