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INVESTIGATION OF STRUCTURAL AND MAGNETIC PROPERTIES OF MOLYBDENUM DOPED ZnO NANOSTRUCTURES PREPARED BY MICROWAVE-ASSISTED WET CHEMICAL METHOD

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The Molybdenum doped zinc oxide nanostructures (Mo_x = 1 wt%, 3 wt%, 5 wt% and 7 wt%) were synthesized by wet chemical synthesis method by using microwave irradiation for 15 minutes. The present work focuses on the effect of molybdenum doping on microstructural and magnetic properties of the ZnO nanomaterials. The prepared samples were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and vibrational sample magnetic spectroscopy (VSM). The XRD pattern reveals that Mo is substituted in the ZnO lattice. The SEM micrograph of pure ZnO shows the presence of dumbbell-shaped nanostructures and it's having average length 4.75µm and diameter 2.65µm which is well matched with TEM results. The SEM and TEM micrographs of Mo-doped ZnO samples reveal that the presence of a spherical shaped particle with an average size of 29nm. The presence of Mo and ZnO compounds were confirmed by EDAX spectrum. The magnetic properties of prepared samples were carried out by VSM studies and Mo-doped ZnO nanostructures exhibit the ferromagnetic behaviour at room temperature.

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Keywords: Microwave irradiation, Nanostructures, Wet chemical synthesis, Zinc oxide, ferromagnetic

1. Introduction

ZnO is an attractive semiconductor oxide material having a wide bandgap and is known for its n-type conduction due to the presence of oxygen vacancies [1]. Nowadays, doped ZnO or ZnO mixed with other oxides play a major role in various industrial fields which includes gas sensors, energy storage device and photocatalyst due to their significant properties with different surface morphologies [2, 3]. Few research works are reported about the effect of dopant on ZnO nanostructures. The dopant affects many properties of zinc oxide such as electrical, magnetic and optical properties without any change in the crystal structure. Several elements were doped with ZnO such as Al [4], Ga [5], in [6], B [7] etc for many applications. Among the various dopants, Mo is one of the most suitable metal oxides owing to its interesting speculier characteristics including direct wide bandgap semiconductor, relatively chemical stability, high refractive index, magnetic and electronic properties [8-10]. The ionic radii of Mo^{6+} is 0.062nm and that of Zn^{2+} is 0.083nm, thus it is theoretically possible for Mo^{6+} to substitute Zn^{2+} in the ZnO lattice. Moreover, Mo is the more beneficial impurity and when doped into the ZnO matrix, it can donate 4 electrons to the free carriers due to the high valence difference between Mo^{6+} ions and substituted Zn^{2+} ions. Furthermore, Mo was doped with several elements such as cadmium, Iron, Cerium, Erbium and Indium [11-15]. It is known that materials with important combinations of properties such as room temperature ferromagnetism and semi-conductive properties are required for spintronic and magnetic-optic device applications. The doping of Mo with ZnO can improve some of the important properties such as electrical conductivity, transparency and ferromagnetism at room

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temperature which pave the way for some interesting spintronic and magnetic-optic devices applications. In the present study, Mo is doped with ZnO by using microwave assisted wet chemical technique. Extensive studies were focussed on ZnO nanoparticles by microwave method because of its simple, quick, cost effective and energy saving which could be scaled up easily for the production of highly pure and crystalline ZnO nanostructures [16,17]. The synthesis of Mo-ZnO nanostructure was carried out with optimal power and on/off radiation cycles, for they may have a great effect on the structure and properties of the products [18,19]. A systematic investigation is conducted to reveal the effect of Mo doping on the structural, morphological and magnetic properties of ZnO nanoparticles by using various characterization techniques.

