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Research Article

Critical Analysis on the Structural and Magnetic Properties of Bulk and Nanocrystalline Cu-Fe-O

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Nanocrystalline and bulk samples of “Fe”-doped CuO were prepared by coprecipitation and ceramic methods. Structural and compositional analyses were performed using X-ray diffraction, SEM, and EDAX. Traces of secondary phases such as CuFe2O4, Fe3O4, and α-Fe2O3 having peaks very close to that of the host CuO were identified from the Rietveld profile analysis and the SAED pattern of bulk and nanocrystalline Cu0.98Fe0.02O samples. Vibrating Sample Magnetometer (VSM) measurements show hysteresis at 300 K for all the samples. The ferrimagnetic Neel transition temperature (TN) was found to be around 465°C irrespective of the content of “Fe”, which is close to the TN value of cubic CuFe2O4. High-pressure X-Ray diffraction studies were performed on 2% “Fe”-doped bulk CuO using synchrotron radiation. From the absence of any strong new peaks at high pressure, it is evident that the secondary phases if present could be less than the level of detection. Cu2O, which is diamagnetic by nature, was also doped with 1% of “Fe” and was found to show paramagnetic behavior in contrast to the “Fe” doped CuO. Hence the possibility of intrinsic magnetization of “Fe”-doped CuO apart from the secondary phases is discussed based on the magnetization and charge state of “Fe” and the host into which it is substituted.

1. Introduction

Oxides such as ZnO, TiO2, and SnO2 are currently explored as host materials for preparing Diluted Magnetic Semiconductors (DMSs) [1–7]. Among these, diamagnetic ZnO (n-type) doped with “3d” transition metal ions is presently explored in detail ([8–13] and references there in). Wide controversies exist in literature reports in explaining the observed results, and the role of preparation methods in deciding the property. CuO (Tenorite), a p-type semiconductor with a band gap of 1.2 eV, is an essential component in a variety of oxide superconductors and is also known for its catalytic and gas sensing properties [14–16]. CuO also being nontoxic and abundant, an attempt has been made to unravel its properties by doping with “Fe” and to find its potential for application in SPINTRONICS. “Cu” has three oxidation states, Cu+, Cu2+, and Cu3+, because of which both hole doping and electron doping are possible. “Fe” doping into CuO has been attempted by researchers [17–21] by different preparation methods and was found to have no definite evidence for “Fe” replacing the “Cu” site in CuO, as the two components are immiscible. Smith et al. have reported that introducing Fe2O3 into CuO by ceramic method is tough and phase segregation results above 0.3% of “Fe” in CuO [17]. Few reports exist on CuO doped with “Mn” [22] and “Fe” [23, 24] from DMS point of view. On the other hand, Cu2O (cuprite), also an eco-friendly p-type semiconductor with a direct band gap value of 2 eV [25], is useful as an energy converter for solar cell applications [26] and as humidity and gas sensor material [27, 28]. Reports also exist on magnetic properties of “Mn-”, “Co-” and “Fe-” doped Cu2O [25, 29, 30]. Comparison of “Fe-doped Cu2O” with “Fe-doped CuO” may throw some light on the understanding of the intrinsic magnetic contribution of the later.

In this work, paramagnetic CuO (antiferromagnetic below 230 K) doped with varying concentration of “Fe”
was characterized in detail for its structural, compositional, and magnetization behavior by X-Ray diffraction (XRD), Rietveld analysis, Scanning electron microscopy (SEM), Energy Dispersive X-Ray analysis (EDAX), Transmission Electron Microscopy (TEM), Vibrating Sample Magnetometer (VSM), Thermogravimetric analyzer (TGA), Mössbauer spectroscopy, and XRD at high-pressures using synchrotron radiation. Presence of other related phases like CuFe2O4/Fe3O4 and Fe2O3, having coincidence with many of the major peak positions of CuO, was not categorized before through the powder X-ray diffraction in detail. Their presence is only discussed based on the Mössbauer spectra [20, 21, 23]. We performed a detailed powder X-ray diffraction study using Rietveld refinement procedure and cross checked the presence of CuFe2O4 from the Neel temperature (TN) measurement using a TGA with a small applied field. High-pressure studies were carried out to identify the presence of any possible secondary phases. We have also discussed the effect of secondary phases in CuO and also compared with 1% and 2% “Fe”-doped Cu2O. The possibility of intrinsic magnetization of “Fe”-doped CuO [24] apart from the ferrite phases is discussed based on the magnetization measurements and the charge state of “Fe” in the host into which it is substituted.

