Studies on Magnetic Behavior of Manganese Doped CuO – CuS Nanocomposites

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ABSTRACT *$CuS_xO_{(1-x)}$ (with x values 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0) nanocomposites doped with 1 mole percent Mn^{2+} was successfully synthesized by solvothermal method using a domestic microwave oven. The as-prepared samples were annealed for about 200 °C and the annealed samples were characterized using by powder X-ray diffraction analysis (PXRD) and the magnetic measurements were carried out at room temperature using a vibrating sample magnetometer (VSM). The structure of the material and particle size was obtained from PXRD analysis. The magnetic measurements indicate paramagnetic nature for all the prepared samples.*

Keywords: *Annealed, microwave, magnetic measurements, solvothermal, nanocomposites.*

I. Introduction

Synthesis and properties of nanostructured materials is one of the most important areas in modern materials science and technology. Nanomaterials are not only a kind of ideal system for the study of many physical properties, but also possess potential applications in fabrication of electronic and optical devices. Nanosize materials exhibit unique electronic, magnetic, optical, catalytic and medicinal properties as compared with the traditional and commercial bulk materials. It is due to its quantum size effect, large surface to volume ratio. Copper oxide and copper sulphide are the p-type narrow band-gap semiconductor material, with capability to form various nanostructured morphologies such as nanotubes (Cao et al 2003, Liu et al 2007), nanowires (Chen et al 2008, Roy and Srivastava 2006), nanoparticles (Yadav and Bajpai 2017, Aparna et al 2012), honeycombs (Liu et al 2007), and hierarchical nanostructures (Li et al 2010, Gao et al 2008) has attracted great deal of attentions for versatile applications such as solar cells (Shuai et al 2018), catalysis (Zhou et al 2006) and photocatalysis (Zhu and Qian 2010, Tanveer 2014), gas sensors (Yang et al 2011), biosensors (Qian et al 2013).

In this article, nanocomposites of Mn^{2+} doped $CuS_xO_{(1-x)}$ (with x values 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0) were prepared by a simple solvothermal method using a domestic microwave oven. Then the samples were characterized structurally and magnetically by PXRD and VSM analysis. The results obtained were reported and discussed.

II. Experiment

A. Metodology

Mn^{2+} doped $CuS_xO_{(1-x)}$ (with x values 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0) nanocomposites were prepared by using the precursors manganese acetate, copper acetate, urea, thiourea and distilled water as solvent. All chemicals used were of analytical reagent (AR) grade. Mn^{2+} doped CuO (when x= 0) nanoparticles were synthesized by taking copper acetate and urea in 1:3 molecular ratio along with 1 mole% of manganese acetate. The precursors are rehabilitated as solution by dissolving them separately in 200 ml distilled water using a magnetic stirrer. Then the urea solution was added drop-wise into the copper acetate solution kept under stirring. The resultant solution was kept in a domestic microwave oven (operated with a frequency of 2.5 GHz and power 800 W). The microwave irradiation was carried out until the solvent gets evaporated and a colloidal precipitate was formed. The colloidal precipitate was washed several times with double distilled water and then with acetone to remove the organic impurities present if any. The washed samples were dried in atmospheric air and then collected as yield. Similarly Mn^{2+} doped CuS (when x= 1) nanoparticles were prepared by taking copper acetate and thiourea. The composites of Mn^{2+} doped $CuS_xO_{(1-x)}$with x = 0.2,0.4,0.5,0.6,0.8 were prepared by taking manganese acetate, copper acetate, urea, thiourea. The method of preparation were same as that used for CuO nanoparticles preparation. A total of seven samples were prepared and annealed at a temperature of 200 ˚C.

B. Characterization

The annealed samples were characterized by powder X -ray diffractometer (XPERT-PRO) using Cu Kα (λ=1.54060 Å) radiation. The magnetic measurements of these samples were analysed using vibrating sample magnetometer.