2. Experimental procedure

The 0.1M concentration of zinc acetate solution was prepared and it was neutralized by liquid ammonia (pH-8) under constant stirring. Then, the as-prepared solution was taken to microwave irradiation for 15 min in a household microwave oven. The obtained precipitates were contained some water molecule and which was dried in a hot plate. The dried samples were heated in a muffle furnace at 120°C. The final product was collected and labelled as (A).

Further, MoO_3 was doped with ZnO in the proportion ratio of 1 wt %, 3 wt %, 5 wt % & 7 wt %. Then, 0.1M of molybdenum oxide solution was prepared and mixed with zinc acetate solution in above mention ratios separately. Then, the solution was kept at vigorous stirring for 1h and undergone to 15 min microwave irradiation. All the precipitates are collected carefully and the presence of water molecules was removed by drying on a hot plate. The dried samples were fatherly heated in a muffle furnace at 120°C for 2h. The final products were named as (B) for 1wt% of MoO_3 doped ZnO sample, (C) for 3wt% of MoO_3 doped ZnO sample, (D) for 5 wt % of MoO_3 doped ZnO sample and (E) for 7wt% of MoO_3 doped ZnO sample. The schematic synthesising process of obtaining molybdenum doped ZnO nanopowder is shown in Fig. 1.

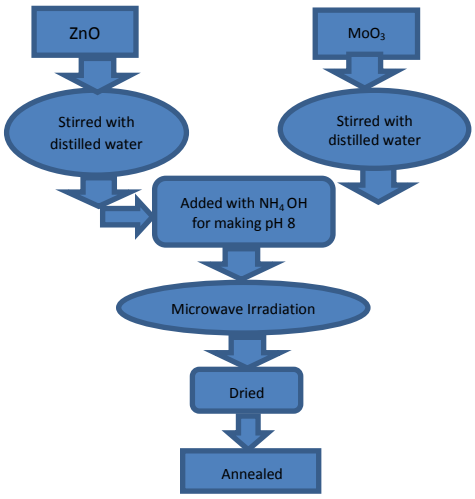


Fig. 1. Schematic diagram of synthesis of molybdenum doped ZnO.

3. Characterization techniques

The as-prepared samples were analysed to know their structure and morphology and its magnetic behaviour was also investigated. The crystal structure and crystalline sizes were analysed by X-ray diffraction technique (XRD, model: PANalytical X' pert Pro). The surface morphology was analysed by scanning electron microscopy (SEM model: Vega-3 S.R.O) and its clear morphology was investigated by transmission electron microscope [TEM, JEOL model:3010]. The

elemental composition of as-prepared samples was analysed by energy dispersive X-ray spectroscopy analysis (EDAX, model: EDAX-EDS-SSD). The vibrating-sample magnetometer (VSM) analysis was performed to evaluate its magnetic behaviour of Mo-doped ZnO samples using [VSM, Lakeshore, USA, model:7407].

4. Results and discussion

4.1. Structure and morphology analysis

The X-ray diffraction patterns of undoped and Mo-doped ZnO nanoparticles are shown in the Fig. 2. The characteristic diffraction peaks of ZnO was observed and carefully indexed. The obtained nanostructures have shown the hexagonal structure corresponding to the JCPDS card number: 89-1397 with (101) as the pretended orientation. In the entire pattern, the characteristic peaks of ZnO such as (100), (002), (101), (102), (110), (113) and (112) were presented. Interestingly, there was no peak corresponding to molybdenum was observed which reveals that the Mo compound has well doped with ZnO compound. Further, any other oxides are not visualised in the XRD patterns which indicated that there is no additional phase presented expect Mo-doped ZnO nanoparticles. In Addition to that, Mo doping has strongly affected the peak intensity of ZnO as seen in Fig. D &E and some small peaks in Fig. A B & C were getting demised due the increasing the doping percentage of Mo compound. The crystallite size D of ZnO-Mo nanostructure was estimated by Scherrer's formula. The crystallite sizes of the nanoparticles were found to be in the ranges from 12 – 25 nm for different ratios of Mo-doped ZnO samples which are shown in Table 1.

