Anomalous magnetic behavior in the transition metal ions doped Cu₂O flower-like nanostructures

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ABSTRACT

Cuprous oxide (Cu₂O) flower-like nanostructures doped with various metal ions i.e. Fe, Co, Ni and Mn have been synthesized by an organic phase solution method. The powder X-ray diffraction study clearly reveals them as single phase simple cubic cuprite lattice. Study of their magnetic properties have shown that these doped samples are ferromagnetic in nature; however, no such property was observed for the undoped Cu₂O sample. The magnitude of the ferromagnetic behavior was found to be dependent on the dopant metal ions amount, which increased consistently with its increase. As total magnetic moment contribution of the doped metal ions calculated was insignificant, it is believed to have originated from the induced magnetic moments at cation deficiency sites in the material, created possibly due to the disturbance of the crystal lattice by the dopant ions. The existence of the defects has been supported by photoluminescence spectra of the doped samples.

1. Introduction

Nanostructured semiconductors have attracted a lot of attention, due to their potential applications in electronic, optical and superconductor devices. The fundamental properties of these nanomaterials are found to be dependent on their architectures, including geometry, morphology and hierarchial structures. Therefore, controlled manipulation of shapes and size of the semiconductor nanomaterials is required to yield the desired properties [1–5]. This is one of the most interesting as well as the most challenging aspect in the synthesis of semiconductor nanomaterials. In the recent times, a lot of effort has been put by the scientific community to develop novel methods to synthesize special nanostructures of the metal oxide semiconductor nanomaterials. It has been reported in the recent literature that unique morphologies exhibit superior electronic, photocatalytic and photonic properties than the conventional morphologies like nanoparticles, nanowires, etc. of the same material [6–9]. The utility of these materials has been extended by introducing additional properties, while retaining the existing properties. Methods for introducing new magnetic, optical, electronic, photophysical or photochemical properties to semiconductor nanomaterials are attracting an intense interest as prospects for nanotechnological applications emerge in the areas of spintronics, opto-electronics, quantum computing, photocatalysis and luminescence labeling. An effective method for manipulating the physical properties of the semiconductors involves impurity doping.

A great deal of attention has been given to doping of semiconductors with transition metal ions, such as Fe, Co, Ni, Mn, etc. These doped nanomaterials have been demonstrated to show coexistence of different physical properties like semiconducting and ferromagnetism [10]. There are many reports in the recent literatures to have achieved ferromagnetism in these materials as a result of doping them with transition metal ions; however, it is still a great challenge to produce room temperature ferromagnetic behavior as these reports are generally observed at low temperatures. There has been an intense research still going on to realize ferromagnetism in semiconductors with Curie temperature at and above the room temperature, because of their usefulness in the area of spintronic devices which are known to exploit spin of the carriers [11]. Spintronics is the technology where an electron spin carries the information rather than conventional electron charges, and therefore can give result in combination of standard electronics with spin dependent effects that arise from the interaction between spin of the carrier and the magnetic properties of the material. It can be said that by addition of spin degree of freedom to conventional semiconductors charge based electronics or using the spin degree of freedom alone will add substantially more capability and performance to electronic devices, which in effect gives advantages of non-volatility, increased data processing speed, decreased electric power consumption and increased integration densities [12].

Among all the semiconductors, cuprous oxide (Cu₂O) has been widely studied for its interesting semiconducting and optical properties. Cuprous oxide, a *p*-type semiconductor metal oxide, has a direct band gap of ~2.1 eV. It crystallizes in simple cubic