2. Sample Preparation and Experimental Details

Nanocrystalline samples of Cu1–xFexO (x = 0.01, 0.02, 0.03, 0.04, and 0.05) were prepared from the stoichiometric solutions of copper nitrate and iron nitrate in deionized water by coprecipitation method after refluxing for 20 hour, 30 hour, 40 hour and 50 hour. Precipitation was done using aqueous NH4OH and peptized with deionized water to remove by-products. The filtrates were then dried, powdered and annealed at various temperatures. Nanocrystalline CuFe2O4 and bulk Cu1–xFexO (x = 0.01, 0.02, 0.03, 0.04, 0.05 and 0.07) were also prepared for comparing the properties. For the preparation of bulk samples, stoichiometric mixtures of oxides were ground in isopropyl alcohol medium, pelleted and sintered at 900°C/12h in air.

Chemical coprecipitation method with subsequent reduction of the precipitates was employed to prepare the samples of Cu2O:Fe (1% and 2%). Copper sulphate and ferric nitrate solutions for the required stoichiometry were prepared with de-ionized water. Aqueous NH4OH (0.15 M) solution was added to the solution with constant stirring. After stirring for 15 minutes, 1.2 M NaOH solution was added in drops to the solution, to form light green precipitates. Further, 2 mL of 10 M N2H4 was added, continued by 5 hour stirring to reduce the sample to form “Fe”-doped Cu2O [30] and Cu2O [31].

2.1. X-Ray Diffraction Results. Nanocrystalline Cu0.95Fe0.05O samples were annealed at 500°C, 700°C, 900°C/2h, and also at 900°C/12h in air. X-Ray diffraction measurements were done using CuKα radiation in the range 10°–80° with a step size of 0.04° (Rich Seifert 2000, transmission geometry). All the peaks could be indexed to the monoclinic structure of CuO. Representative XRD patterns of 50 hours refluxed Cu0.95Fe0.05O sample annealed at different temperatures are shown in Figure 1. The samples annealed at 700°C/2h presented Fe2O3 peaks of small intensity around 31° and 33°. However, after annealing the samples at 900°C those peaks vanished and only lines of CuO phase were evident. Hence all the nanocrystalline Cu1–xFexO (x = 0.01, 0.02, 0.03, 0.04, and 0.05) samples and Cu0.95Fe0.05O samples refluxed for 20 hour, 30 hour, 40 hour, and 50 hour were annealed at 900°C/2h. Based on these results the samples were first considered as single phase and the magnetization and other measurements were performed. However, most of the reflections of monoclinic CuO (Monoclinic, JCPDS # 65-2309) match with those of ferrimagnetic CuFe2O4 (Cubic, JCPDS file No. 77-0010), Fe2O3 (Cubic, JCPDS file No. 85-1436), and paramagnetic Fe2O3 (Rhombohedral, JCPDS file No. 80-2377). Some of the peaks of CuFe2O4/Fe2O3 having same hkl planes and position very close to that of the host CuO are tabulated in Table 1. This overlap of reflections presented the problem of identifying hidden impurity phases.