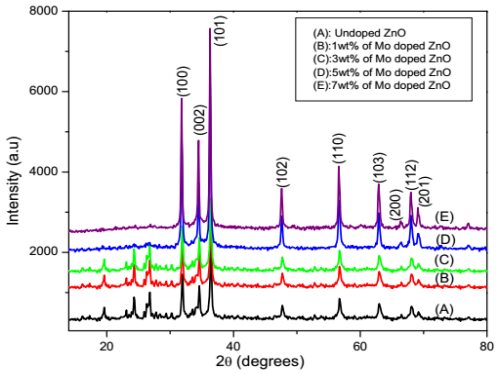


Fig.2. XRD pattern of Mo-doped ZnO nanostructures.

Table 1. XRD Analysis of undoped and Mo doped ZnO.

S.no	***Sample***	***Average particle size in nm***	***d spacing (Å)***
1	A	35.44	2.82036
2	B	31.32	2.81266
3	C	28.84	2.81265
4	D	27.89	2.81110
5	E	27.66	2.80268

Fig. 3 shows the surface topography of the undoped and Mo-doped ZnO nanostructures. The SEM images clearly indicate that the as-synthesized samples were well defined and distinguished from each other. The crystal size of the ZnO changes with doping of Mo. The results also show agglomerated particles of ZnO with Mo doping. The variation of surface morphology occurs due to excess of Mo concentration react with microwave irradiation. EDAX measurements

were performed in order to confirm the presence of molybdenum in the synthesized ZnO-Mo nanostructures and to determine their compositions. Fig. 4 shows the EDAX spectrum of as-prepared samples which demonstrate the presence of various elements in as-prepared undoped and doped samples which provides a precise composition of the elements. Each peak shown in the figure corresponds to elements like Zn, O and Mo with different concentrations. Table 2 shows the percentage of each element for various concentrations. From Fig. 4 it is observed that the distributions of O and Zn elements are homogeneous and exhibits the identical spatial distributions. Moreover, the Mo element is in uniform distribution with ZnO microstructures which indicates that Mo element is loaded on ZnO nanostructures.