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lattice with space group $Pn3m$, where Cu atoms are located at conventional face centered cubic lattice and O atoms at the (¼, ¼, ¼) and (^{3}/$_4$, ^{3}/$_4$, ^{3}/$_4$) positions [13]. It is one of the first semiconductors studied in the solid state electronics as it has several advantages over other semiconductors. It is one of the most abundant and accessible semiconductor materials in addition to being quite inexpensive and environment friendly. It is a potential material for low cost solar cells. It has been used for catalysis in water splitting experiments in the presence of visible light. It has also been utilized for photo-degradation of various dye molecules and in the gas sensor technology [14–17]. Cuprous oxide basically is a diamagnetic material as the d shell of Cu^+ is full and neither Cu^+ nor O^{2-} is a magnetic ion; however, anomalous magnetic behaviors have been reported in the recent literature for the undoped Cu_2O nanomaterials, and also for the metal ion doped Cu_2O samples, attributed to the defects created, due to the cation deficiency in the material. These defects are known to have induced magnetic moments, which may give rise to stable ferromagnetically coupled ground state. If the defects are present in sufficient concentration, these couplings may result in change of magnetic property from diamagnetic to paramagnetic or ferromagnetic behavior, due to conjunction effect of the induced magnetic moments in the material [18–26]. It has also been investigated theoretically on the basis of ab $initio$ calculations, using density functional theory that doping of transition metal ions in the cuprous oxide lattice may result in the generation of defects and these defects which are either cation or anion vacancies, may further result in culmination of ferromagnetism in the material [27].

Recently, there are some recent reports in the literature to have achieved ferromagnetism in the Cu_2O nanomaterials, which they have attributed to the induced magnetic moments at the defect sites. For example, Chen et al. [28] have reported ferromagnetic behavior for their Cu_2O samples at 5 K temperature. Similarly, Liao et al. [29] have reported an observation of ferromagnetism in Cu_2O nanowires at room temperature. However, these works are either done at low temperature or their magnetic properties i.e. coercivity and saturation magnetization are not significant enough, making them unusable for the practical purposes in the applications. We also have reported recently that the observation of room temperature ferromagnetism in the Cu_2O nanorods doped with different metal ions like Fe, Co, Mn and Ni [30,31], with good values of coercivity and saturation magnetization, due to the creation of cation deficiency at various defect sites, because of the presence of the doped metal ions. Herein, we report the study of the magnetic property of the Cu_2O flower-like nanostructures doped with various transition metal ions i.e. Fe, Co, Ni and Mn at room temperature, synthesized by an organic phase solution method. It is still a great challenge to produce room temperature ferromagnetism in the cuprous oxide material. Also, to the best of our knowledge, Cu_2O flower-like nanostructures doped with transition metal ions have not been reported for their study of magnetic property. We observed the ferromagnetic behavior at room temperature for the doped samples. It may be proposed that defects created as cation vacancy in the nanomaterial by the dopant ions contributed to give rise to ferromagnetism. The total magnetic moment contribution from the dopant ions was too insufficient to account for the observed magnitude of the ferromagnetism in the doped samples.

2. Experimental

2.1. Chemical used

Copper nitrate ($Cu(NO_3)_2 \cdot 6H_2O$), ethylene glycol, sodium dodecyl sulphate (SDS), polyethylene glycol sorbitan monooleate (Tween 80), Ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), cobalt acetate ($Co(CH_3COO)_2 \cdot 4H_2O$), nickel acetate ($Ni(CH_3COO)_2 \cdot 4H_2O$), manganese acetate ($Mn(CH_3COO)_2 \cdot 4H_2O$), ethanol and acetone were purchased from S.D. fine Ltd. (India) and used as received without further purification. All of the chemical reagents used in this experiment were of analytical grade.

2.2. Methods

Synthesis of the Cu_2O flower-like nanostructures doped with Fe, Co, Ni and Mn metal ions was done by adopting the well known polyol method. The typical experiment for the synthesis was as follows: the three necked round bottom flask containing 40 mL of the solvent (ethylene glycol) was fitted with water condenser and magnetic stirrer and was heated at 160 °C for 2 h in air. Then, argon gas was introduced into the system and constant flow of which was maintained afterwards throughout the reaction. After purging the solution for few minutes, required amount of 0.06 M solution of $Cu(NO_3)_2 \cdot 6H_2O$ in ethylene glycol was added to it along with the calculated amount of the dopant metal ion precursor. Iron nitrate, cobalt acetate, nickel acetate and manganese acetate were used as the precursor for Fe, Co, Ni and Mn ions, respectively. Surfactants SDS and Tween 80 were then added in the relative ratio of 1:2 into the solution. The reaction mixture was constantly stirred magnetically throughout the reaction. Heated the solution again at 160 °C for further 2 h. Cooled down the solution flask to room temperature and the product was washed with ethanol and acetone, followed by centrifugation several times to remove excess surfactants or any other residue left from the reaction. It was dried in vacuum overnight. The undoped sample was also prepared, following the same procedure without the addition of dopant precursors.

