

Intrinsic Ferromagnetic Behavior in Fe-doped Cu₂O Octahedra Due to Cation Vacancy Defects

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Cu₂O octahedra doped with Fe ions were prepared by simple room temperature synthesis. They were found to exhibit paramagnetism at room temperature and ferromagnetic behavior at 77 K. The room temperature Mössbauer spectra indicate that iron is present only in the form of paramagnetic Fe²⁺ ions. The magnetic moments were observed to be increasing with increase of Fe ions in the materials, therefore suggesting that ferromagnetic behavior might have originated from defects created due to the dopant ions and not from the metal ion itself. The photoluminescence and EPR spectra fully supported the existence of the defects in the lattice.

Keywords: Octahedra, Cuprous oxide, Ferromagnetism, Mössbauer spectroscopy.

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1. INTRODUCTION

Semiconductor nanomaterials are of immense potential in the current era as they are very useful in different kinds of applications such as electronic and optical properties. Currently, there has been extensive research in the field of spintronics as different physical properties of ferromagnetism and semiconducting properties co-exist [1]. There are some reports in the current literature of achieving ferromagnetism at low temperatures for these systems; however, achieving ferromagnetism behavior at room temperature and above is still a great challenge to the scientists.

The possibility of having materials with ferromagnetism with high T_C using first principle calculations was predicted by K. Sato et al. in 2002 [2]. Therefore, a wide variety of semiconductor nanomaterials like zinc oxide (ZnO), titanium oxide (TiO₂), gallium nitride (GaN) have been studied for the potential possibility of observing ferromagnetism at room temperature and above [3-5]. Following this theoretical prediction, there has been extensive research to achieve ferromagnetism at room temperature and above in a lot of electronic oxide materials for potential applications in the field of spintronic devices, in which the spin of the carriers can be exploited, in addition to their existing attractive applications in transport electronics, ultra-violet light emission, gas sensing, varistors and surface acoustics wave devices and low threshold spin-lasers [6]. In recent literature, there are many attempts to doped cuprous oxide nanomaterials with a variety of metal ions [7-11]. However; it is still a challenging task to achieve to ferromagnetic behavior in the originally diamagnetic Cu₂O due to the limited solubility of the transition metal ions, stabilization of single phase and difficult preparation methods. Here we report, room temperature synthesis of Cu₂O octahedra with Fe

metal ions impurities and observation of ferromagnetic property at 77 K and paramagnetic property at room temperature.

2. EXPERIMENTAL SECTION

In a typical procedure, 0.5 g of CuSO₄·5H₂O (2 mmol) and 0.361 g of D-glucose (2 mmol) were completely dissolved in 100 mL of double distilled water in a 250 mL round bottom flask fitted with Ar gas flow and started magnetic stirring. Required amounts of cupric acetate monohydrate (Cu(CH₃COO)₂·H₂O) and the metal ion dopant precursor was also then added to it. Iron nitrate (Fe(NO₃)₃·9H₂O) was taken as precursor for Fe ions. The atomic percentage of the dopant metal ions was calculated with respect to Cu atomic composition in the experiments. After 15-20 minutes of stirring, 2 mL of 10 M NaOH was added in a drop wise manner with the help of dropping funnel into the solution and a blue colored solution of Cu(OH)₂ was soon produced. After stirring for 30 minutes, 3 mL of 2 M N₂H₄·H₂O solution was dropped into this solution, color of the solution gradually changed from blue to brick red. The solution was stirred until the Cu(OH)₂ precipitates were completely reduced by the hydrazine hydrate. The brick red precipitates were collected by centrifugation at 8000 rpm for 30 minutes, washed with methanol (HPLC grade) several times and centrifuged afterwards. Then it was dried in vacuum oven at 60 °C for 3 hours.

3. RESULTS AND DISCUSSIONS

The powder X-ray diffraction pattern of the Cu₂O octahedra is given in Figure 1. All the peaks can be indexed to single phase crystalline Cu₂O cubic lattice. The average crystallite size was calculated between 21-

30 nm for different samples using the Scherrer's equation. FESEM image in Figure 2 clearly shows the morphology of the synthesized nanomaterials as octahedral in the range of 100-150 nm size. As the XRD patterns and morphology were almost identical for the undoped and various doped samples, only representative XRD pattern and FESEM image is given here. The field dependent magnetization measurements were carried out by vibrating sample magnetometer on the doped and the undoped samples