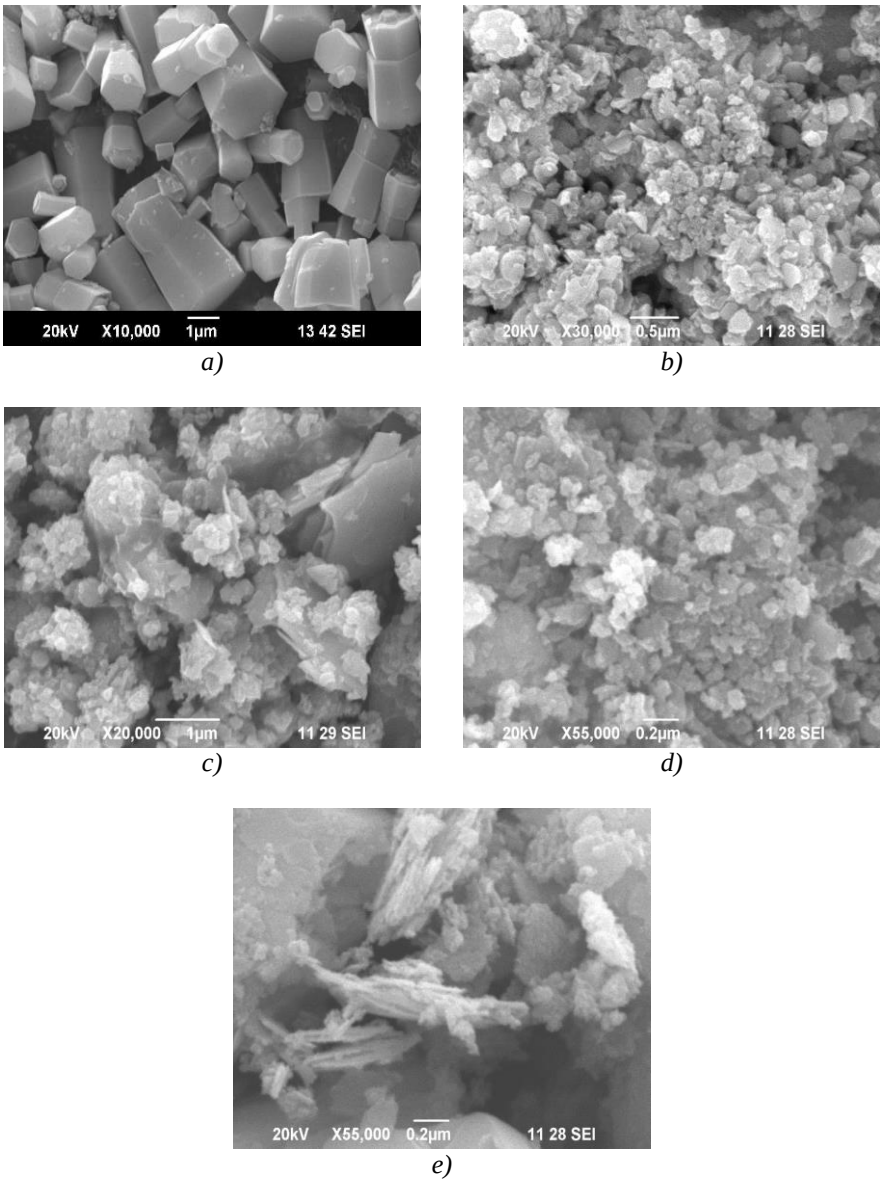
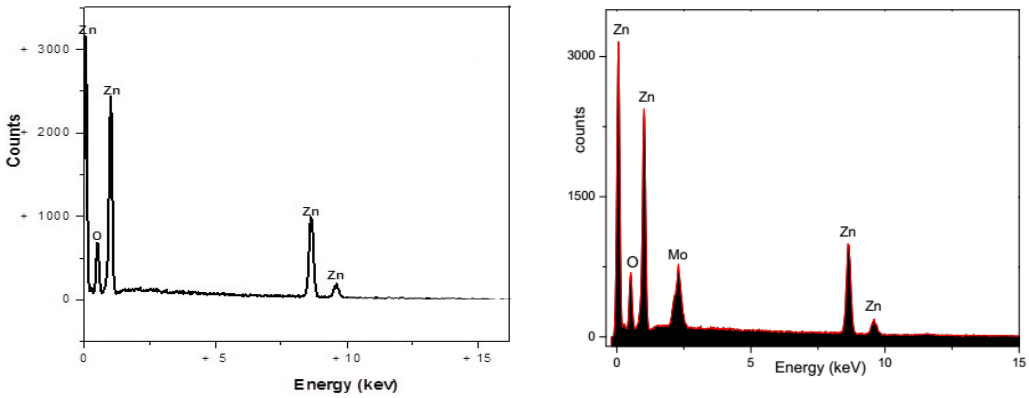


Fig. 3. Shows SEM images of ZnO (a) and Mo-doped ZnO nanostructures (b, c, d, e).