III. Results and discussions

3.1 PXRD analysis

Figure 1 shows the PXRD pattern recorded for the Mn^{2+} doped $CuS_xO_{(1-x)}$ (with x values 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0) nanocomposites. The diffraction peaks obtained in the spectra were indexed by the using of the standard JCPDS data (card no: 78-2391 for CuS, 89-2531 for CuO). The broadening of the peaks in the PXRD pattern indicates the nanocrystalline nature of samples. The diffraction peaks obtained in the spectra corresponding to the x values 1.0 and 0.0 possess hexagonal structure of CuS (Chen et al 2006) and monoclinic structure of CuO (Kannaki et al 2012) respectively. The diffraction peak obtained in the spectra corresponding to the x value 0.2, 0.4, 0.5, 0.6, and 0.8 comprises mixed phase of CuS and CuO which confirms the formation of nanocomposites. No diffraction peaks corresponding to manganese are observed in the PXRD pattern of Mn^{2+} doped $CuS_xO_{(1-x)}$nanocomposites. Moreover the Mn ions are fused into the lattice of the host material which produces a small shift in the diffraction peak to the lower angle side. This can be ascribed by Vegard's law, which state that the dopant alone cannot produce individual peak other than the host peaks, but can generate adequate shift in the position of host peaks (Chaki et al 2014,Elango et al 2012). The obtained PXRD pattern indicates that the decreasing concentration of oxygen sharpens the diffraction peaks, which in turn increases the particle size. The average particle size were calculated by Scherer relation (Kannaki et al 2012) and it was found to be 27.04 - 43.04 nm.