2.3. Measurements

The samples were characterized by powder X-ray diffraction (XRD) using X'pert PRO (PANalytical) X-ray diffractometer Cu $K\alpha$ radiation and Ni-filter in the 2θ range 35–120°. Morphology of the samples were characterized by Ziess, Supra-40 VP Field Emission Scanning Electron Microscopy instrument (FESEM). The room temperature photoluminescence spectra were recorded by using Fluorolog (R)-3 Spectrofluorometer. The magnetic measurements were done at room temperature by Vibrating Sample Magnetometer (VSM).

3. Results and discussion

The powder XRD patterns (Fig. 1) of the synthesized samples were analyzed and found to be single phase crystalline in nature and can be easily indexed to cubic Cu_2O lattice (JCPDS, $Joint$ $Committee$ on $Powder$ $Diffraction$ $Standards$, file 34–1354). There were no detectable impurities or extra phases in the XRD patterns; therefore, only representative XRD pattern is given here. The average crystallite size calculated from Scherrer's equation was approximately 40 nm. The samples doped with more than 0.5% concentration were found to have impurity phase apparently due to the phase separation. An FESEM image in Fig. 2 clearly displays the morphology of the samples, where beautiful flower-like nanostructures of 70–80 nm size were observed. As the morphology of the nanostructures was almost identical for the various doped samples and the undoped sample, only representative electron microscopy image is given here.

The field dependent magnetization measurements at room temperature were studied by vibrating sample magnetometer on the Fe, Co, Ni and Mn metal ion doped samples along with the undoped samples to study their magnetic behavior. The
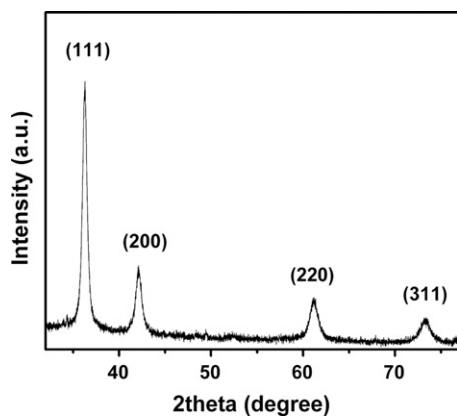
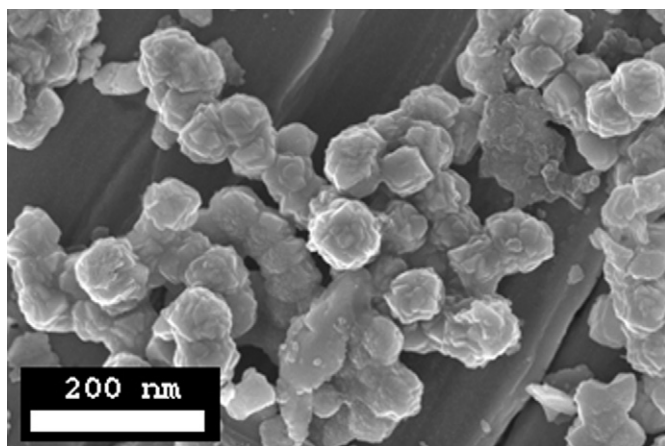**Fig. 1.** Powder X-ray diffraction pattern.

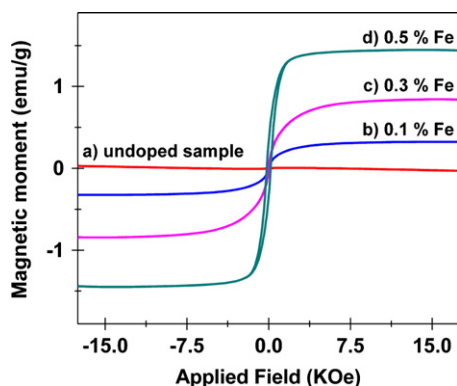**Fig. 2.** Electron microscopy image of Cu$_2$O nanoflowers.