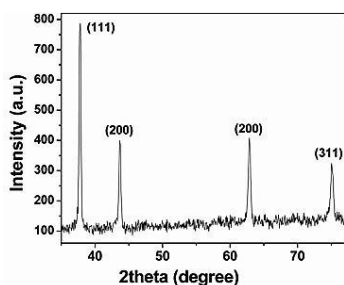


Fig. 1 – Powder X-ray diffraction pattern

to study their magnetic property at room temperature and low temperature (77 K). The same measurement in identical conditions for the undoped sample was also carried out at room temperature to confirm whether the room temperature paramagnetism and low temperature ferromagnetism originated from the cuprous oxide and not from the unintentionally introduced magnetic impurities. The Magnetization *vs.* applied field curve for the undoped sample can be clearly seen in the Figures 3 and 4 (hysteresis loop a in both) which exhibits the expected diamagnetic behavior of cuprous oxide semiconductor, both at room temperature and at 77 K.

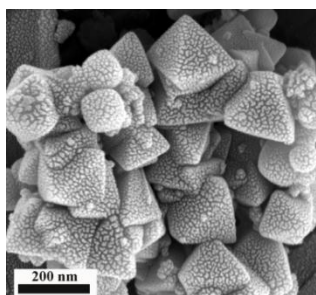


Fig. 2 – FESEM image of the Cu₂O octahedra

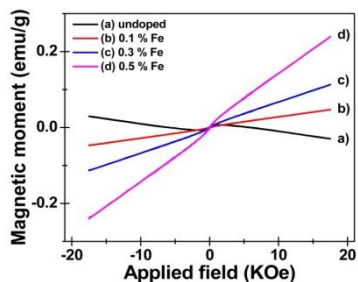


Fig. 3 – Magnetization curve at room temperature

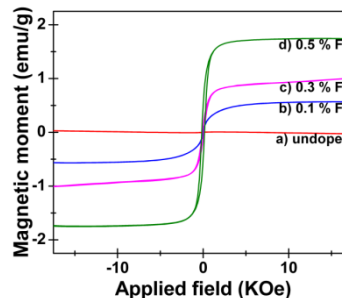


Fig. 4 – Magnetization curve at 77 K

Unexpected ferromagnetic and paramagnetic behavior was observed at low temperature of 77 K and room temperature respectively (Figure 3 and 4). The magnitude of the magnetic moments in the M-H curves for different doped samples at room temperature were found to be very low; nevertheless found to be increasing with increased dopant amount as can be seen in the Figure. On the other hand, at 77 K temperature, clear ferromagnetic signals were observed for the different doped samples. For 0.1, 0.3 and 0.5 % Fe doping (Figure 4, hysteresis curves b, c and d respectively), the values of the saturation magnetization (M_s) were 0.565, 1.005 and 1.734 emu/g respectively. The values of coercivity (H_c) for the same were 0.019, 0.093 and 0.159 kOe respectively. 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.

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: $\chi = n\mu_{\text{eff}}^2 / 3k_B T$, where n is the Fe concentration, and μ_{eff} represents the effective magnetic moment of the metal ion. The values of μ_{eff} for the magnetic ions Fe is $4 \mu_B$ (per atom) [12]. The magnetic susceptibility values calculated from this equation for Fe are 0.1, 0.3 and 0.5 % Fe dopant amounts were 0.93 , 2.79 and $4.66 \times 10^{-7} \text{ emu Oe}^{-1} \text{g}^{-1}$ 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. Hence, we can say that the ferromagnetism in the cuprous oxide octahedra was generated not from the intentionally doped magnetic ions in the material, but from the material itself.

To investigate the origins of this anomalous magnetic behavior, Iron-57 Mössbauer spectroscopic measurements at room temperature were performed on

0.5 % Fe doped sample. The presence of the Fe ions in the material, not indicated by the XRD results perhaps due to the low amount, was confirmed by Mössbauer spectroscopy. The de-convoluted spectra exhibit presence of two doublets which represents two different paramagnetic sites of iron ions in the lattice as shown in the Figure 5. The two doublets in the spectra show that the iron impurities are present as Fe^{3+} ions in the octahedral type environment in the neighborhood of six oxygen atoms, perhaps at the face center and tetrahedral type environments neighborhood of four oxygen atoms, possibly at the vacant tetrahedral sites of the distorted cubic lattice. The intensity of the spectrum corresponding to the Fe^{3+} ions in the octahedral type environment was very weak, indicating that the Fe^{3+} ions are preferably residing in the tetrahedral type environment rather than the octahedral type environment. Interestingly while it confirms the existence of paramagnetic iron ions, there was no evidence of any magnetic iron ions present in the system contributing to the ferromagnetic character of the sample as the spectra was devoid of any magnetic sextets (six finger pattern) which represent the presence of magnetic iron sites.¹³ Hence it confirms the presence of only paramagnetic contribution from Fe ions.