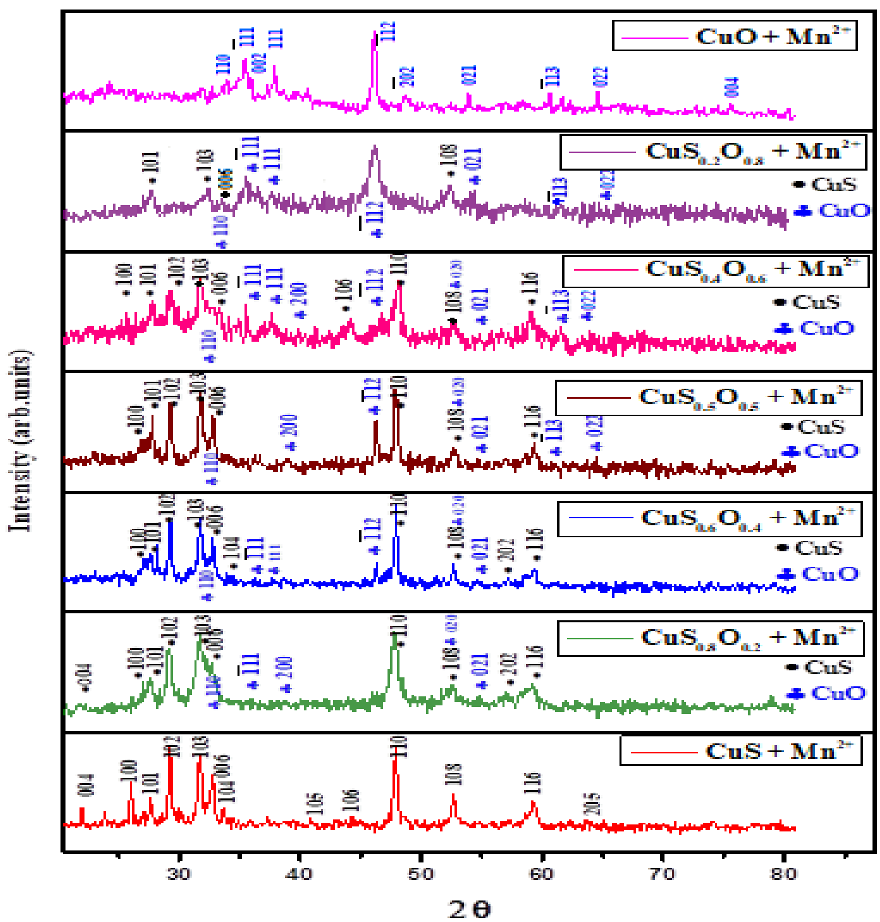


Figure 1: PXRD pattern of Mn^{2+} doped$CuS_xO_{(1-x)}$ nanocomposites

3.2 VSM measurements

Figures 2 – 8 show the plots of the magnetization 'M' versus applied field 'H' recorded at room temperature ranges from −15000 G and +15000 G of the Mn^{2+} doped $CuS_xO_{(1-x)}$nanocomposites. The hysteresis loop of Mn^{2+} doped $CuS_xO_{(1-x)}$nanocomposites are found to have a paramagnetic nature that is revealed by the linear magnetic hysteresis behaviour shown by the samples. The obtained coercivity and remanent magnetization values, also exhibits paramagnetic behavior (Freeda and Mahadevan 2017) of the prepared samples. The observed values of saturated magnetization (M_s), remanent magnetization (M_r), coercivity (H_c) and squareness ratio (M_r/M_s) data are given in Table 1. It reveals that the squareness ratio and coercivity for Mn^{2+} doped $CuS_{0.5}O_{0.5}$nanocomposite is minimum. While squareness ratio is maximum for Mn^{2+} doped CuS nanoparticle. The coercivity and remanent magnetization is maximum for Mn^{2+} doped $CuS_{0.2}O_{0.8}$nanocomposite. The remanent magnetization is minimum for Mn^{2+} doped $CuS_{0.6}O_{0.4}$nanocomposite. When the concentration of x decreases from 1 to 0, the saturated magnetization (M_s) increases except CuO (x = 0). Low saturated magnetization was observed for Mn^{2+} doped CuS nanoparticles, and high saturated magnetization was observed for the middle composition that is, $CuS_{0.5}O_{0.5}$ (x = 0.5). The observed values also indicates that the nanocomposites prepared are considered as an interesting magnetic material.

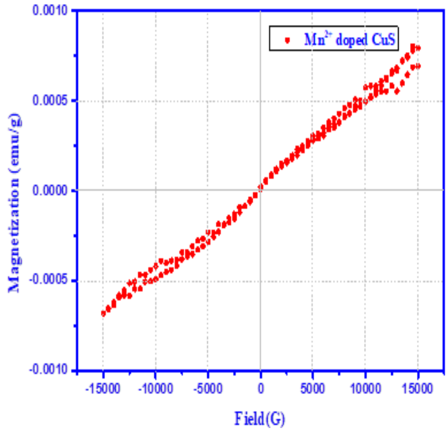
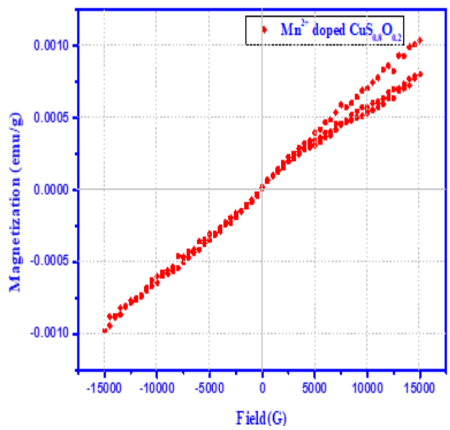


Figure – 2



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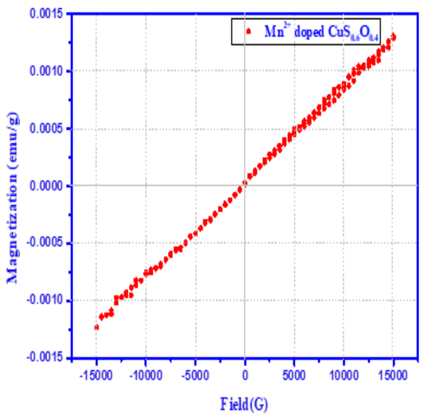

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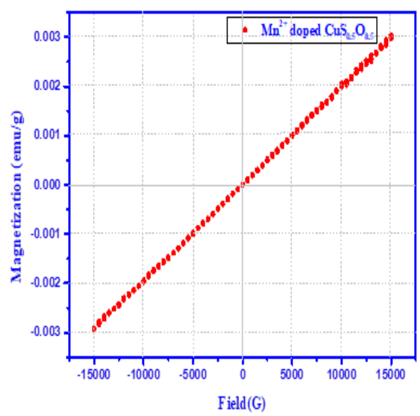