Fig. 3. Magnetization vs. applied magnetic field curves at room temperature: (a) undoped sample, (b) 0.1% Fe doped sample, (c) 0.3% Fe doped sample and (d) 0.5% Fe doped sample.

Fig. 4. Magnetization vs. applied magnetic field curves at room temperature: (a) undoped sample, (b) 0.1% Co doped sample, (c) 0.3% Co doped sample and (d) 0.5% Co doped sample.

Fig. 5. Magnetization vs. applied magnetic field curves at room temperature: (a) undoped sample, (b) 0.1% Ni doped sample, (c) 0.3% Ni doped sample and (d) 0.5% Ni doped sample.

Fig. 6. Magnetization vs. applied magnetic field curves at room temperature: (a) undoped sample, (b) 0.1% Mn doped sample, (c) 0.3% Mn doped sample and (d) 0.5% Mn doped sample.

diamagnetic behavior of the undoped sample was confirmed as expected conventionally for cuprous oxide by its magnetization vs. applied magnetic field (M–H) curve in Figs. 3–6 (hysteresis loop a in all). In the case of Fe doped samples, unexpected ferromagnetic behavior was observed, magnitude of which increases with dopant Fe ions amount in the material. For 0.1%, 0.3% and 0.5% Fe doping (Fig. 3, hysteresis curves b, c and d, respectively), the values of the saturation magnetization (M_s) were 0.324, 0.842 and 1.443 emu/g, respectively. The values of coercivity (H_c) for the same were 0.016, 0.032 and 0.198 KOe. It can be easily understood from these values
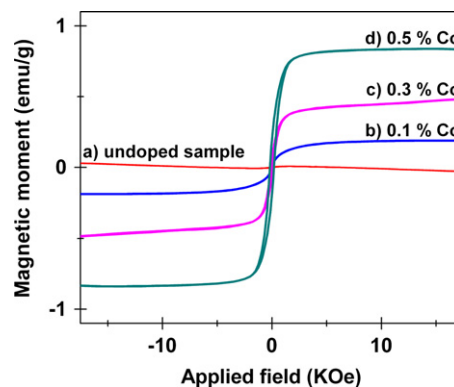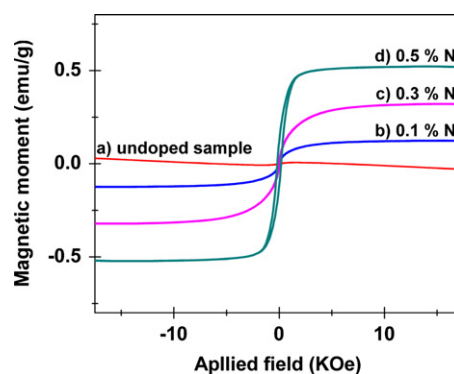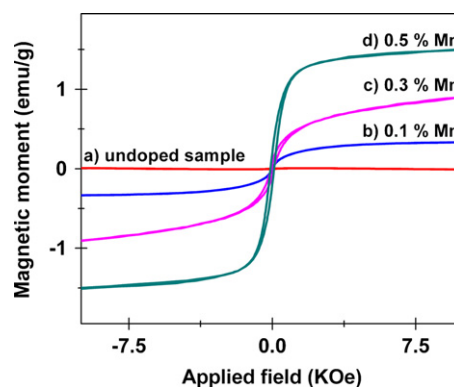
that 0.1% Fe doped samples exhibited weak ferromagnetism, while 0.3% Fe doped sample showed quite good ferromagnetic behavior. The 0.5% Fe doped sample shows substantial magnitude of ferromagnetism; however, doping beyond 0.5% did not yield the desired magnetic property, perhaps due to limited solubility and phase separation.