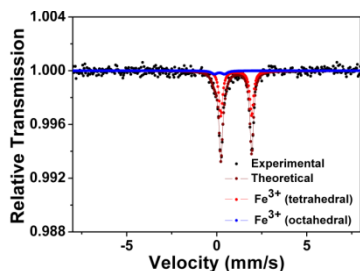


Fig. 5 – Mössbauer spectra of 0.5 % Fe doped sample

As clear from the above discussion, the magnetic moment contribution directly from the doped metal ions is miniscule if it's compared to the observed magnitude of the ferromagnetism in all the Fe doped samples. 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, where we have observed ferromagnetic behavior in the Fe, Co, Ni and Mn doped Cu_2O nanorods and nanoflowers [14-16]. The induced magnetic moment at defect sites might give rise to high magnetic moment [17]. Recently, Soon et al. 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.¹⁸ 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 defects created by the cation deficiency at the surface and the grain boundary [12, 19].

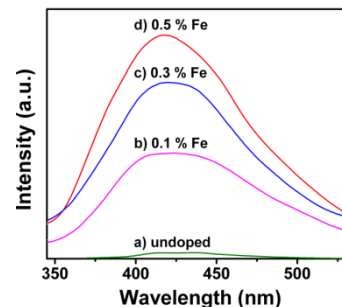


Fig. 6 – Photoluminescence spectra at room temperature

It is well known that *p*-type conduction in Cu_2O is caused by copper vacancies as the Cu vacancy hole producer V_{Cu} has a low formation energy in the cuprite structure [20-23]. As we introduce dopant ions in the Cu_2O octahedral, there is increased formation of cation vacancy. These defects can be called as V_{O} defects according to the Kroger-Vink notation [24]. The existence of these defects in the doped materials has been supported by the photoluminescence (PL) spectroscopic measurements in the earlier reports [14-16, 19, 25, 26]. In this work, photoluminescence spectra have been recorded at room temperature for all the doped samples (Figure 6) in reference to the undoped Cu_2O sample (curve a). Strong photoluminescence was observed at room temperature for the doped samples suggesting high efficiency of photon-electron and /or exciton coupling in the nanomaterials. It is observed in all the Fe doped samples, 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

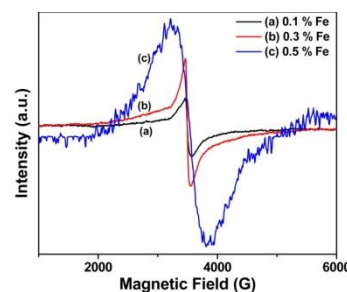


Fig. 7 – EPR spectra at room temperature

intensity, indicating more photoluminescence with increase of dopant ions.

These defects are expected to appear at around *g*-

factor value of 2.0 in the EPR spectra. The EPR spectra for the Fe doped samples were recorded at room temperature as shown in Figure 7. The values of g-factor for 0.0, 0.1, 0.3 and 0.5 % Fe doped octahedra samples were calculated to be 0.0, 2.0077, 2.0074 and 2.0068 respectively. These values close to 2.0 suggested that these signals are originated from the V_o defects, which are believed to be the recombination centres (F^+ type centres) for the luminescence processes [27]. It is expected that the concentration of the cation vacancies should be high enough because of their low formation energy and hence their concentration should be above the required threshold to mediate long range ferromagnetic ordering [28].

The increased formation of defects might 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 crystal lattice is disturbed and results in the generation of more 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 and EPR signals and subsequently to induce magnetic moment. So, it resulted in more contribution to the ferromagnetic moments with increase of dopant ions in the material after achieving certain critical amount of the cation deficiency sites. We may easily correlate that increase in PL and EPR peak intensity is in coherence to the magnitude of the ferromagnetism in the doped samples.

4. CONCLUSIONS

Single phase Cu_2O octahedra doped with Fe metal ions were prepared by simple room temperature synthesis. They were found to exhibit ferromagnetic behavior at 77 K. The room temperature Mössbauer spectra indicate that there only iron is present only in the form of paramagnetic Fe^{2+} ions. The magnetic moments were observed to be increasing with increase of Fe ions in the materials, therefore suggesting that ferromagnetic behavior might have originated from defects created due to the dopant ions and not from the metal ion itself. The photoluminescence and EPR spectra fully supported the existence of these defects in the lattice.

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