2.2. Rietveld Analysis. XRD measurement with a step size of 0.01° with an exposure time of 8 seconds was performed on the as-mixed powders of CuO:Fe2O3 (2%) and on the same mixtures but sintered at 900°C/12h in air. Interestingly, from the close scan XRD spectrum, the subtle merged peaks belonging to the ferrimagnetic cubic CuFe2O4 phase were identified. The full-scale view of the close scan XRD pattern of as-mixed CuO:Fe2O3 (2%) presents peaks of CuO and Fe2O3. On sintering at 900°C/12h in air, all the lines of Fe2O3 vanished indicating the substitution of “Fe” into the copper site and the CuO main phase lines were alone evident. The phase quantification by Rietveld refinement using a program called MAUD [32], which combines the Rietveld method and a Fourier transform analysis, also indicated the existence of 0.2% of CuFe2O4 in the samples. The results of refinement are given in Table 2. The observed pattern matches with that

![XRD patterns of 50-hour refluxed nanocrystalline Cu0.95Fe0.05O annealed at different temperatures.](image-url)
of the monoclinic CuO phase there by indicating that the dopants were incorporated into the CuO matrix. The profile analysis and the difference pattern of as-mixed and sintered 

CuO:Fe$_2$O$_3$ (2%) along with the vertical lines indicating the peak position of the CuO main phase and the CuFe$_2$O$_4$ impurity phase are shown in Figure 2. The square root of the monoclinic CuO phase is here indicating that the as-prepared sample shows particles with rod-like and disc-shaped morphologies (Figure 3), and their thickness increases when annealed at 500°C/2h in air; however it was less than a micrometer. The thickness and length of the rod shaped particles alone were measured. A Gaussian fit was given and the average value of thickness was found to be 78 nm with an average length of 0.366 μm. As the temperature was raised to 700°C/2h, the rod-like morphology vanishes and the particles grow in size. At 900°C/2h the particle morphology transforms to platelets due to temperature-induced agglomeration and growth (not shown here). Compositional analysis by EDAX confirmed the desired composition of “Fe” in the entire batch of samples (not presented here). The nominal variation in composition is due to the random alloying of the magnetic dopants.

The observation of two different particle morphologies, rod-like and platelet-like may be an indication of existence of two different phases. Rod- and platelet-like morphology may be the undoped CuO and CuFe$_2$O$_4$ phases, respectively. This argument is supported by the magnetization results which are discussed in the following sections. The samples annealed at lower temperature are found to have paramagnetic component [24] without saturation superimposed with the hysteresis behavior (bottom inset of Figure 10). This is because the temperature is not sufficient for the CuFe$_2$O$_4$ to crystallize out. Hence, after annealing at 900°C in air, the magnetization curve becomes smooth and the corresponding SEM micrograph presented only platelet-like particles (not presented here).

2.4. TEM Results. The selected area electron diffraction (SAED) on bulk Cu$_9$O$_9$Fe$_9$O$_5$O (900°C/12h) was performed by selecting samples from three different locations in a JEOL EX2000. The TEM micrograph and SAED pattern (inset) is shown in Figure 4. All the $d_{hkl}$ values corresponding to the streaky spot pattern were calculated and compared with the $d_{hkl}$ values of the host CuO (JCPDS 65-2309), and possible secondary phases such as cubic CuFe$_2$O$_4$ (JCPDS 77-0010), cubic Fe$_3$O$_4$ (JCPDS 85-1436), and rhombohedral $\alpha$-Fe$_2$O$_3$ (JCPDS 80-2377). The $d_{hkl}$ and corresponding hkl values of Cu$_9$O$_9$Fe$_9$O$_5$O and possible secondary phases are listed in Table 3. This is also confirmed from SAED patterns for samples taken from three different locations (not shown here). From the above result, it is seen that Cu$_9$O$_9$Fe$_9$O$_5$O sample has the secondary phases of CuFe$_2$O$_4$/Fe$_3$O$_4$ and $\alpha$-Fe$_2$O$_3$.

Table 2: Structural and compositional parameters of bulk as-mixed and sintered CuO:Fe$_2$O$_3$ (2%) along with possible secondary phases from Rietveld Refinement of the X-ray data.