Figure – 5

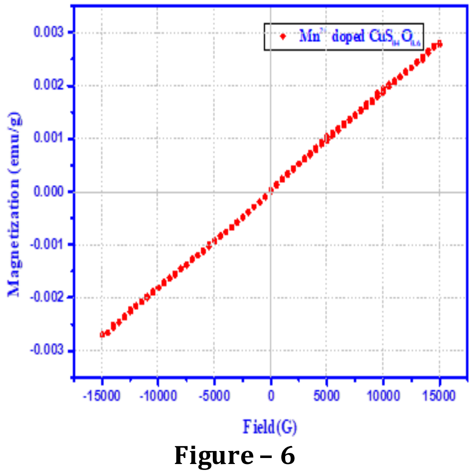
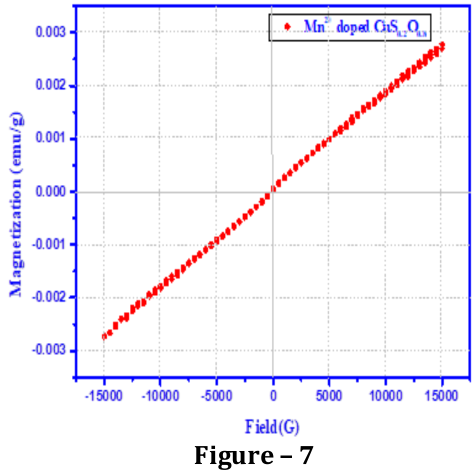


Figure – 6



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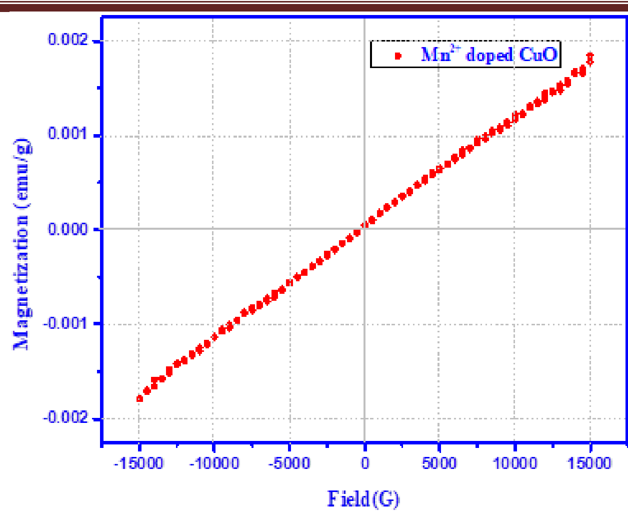

Figure – 8

Figure 2 – 8 M-H plots for Mn^{2+} doped $CuS_xO_{(1-x)}$nanocomposites

Table 1:
Summery of saturated magnetization (Ms), remanent magnetization (M_r) coercivity (H_c) and Squareness ratio (M_r/M_s) data (observed from VSM) of Mn^{2+} doped $CuS_xO_{(1-x)}$nanocomposites

System	CoercivityH_c(G)	Remanent magnetization M_r (x10^{-6} emu)	Saturated magnetization M_s(x10^{-3} emu)	Squareness ratio (M_r/M_s)(x10^{-3})
CuS + Mn^{2+}	59.732	6.562	0.741	8.556
$CuS_{0.8}O_{0.2}$ + Mn^{2+}	37.431	2.744	1.008	2.722
$CuS_{0.6}O_{0.4}$ + Mn^{2+}	15.474	1.749	1.269	1.378
$CuS_{0.5}O_{0.5}$ + Mn^{2+}	13.155	3.888	2.979	1.305
$CuS_{0.4}O_{0.6}$ + Mn^{2+}	15.695	5.353	2.743	1.951
$CuS_{0.2}O_{0.8}$ + Mn^{2+}	76.226	20.587	2.752	7.480
CuO + Mn^{2+}	29.433	3.516	1.820	1.931

IV. Conclusion

In this article, nanocomposites of Mn^{2+} doped $CuS_xO_{(1-x)}$ (with x values 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0) were successfully synthesized using a facile microwave assisted solvothermal method and their structural and magnetic features were discussed. The PXRD results revealed that the decreasing concentration of oxygen sharpens the diffraction peaks, which in turn increases the particle size. M-H plots shows that the Mn^{2+} doped $CuS_xO_{(1-x)}$nanocomposites are found to have a paramagnetic nature that is revealed by the linear magnetic hysteresis behavior shown by the samples. The magnetic measurements revealed that the nanocomposites prepared are considered as an interesting magnetic material and also, it could be understood that the nanocomposites prepared are expected to be useful in poultry roofs, solar cells, electro-optical devices, etc.

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