We have also attempted doping of these flower-like nanostructures with other common magnetic transition metal ions like Co and Ni. In the case of Co doped samples, we again observed

ferromagnetic behavior, magnitude of which increases with dopant Co ions amount. For 0.1%, 0.3% and 0.5% Co doping, the values of the saturation magnetization (M_s) were 0.189, 0.481 and 0.836 emu/g, respectively, as can be seen in Fig. 4 (hysteresis curves b, c and d, respectively). The coercivity values (H_c) for these samples were found to be 0.020, 0.091 and 0.179 KOe for 0.1%, 0.3% and 0.5% Co doped samples, respectively. It can be concluded that while 0.1% Co doped sample exhibited weak ferromagnetism and 0.3% Co doped sample showed quite good ferromagnetic behavior, the 0.5% Co doped sample was observed to display significant ferromagnetism. Anomalous ferromagnetic behavior was also seen in the case of Ni doped samples, which again was dependent on the dopant Ni ion amount. The values of the saturation magnetization (M_s) for 0.1%, 0.3% and 0.5% Ni doping (Fig. 5, hysteresis curves b, c and d, respectively) were 0.124, 0.321 and 0.521 emu/g, respectively. The values of coercivity (H_c) for the same were 0.015, 0.025 and 0.183 KOe. On the basis of these values, we can say that 0.1% Ni doped samples exhibited very weak ferromagnetism, while 0.3% Ni doped sample showed quite fair ferromagnetic behavior. The 0.5% Ni doped sample showed respectable ferromagnetism magnitude. It may noted here that doping Co and Ni ions beyond 0.5% did not yield the desired ferromagnetic property, perhaps due to the phase separation and limited solubility.

Also we tried for doping the flower-like nanostructures with non-magnetic metal ion i.e. Mn ions, where again we witnessed an unexpected ferromagnetic behavior for the doped samples. The magnitude of ferromagnetism was increased when the dopant Mn ion amount was increased. For 0.1%, 0.3% and 0.5% Mn doping (Fig. 6, hysteresis curve b, c and d, respectively), the values of the saturation magnetization (M_s) were 0.334, 0.888 and 1.492 emu/g, respectively. The values of coercivity (H_c) for these samples were 0.017, 0.065 and 0.091 KOe. It can be easily understood from these values that 0.1% Mn doped samples exhibited weak ferromagnetism, while 0.3% Mn doped sample showed quite good ferromagnetic behavior. The 0.5% Mn doped sample showed substantial magnitude of ferromagnetism; however, doping beyond 0.5% did not yield the desired magnetic property, possibly due to limited solubility and phase separation.

It may be assumed preliminarily that this kind of anomalous magnetic behavior was due to the presence of the magnetic metal ions in the case of Fe, Co and Ni ions doped samples; however, this kind of argument does not hold water in case of non-magnetic Mn ion doped samples. To verify whether observed magnetic moments in case of magnetic ion doped samples were due to the presence of magnetic ions only, the contributions of the magnetic moments of the dopant metal ions were determined. The magnetic susceptibility values were calculated according to the following equation:

$$\chi = n\mu_{eff}^2 / 3k_b T$$

where n represents concentration of the magnetic impurities and μ_{eff} represents the effective magnetic moment of the metal ion. The values of μ_{eff} for the magnetic ions Fe, Co and Ni are 4, 3 and 2 μ_B (per atom), respectively (28). The magnetic susceptibility values calculated from this equation for 0.1%, 0.3% and 0.5% Fe dopant amounts were 0.93, 2.79 and 4.66×10^{-7} emu Oe^{-1} g^{-1}, respectively. Therefore, it can be easily said that the total magnetic moments calculated for the doped Fe ions were too negligible in comparison to the observed magnitude of the magnetism. Similarly, values obtained for 0.1%, 0.3% and 0.5% Co ion amounts were found to be 0.52, 1.57 and 2.62×10^{-7} emu Oe^{-1} g^{-1}, respectively. For 0.1%, 0.3% and 0.5% Ni amounts, the calculated values were 0.23, 0.69 and 1.16×10^{-7} emu Oe^{-1} g^{-1}, respectively. Therefore, in the case of Co and Ni doped samples also, the total magnetic moments calculated were too insignificant as compared to the magnitude of the observed ferromagnetism. In the case of Mn doped samples,

there could not be any kind of magnetic contribution because Mn ions are non-magnetic in nature. Even though, Mn_3O_4 clusters in the semiconductor oxides are known to display ferromagnetic behavior, but at low temperature. Also, the magnitude of the observed ferromagnetism was much higher than any possible magnetic contribution of the Mn_3O_4 clusters. Ferromagnetic behavior due to contamination with other impurities was ruled out because the undoped sample prepared in the identical manner as the doped samples exhibited no detectable magnetic moment. Hence, we can say that the ferromagnetism in the cuprous oxide nanoflowers was generated not from the intentionally doped magnetic ions in the material, but from the material itself.