<table>
<thead>
<tr>
<th>Phase</th>
<th>As-mixed</th>
<th>Sintered (900°C/12h in air)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>$a = 4.694$ Å</td>
<td>$a = 4.688$ Å</td>
</tr>
<tr>
<td></td>
<td>$b = 3.433$ Å</td>
<td>$b = 3.425$ Å</td>
</tr>
<tr>
<td>Monoclinic (C2/C)</td>
<td>$c = 5.144$ Å</td>
<td>$c = 5.134$ Å</td>
</tr>
<tr>
<td></td>
<td>$\beta = 99.43$</td>
<td>$\beta = 99.47$</td>
</tr>
<tr>
<td></td>
<td>% of CuO = 97.3%</td>
<td>% of CuO = 99.8%</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>$a = 5.034$ Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$c = 13.802$ Å</td>
<td>% of Fe$_2$O$_3$ = 2.7%</td>
</tr>
<tr>
<td>Cubic (Fd$\bar{3}$m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>% of CuFe$_2$O$_4$ = 0.2%</td>
<td></td>
</tr>
<tr>
<td>Overall R factor</td>
<td>8.038</td>
<td>1.760</td>
</tr>
<tr>
<td>Overall goodness of the fit ($\sigma$)</td>
<td>1.223</td>
<td>2.643</td>
</tr>
</tbody>
</table>

Table 1: Peak position, intensity, and hkl values of possible secondary phases in Fe-doped CuO from XRD pattern.

<table>
<thead>
<tr>
<th>CuO</th>
<th>CuFe$_2$O$_4$</th>
<th>Fe$_3$O$_4$</th>
<th>Fe$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2θ</td>
<td>Int</td>
<td>2θ</td>
<td>Int</td>
</tr>
<tr>
<td>35.663</td>
<td>999</td>
<td>35.543</td>
<td>999</td>
</tr>
<tr>
<td>46.401</td>
<td>14</td>
<td>47.299</td>
<td>009</td>
</tr>
<tr>
<td>53.615</td>
<td>71</td>
<td>53.596</td>
<td>076</td>
</tr>
<tr>
<td>56.863</td>
<td>06</td>
<td>57.135</td>
<td>259</td>
</tr>
<tr>
<td>65.989</td>
<td>96</td>
<td>65.974</td>
<td>010</td>
</tr>
<tr>
<td>75.235</td>
<td>35</td>
<td>75.244</td>
<td>027</td>
</tr>
<tr>
<td>87.103</td>
<td>09</td>
<td>87.051</td>
<td>022</td>
</tr>
<tr>
<td>90.064</td>
<td>15</td>
<td>89.964</td>
<td>081</td>
</tr>
</tbody>
</table>

2.3. SEM and EDAX Results. SEM measurements were performed on nanocrystalline Cu$_9$O$_9$Fe$_9$O$_5$O samples obtained after refluxing for 40 hour. The image corresponding to the as-prepared sample shows particles with rod-like and disc-shaped morphologies (Figure 3), and their thickness increases when annealed at 500°C/2h in air; however it
The TEM micrograph of nanocrystalline Cu_{0.95}Fe_{0.05}O (900°C/2h) shown in Figure 5 has agglomerates of smaller particles due to annealing of the sample. The SAED pattern (inset of Figure 5) shows well-defined spots indicating formation of highly crystalline particles on annealing. The \( d_{hkl} \) and hkl values are tabulated in Table 4. All the \( d_{hkl} \) values match with those of the parent CuO except for the 3.310 Å \( d_{hkl} \), which has good coincidence with that of (012) plane of \( \alpha \)-Fe_{2}O_{3}. Hence the nanocrystalline Cu_{0.95}Fe_{0.05}O sample also has the possible secondary phases as observed in the SAED of bulk Cu_{0.95}Fe_{0.05}O. The equation representing the sample formation with possible secondary phases is given as follows:

\[
\text{CuO + Fe}_{2}\text{O}_{3} \xrightarrow{900\,^\circ\text{C}/12\,\text{h}} \text{Cu}_{(1-x)}\text{Fe}_{x}\text{O} + \text{CuFe}_{2}\text{O}_{4}\text{(cubic)} + \text{Fe}_{2}\text{O}_{3}\text{(Rhombohedral)} + \text{CuO}.
\]
Table 4: $d_{hkl}$ and hkl values of nanocrystalline Cu$_{0.95}$Fe$_{0.05}$O shown in comparison with possible secondary phases to indicate the closely situated $d_{hkl}$ planes.

<table>
<thead>
<tr>
<th>$d_{hkl}$ (Å) of Cu$<em>{0.95}$Fe$</em>{0.05}$O from SAED</th>
<th>Monoclinic CuO JCPDS 65-2309</th>
<th>Cubic CuFe$_2$O$_4$ JCPDS 77-0010</th>
<th>Cubic Fe$_3$O$_4$ JCPDS 85-1436</th>
<th>Rhombohedral $\alpha$-Fe$_2$O$_3$ JCPDS 80-2377</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{hkl}$ (Å)</td>
<td>hkl</td>
<td>$d_{hkl}$ (Å)</td>
<td>hkl</td>
<td>$d_{hkl}$ (Å)</td>
</tr>
<tr>
<td>3.310</td>
<td>—</td>
<td>3.682</td>
<td>0 1 2</td>
<td>2.699</td>
</tr>
<tr>
<td>2.685</td>
<td>2.515</td>
<td>1 1 0</td>
<td>2.530</td>
<td>3 1 1*</td>
</tr>
<tr>
<td>2.341</td>
<td>2.315</td>
<td>1 1 1</td>
<td>2.416</td>
<td>2 2 2</td>
</tr>
<tr>
<td>2.086</td>
<td>1.955</td>
<td>1 1 2</td>
<td>2.092</td>
<td>4 4 0</td>
</tr>
<tr>
<td>2.078</td>
<td>1.959</td>
<td>2 0 2</td>
<td>1.920</td>
<td>3 3 1</td>
</tr>
<tr>
<td>1.684</td>
<td>1.708</td>
<td>0 2 0</td>
<td>1.708</td>
<td>4 2 2</td>
</tr>
<tr>
<td>1.616</td>
<td>1.617</td>
<td>0 2 1</td>
<td>1.610</td>
<td>5 1 1</td>
</tr>
<tr>
<td>1.514</td>
<td>1.501</td>
<td>0 1 1</td>
<td>1.479</td>
<td>4 4 0</td>
</tr>
<tr>
<td>1.368</td>
<td>1.375</td>
<td>1 1 3</td>
<td>1.414</td>
<td>5 3 1</td>
</tr>
<tr>
<td>1.217</td>
<td>1.257</td>
<td>2 2 2</td>
<td>1.208</td>
<td>4 4 4</td>
</tr>
<tr>
<td>1.053</td>
<td>1.070</td>
<td>1 3 1</td>
<td>1.089</td>
<td>7 3 1</td>
</tr>
<tr>
<td>0.917</td>
<td>0.951</td>
<td>3 3 1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.748</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>0.636</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*Indicates the respective 100% peak.

Figure 3: SEM micrograph of 40-hour refluxed nanocrystalline Cu$_{0.95}$Fe$_{0.05}$O showing the mixture of rod-like and platelet-like particles.

Figure 4: TEM micrograph and SAED pattern of bulk Cu$_{0.95}$Fe$_{0.05}$O (900°C/12h).

Figure 5: TEM micrograph and SAED pattern of nanocrystalline Cu$_{0.95}$Fe$_{0.05}$O (900°C/2h).