a) *b)*

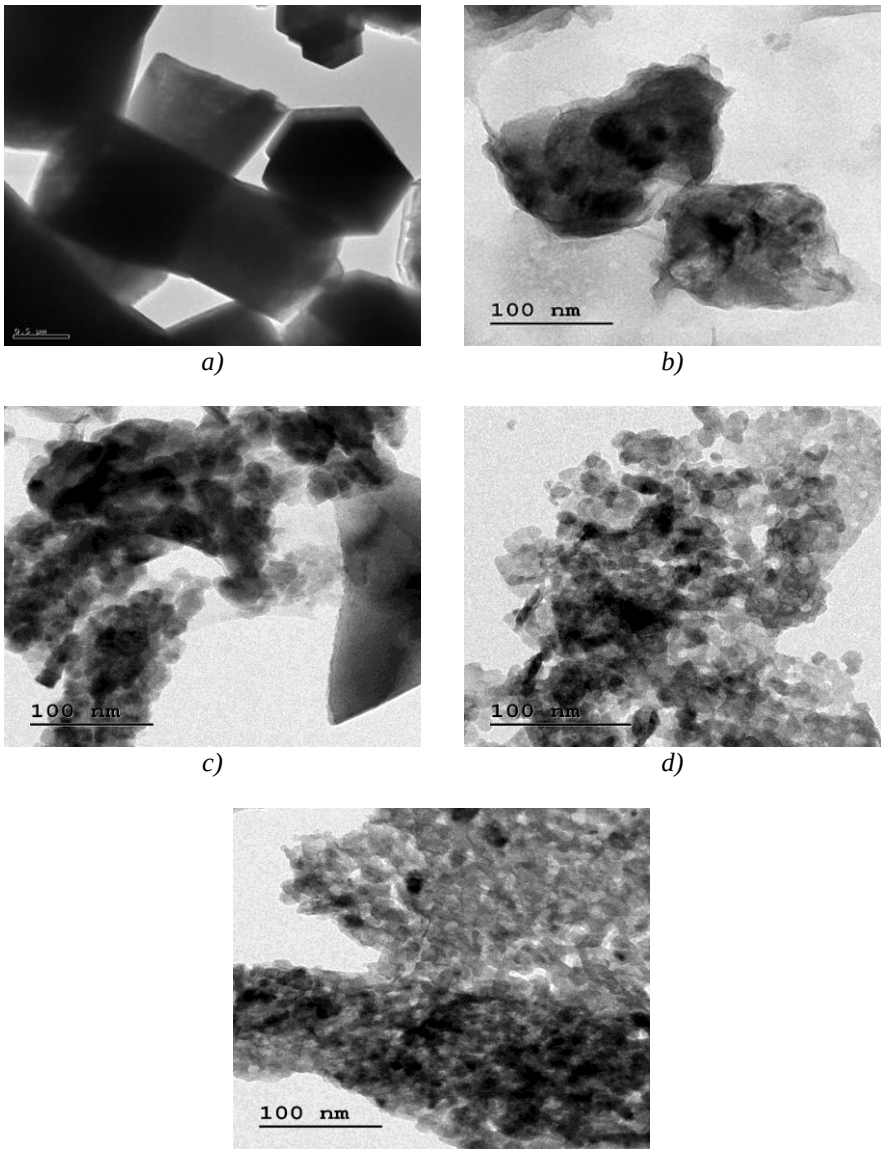
Fig. 4. Shows EDAX spectrum of ZnO (a) and Mo-doped ZnO nanostructures (b).

Table 2. EDAX analysis of undoped and Mo-doped ZnO.

S.No	***sample***	***Zn wt%***	***O wt%***	***Mo wt%***
1	A	92.89	7.11	-
2	B	81.27	18.18	0.55
3	C	75.70	23.75	0.54
4	D	71.91	24.73	3.36
5	E	64.83	24.42	10.75

Fig. 5 shows the TEM micrograph of undoped and Mo-doped ZnO nanoparticles for various concentrations. The morphology of undoped ZnO nanostructures has shown irregular share shape. When the doping concentration is increased from 1 wt % to 7wt%, the morphology of ZnO has shown the unclear and agglomerated structures. This might be ascribed to the microwave irradiation which created hot spot over the surface of samples and distracted the structure of ZnO. Along with that, the doping of Mo compound has also caused this structural variation.