As clear from the above discussion, the magnetic moment contribution directly from the doped metal ions is miniscule if it is compared to the observed magnitude of the ferromagnetism in all the doped samples i.e. Fe, Co and Ni doped and therefore it has been proposed that the observed ferromagnetism might have been originated from the cation deficiency sites, formed due to the doped metal ions in the material. This has been confirmed by our earlier work [30,31], where we have observed ferromagnetic behavior in the Fe, Co, Ni and Mn doped Cu_2O nanorod samples. The induced magnetic moment at defect sites might give rise to high magnetic moment [32,33]. Recently, Soon et al. [34] have reported on the basis of theoretical density functional theory calculations that it can be proved that Cu_2O lattice indeed contains cation deficiency in the material, and these cation deficiency sites may lead to induced magnetic moments, which may conjure up to yield favorable ferromagnetically coupled ground state if present in sufficient concentration in the material as the observed magnetism in the samples could not be simply explained by the magnetic impurities present. There are some recent reports in the literature, which claimed to have achieved ferromagnetism in the cuprous oxide material with or without magnetic impurities, due to the defects created by the cation deficiency at the surface and the grain boundary [28,29] e.g. Chen et al. have reported recently ferromagnetism in the cuprous oxide observed at a low temperature of 5 K, while ferromagnetic behavior was seen in the Cu_2O nanowires at room temperature by Liao et al. We can see easily that our reported ferromagnetism has better magnitude than previous reports; moreover it is observed at room temperature which makes it potential material for practical applications.

The existence of the defects as cation deficiency in the doped materials has been supported by the photoluminescence (PL) spectroscopic measurements in the earlier reports [30,31,35,36]. Here in this work, photoluminescence spectra have been recorded at room temperature for all the doped samples (Figs. 7–10) in reference to the undoped Cu_2O sample (Curve a in all). Strong photoluminescence was observed at room temperature for the doped samples suggesting high efficiency of photon–electron and/ or exciton coupling in the nanomaterials perhaps. Photoluminescence in the undoped as well as doped samples was observed due to the inherent defects as cationic deficiency present in the material. Therefore, intensity of the PL peak increases as the amount of the dopant ion was increased as the defects formation increased too. It is observed in all doped samples i.e. Fe, Co, Ni and Mn, as we increase the amount of the dopant metal ion, the intensity of the PL peak gets increased regularly in reference to the undoped sample. It may be concluded that with more doped ions in the material, the defects formation is more; therefore, the defects contributing to the PL signal are increased. Hence, we see broadened PL peak with more intensity, indicating more photoluminescence with an increase of dopant ions. The defects formation may be due to the result of difference between the ionic radii of the dopant ions and the Cu^+ ions. Also, there is charge disparity between the +1 oxidation state of copper ions and that of dopant ions. Therefore, we can say that long range crystallographic ordering of the cuprite
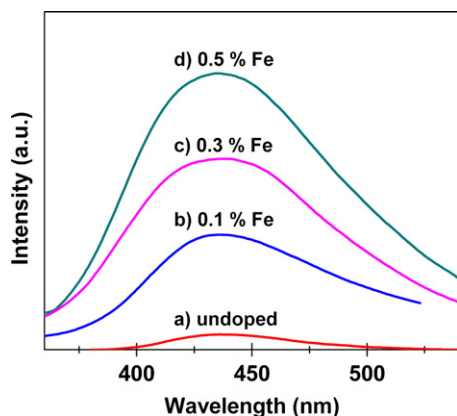
Fig. 7. Photoluminescence spectra at room temperature: (a) undoped sample, (b) 0.1% Fe doped sample, (c) 0.3% Fe doped sample and (d) 0.5% Fe doped sample.
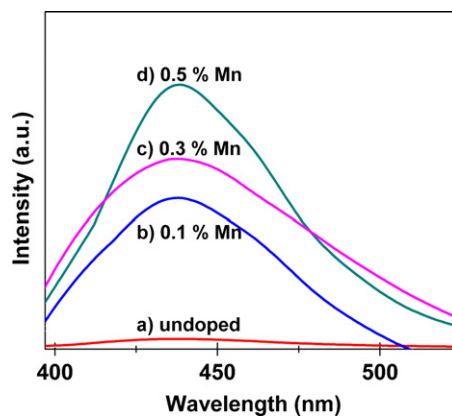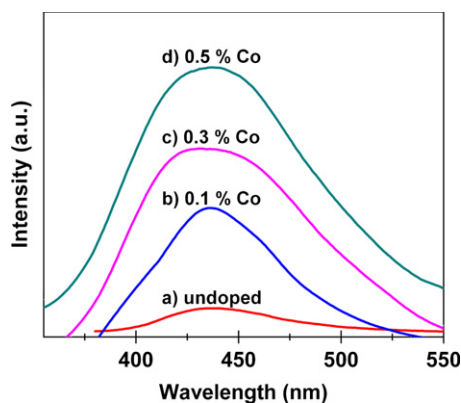