2.5. High-Pressure X-Ray Diffraction Using Synchrotron Radiation. Pressure is a fundamental thermodynamic degree of freedom available for basic investigations as well as for processing of materials. The effects of pressure are a result of changes in the band structure and of the energy content of a material produced by the reduction of interatomic spacing. The study of the behavior of materials at high-pressures has been useful in the observation of new features of the physical and chemical properties. In order to produce appreciable effects on the properties of condensed phases, high-pressures of the order of hundreds or thousands of bars are required. Synchrotron radiation is a photon light source generated by high-energy electrons that are centripetally accelerated to relativistic velocities in the magnetic fields of a storage ring and are emitted in a narrow cone tangent to the orbit. Synchrotron radiation,
because of unique properties like high brightness, wide energy spectrum, high degree of polarization, and high collimation has allowed extensive investigation of a variety of materials. The remarkable qualities of diamond such as high yield strength and transparency to radiation over a wide range of wavelengths have made it an obvious choice for the anvil materials making it possible to conduct high-pressure X-ray diffraction measurements on materials at few hundreds of giga Pascal (GPa) using synchrotron radiation. Presence of secondary phases can be evidenced from the high-pressure X-ray diffraction measurements due to the fact that the elastic properties of CuO, Fe, and CuFe$_2$O$_4$ are different. Hence, we are motivated to study the sample at high-pressures to identify the presence of any hidden secondary phases.

High-Pressure XRD measurements were conducted in angle dispersive geometry using Mao-Bell type Diamond Anvil Cell. Experiment was performed using the synchrotron source at beamline 16IDB, High-Pressure Collaboration Access Team (HPCAT), Advanced photon source, Chicago, with a wavelength of 0.4564 Å. Bulk CuO: Fe (2%) powder was loaded along with a few grains of platinum which acts as a pressure standard [33]. A stainless steel gasket of 50 μm thickness indented using diamond anvils of culet size 300 μm, wherein a 100 μm hole drilled serves as the sample chamber. The size of the incident beam was 10 × 10 μm$^2$ and the diffracted beam was recorded on a Mar 3450 image plate. The diffraction measurements were carried out from 0.5 GPa to 44 GPa at room temperature and are shown in Figure 6. Each pattern was fitted and refined to monoclinic structure of CuO with space group C2$_1$/c using the software GSAS [34] with(EXPGUI) [35]. Though no structural transitions had been reported up to 100 GPa in monoclinic CuO [36–40], the study helps in identifying the hidden phases based on the variation in compressibility.

In the case of 2% Fe-doped CuO, application of pressure causes a shift in the diffraction peaks towards higher angle indicating reduction in cell volume. Relative variation of refined lattice parameters as a function of pressure is shown in Figure 7. The overall trend on application of pressure on the “b” and “c” lattice parameters is to decrease them with increasing pressure and that “a” increases gradually (Figure 7). The cell volume obtained from the refinement is found to decrease with pressure (Figure 8) and no abrupt change is
observed indicating absence of structural transition. Literature reports indicate absence of structural transition from high-pressure electrical resistivity measurements in monoclinic CuO up to 100 GPa [36, 40].

Upon increasing the pressure, at 3.98 GPa, a peak clearly separates out from the (200) plane. Hence, when CuO gets compressed and shifts towards higher angle, an unknown peak becomes evident. With further increasing pressure, we observed that the (−111) peak of monoclinic CuO shifts towards higher angle and tends to overlap with the unknown peak. As the pressure is further increased, the intensity of the unknown peak gradually decreases and completely vanishes at 26.02 GPa before overlapping with the (−111) plane of CuO. Similar behavior has been observed in pure CuO itself (the results will be published elsewhere).