The size of the particles was measured and showed a similar decreasing crystallite size obtained by XRD measurements with the increase in Mo content. The particles did not exhibit definite shape for the investigated samples. When the reaction is accomplished with microwave irradiation, the synthesized ZnO nanoparticles have an absence of definite shape and size which indicates the destruction of recrystallization of ZnO nanoparticles. The TEM image showed agglomeration of the synthesized nanoparticles when the doping level of molybdenum reaches a concentration of 7 wt %.



a) *b)* *c)* *d)* *e)*

Fig. 5. Shows the TEM micrograph of ZnO (a) and Mo-doped ZnO nanostructures (b, c, d, e).

4.2. VSM analysis

The plot of magnetization (M) versus applied a magnetic field (H) at room temperature is shown in Fig. (6). The M-H curve for the undoped ZnO nanoparticles shows a negative moment with an increasing field indicating diamagnetic behaviour of ZnO. The coercivity of Mo-doped ZnO nanoparticles is found to decrease with the increase in Mo doping and this is expected for any ferromagnetic material due to the dilution of the magnetic lattice as a function of doping with a non-magnetic element such as Mo. Interestingly, on the other hand, MPs shows non-monotonic behaviour as a function of Mo doping. First Ms increases upon 3%,5% doping of Mo and then decreases as the doping increases further. The values of saturation magnetization (Ms), coercivity (Hc)and retentivity (Mr) are summarized in Table 3 for different molar concentrations of molybdenum doped zinc oxide nanoparticles. From Fig. 5, it can be observed that the value of the magnetization increases with increasing Mo content due to the fact that the individual Mo ions act as centres of magnetization [20]. Thus the injection of Mo into ZnO induces strong magnetic moment without any distractions in the geometrical symmetry. Comparatively, the ZnO and Mo-doped ZnO samples were showed distinctly hysteresis loop which indicating the samples ferromagnetism at room temperature. The mechanism responsible for the observed ferromagnetism

at room temperature in transition metal-doped ZnO is not clear and has been debated over the years. Nevertheless, a few researchers have claimed to observe ferromagnetic behaviour arising only from a secondary phase and not from the intrinsic property of the material itself. There are several mechanisms proposed in the literature, such as ferromagnetism induced by structural changes [21-24]. In a recent report, Coey *et al*. [25] proposed a ferromagnetic exchange mechanism involving oxygen vacancies (V_O), which form F-centers with a trapped electron, for the observed ferromagnetism in transition metal-doped oxide semiconductors. Overlap of the F-center electron orbitals with the *d* orbitals of the neighbouring transition metal spins (TMs) to form TMs-V_O-TMs groups is crucial for the proposed ferromagnetism coupling. From the discussion above, the ferromagnetic exchange mechanism involving oxygen vacancies model is an appropriate explanation for the observed RTFM behaviour in our Mo-doped samples. It would indicate that the oxygen vacancies are present in our transition metal doped ZnO.