Fig. 8. Photoluminescence spectra at room temperature: (a) undoped sample, (b) 0.1% Co doped sample, (c) 0.3% Co doped sample and (d) 0.5% Co doped sample.
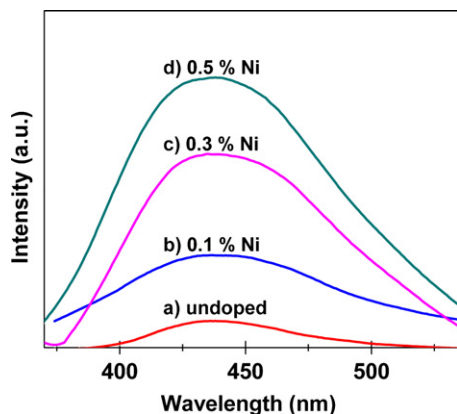

Fig. 9. Photoluminescence spectra at room temperature: (a) undoped sample, (b) 0.1% Ni doped sample, (c) 0.3% Ni doped sample and (d) 0.5% Ni doped sample.

crystal lattice is disturbed and results in the generation of cation deficiency in the material. This argument is consistent with the fact that with more doping of metal ions in the material, there are more disturbances in the crystal lattice, giving rise to more deficiency of cations. Now these defect sites contribute to increase the PL signal and also induce magnetic moment. So, it results in more contribution to the ferromagnetic moments with an increase of dopant ions in the material after achieving certain critical amount of the cation deficiency cites. We may easily correlate that an increase in PL peak intensity is in coherence to the magnitude of the ferromagnetism in

Fig. 10. Photoluminescence spectra at room temperature: (a) undoped sample, (b) 0.1% Mn doped sample, (c) 0.3% Mn doped sample and (d) 0.5% Mn doped sample.

the doped samples. There is more defects formation in the nanomaterials than the bulk counterpart at the surface. Therefore, we may say that this kind of anomalous magnetic behavior is perhaps due to the combined effect of the size effect, which helps in the formation of more defects in the material and also due to the dopant ion presence.

4. Conclusions

Flower-like nanostructures of cuprous oxide doped with Fe, Co, Ni and Mn metal ions were prepared by an organic phase solution method. They were found to be single phase simple cubic Cu_2O lattice structure. Their magnetic studies have shown that these are ferromagnetic in nature at room temperature; however, no such property was observed for the undoped Cu_2O sample. The magnitude of the ferromagnetic behavior was found to be dependent on the amount of dopant ions, which increased consistently with its increase. The magnetic moment contribution from the doped metal ions was calculated and found to be insignificant. Therefore, ferromagnetism might be due to the induced magnetic moments at cation deficiency sites in the material. The existence of the defects was supported by room temperature photoluminescence spectra. Further detailed investigations, both theoretical and experimental, to understand the effect of doping the metal ions are needed. Efforts are going on in this direction.

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