Reimann and Syassen [41] observed changes in the Raman modes of pure CuO in high-pressure Raman measurements up to 34 GPa which they explain as the changes in the internal structure parameter. Reimann and Syassen also report Malinowski to observe a structural anomaly in his X-ray diffraction measurement around 10 GPa (referred as private communication in back reference of [41]). High-pressure neutron diffraction studies by Ehrenberg et al. [38] suggest Jahn Teller type structural distortion seen below 8 GPa in pure CuO. Hence, appearance and suppression of an additional peak in the high-pressure XRD of 2% Fe-doped CuO sample is also characteristic of pure CuO. The phase transformation is similar to Jahn Teller-like distortion which occurs at high-pressure related to the variation of the bond angle with pressure. In addition to this observation, the absence of any other additional peaks evidences absence of secondary phases of them to be present below the limit of detection. The conclusion was drawn based on the variation of the bulk modulus of CuO and various secondary phases.

The (−111) peak which was the maximum intensity peak at 0.5 GPa loses its intensity gradually with increasing pressure, and at the same time, the (200) peak gain intensity. This may be due to the pressure-induced preferred orientation. This small internal structural distortion [37, 38, 41] is found to be reversible upon releasing the pressure. However, there is a slight shift towards higher angle in the peak positions along with broadening, also, after releasing the pressure, the (200) plane becomes the peak with maximum intensity instead of (−111) plane which may be due to the pressure-induced lattice strain and preferred orientation. However, pressure-induced substitution of a fraction of “Fe” at the “Cu” site might have also resulted which can be understood in more detail from high-pressure neutron diffraction measurement which is more sensitive to the magnetic moment of the elements in the sample when performed in the similar pressure range. The PV-equation of state fitted using the third-order Birch-Murnaghan equation of state (BM-ecos) is given by

\[ P = \frac{3K_0}{2} \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \]

\[ \times \left[ 1 + \frac{3}{4} \left( K'_0 - 4 \right) \left( \left( \frac{V_0}{V} \right)^{2/3} - 1 \right) \right], \]

where \( K_0 \) is bulk modulus, \( K'_0 \) is derivative of bulk modulus with pressure, \( V_0 \) is zero pressure volume, and \( V \) is volume at pressure \( P \). The value of \( K'_0 \) set to 4 shown in Figure 8 indicates a steady decrease in volume on increasing the pressure with no abrupt change indicating absence of phase transition. Hence, absence of secondary phases is evident from the high pressure XRD data and even if present, it is well below the level of detection.

2.6. TGA Results. To identify the effect of “Fe%” doping on the \( T_N \) of the samples, the TGA measurements were performed with a small applied field (≈20 Oe) to determine the \( T_N \) as a function of temperature. The measurement was performed in N₂ atmosphere with a heating rate of 10°C/min up to 600°C. For the 50 hour refluxed nanocrystalline Cu₀.₉₅Fe₀.₀₅O sample, the \( T_N \) was found to increase with decreasing crystallite size (Figure 9). The increase in magnetization prior to \( T_N \) in the TGA curves observed for Cu₀.₉₅Fe₀.₀₅O is due to Hopkinson effect which is also reported in the case of NiFe₂O₄ [42]. The bulk Cu₀.₉₅Fe₀.₀₅O had a \( T_N \) of 458°C, whereas a \( T_N \) of 479°C (900°C/12h) for the 49 nm sample and that of 486°C (900°C/2h) for the 25 nm sample were observed. Thus the decrease in crystallite size increases the \( T_N \). However, this variation of \( T_N \) may be due to the size effect of the copper ferrite phase that has formed within the sample. To avoid the effect of particle size on \( T_N \), we studied the bulk samples prepared by ceramic method to trace the original trend of variation of \( T_N \) with “Fe” concentration in CuO. The \( T_N \) observed for “Fe”-doped CuO bulk samples is shown in Table 5. There was no noticeable trend in the variation of \( T_N \). The \( T_N \) remained around 460°C irrespective of the “Fe%”, indicating that one major secondary phase had formed within the sample. This \( T_N \) value has good coincidence with the \( T_N \) of cubic CuFe₂O₄, which is 465°C [43], whereas the \( T_N \) of cubic CuFe₂O₄ is 585°C. This observation is a clear experimental evidence that the observed hysteresis behaviour is from the phase-segregated CuFe₂O₄. This confirms that the “Fe” does not get substituted into the substitutional site of CuO even for 1% of “Fe” in CuO to effect any change in the property of CuO; rather it favors the formation of cubic CuFe₂O₄ as segregates within the sample whereas Park et al. [24] do not report any ferrite impurity phase; they instead discuss intrinsic ferromagnetic behaviour in 2% “57Fe”-doped CuO mediated by carriers localized around the oxygen vacancies studied by Mössbauer measurements.