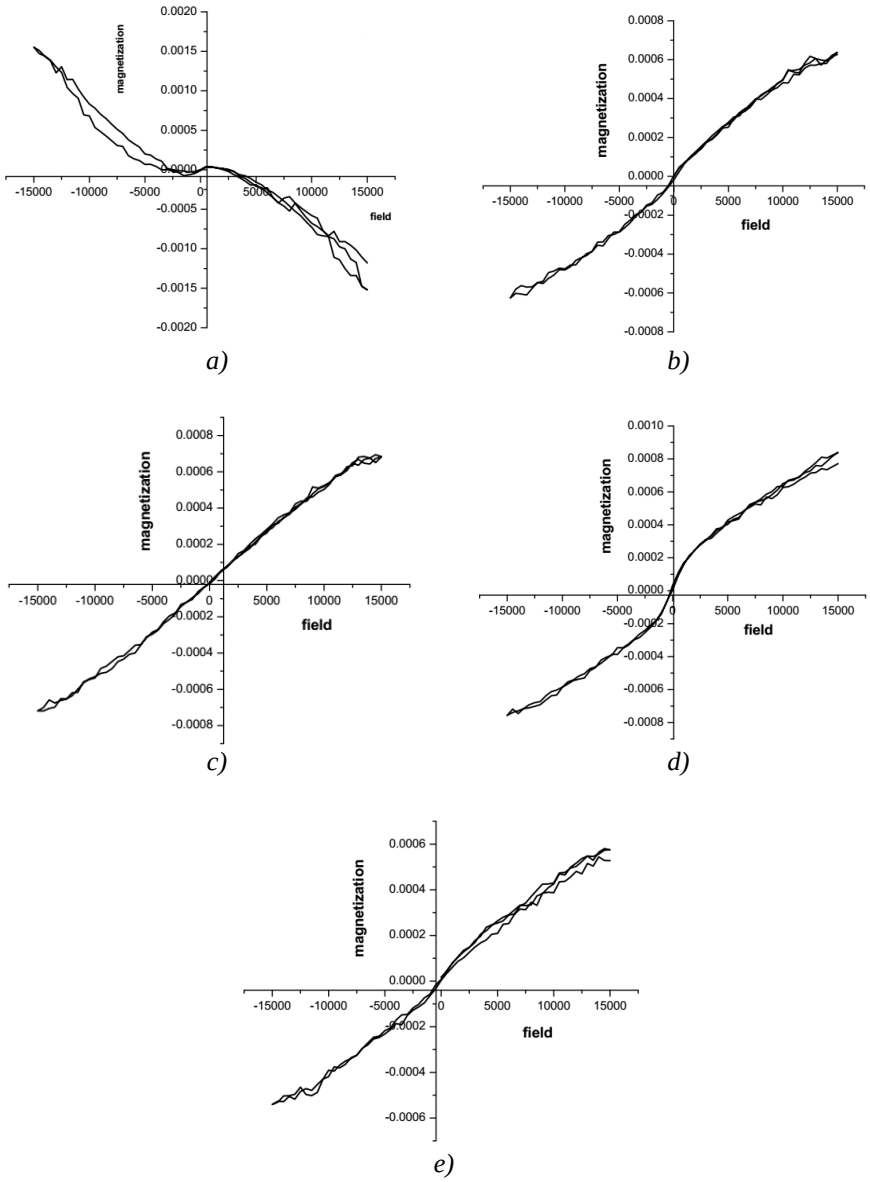


Fig. 6. VSM results of pure and Mo-doped ZnO: (A) – ZnO, (B) ZnO- Mo (1 wt %), (C) ZnO-Mo (3 wt %), (D) ZnO-Mo (5 wt %), (E) ZnO-Mo (7 wt %).

Table 3. VSM analysis of undoped and Mo-doped ZnO.

S.No	*Sample*	*Magnetisation (Ms) in 10^{-6} emu*	*Coercivity (Hc) (Gauss)*	*Retentivity (Mr) 10^{-6} emu*	*Squareness of the M-H curve*
1	A	1536.2	105.77	6.044	0.0039
2	B	631.89	117.60	10.300	0.0163
3	C	706.92	45.663	0.574	0.0008
4	D	798.57	64.165	13.282	0.0166
5	E	560.32	48.132	1.816	0.0324

5. Conclusions

The undoped ZnO and molybdenum doped ZnO with different concentrations were synthesized by wet chemical method. The effect of Mo doping on the structural, morphological, and magnetic properties of ZnO nanoparticles was studied. The XRD analysis shows that Mo-doped ZnO nanoparticles possess a hexagonal structure with (002) preferred orientation.

The microscopic analysis revealed that the surface morphology of the ZnO nanoparticle is disturbed due to various Mo doping percentage and microwave irradiation due to hotspot creation during the irradiation. In order to understand the magnetic properties, VSM study was carried out at room temperature. All the samples were found to exhibit room temperature ferromagnetism. The specific magnetization values were found to increase with increasing Mo concentration.

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