For “Fe”-doped bulk CuO, the \( T_N \) is found to be around 460°C. The \( T_N \) of Fe₃O₄ is 585°C and is higher than the \( T_N \) observed for bulk Cu₀.₉₅Fe₀.₀₅O whereas the \( T_N \) of cubic CuFe₂O₄ is 465°C [43]. The \( T_N \) of bulk CuO doped with Fe to various extents was very close to that of cubic CuFe₂O₄. Hence no appreciable variation in \( T_N \) was found with varying “Fe” concentration. Hence, even the 1% and 2% “Fe”-doped CuO is inevitably found to possess copper ferrite phase. CuFe₂O₄ when quenched or rapidly cooled (from above 760°C), takes cubic structure with \( a = 8.37 \) Å. If cooled slowly, it attains tetragonal phase with \( a = 8.22 \) Å and \( c = 8.70 \) Å [43]. Since all the samples were furnace cooled from
Table 5: Neel transition temperature of bulk CuO with “Fe” doped to various extent and pure CuFe$_2$O$_4$.

<table>
<thead>
<tr>
<th>% of “Fe” in CuO</th>
<th>Neel transition temperature ($T_N$) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{0.99}$Fe$</em>{0.01}$O</td>
<td>463</td>
</tr>
<tr>
<td>Cu$<em>{0.98}$Fe$</em>{0.02}$O</td>
<td>464</td>
</tr>
<tr>
<td>Cu$<em>{0.97}$Fe$</em>{0.03}$O</td>
<td>456</td>
</tr>
<tr>
<td>Cu$<em>{0.96}$Fe$</em>{0.04}$O</td>
<td>480</td>
</tr>
<tr>
<td>Cu$<em>{0.95}$Fe$</em>{0.05}$O</td>
<td>458</td>
</tr>
<tr>
<td>Cu$<em>{0.94}$Fe$</em>{0.06}$O</td>
<td>481</td>
</tr>
<tr>
<td>CuFe$_2$O$_4$</td>
<td>483</td>
</tr>
</tbody>
</table>

above 900 °C, the cubic phase of CuFe$_2$O$_4$ is predominantly observed. Hence the observed magnetic property for these samples is not fully intrinsic in nature; instead they have a major contribution from the cubic CuFe$_2$O$_4$ phase leading to a “pinned type” composite magnetic material. Similar observation of contribution from NiFe$_2$O$_4$ phase has also been reported in the case of Fe-doped NiO by Douvalis et al. from Mössbauer measurements [44].

2.7. Magnetization Results. The magnetization measurements were performed in a Vibrating Sample Magnetometer (VSM) (EG and G Princeton Applied Research VSM 4500) at 300 K. The Cu$_{0.95}$Fe$_{0.05}$O samples show clear hysteresis behaviour at room temperature (Figure 10) whereas Borzi et al. had observed paramagnetic behaviour from the Mössbauer measurements for “Fe”-doped CuO, at room temperature [23]. Park et al. [24] have reported ferromagnetic hysteresis behavior for annealing above 500 °C; however they explain it as intrinsic behavior due to indirect coupling among the Fe$^{2+}$ ions via a localized carrier at oxygen vacancy. Treatment at 500 °C is not sufficient to completely crystallize out CuFe$_2$O$_4$. We could also observe a paramagnetic-like behaviour for the samples annealed at 500 °C/2h from VSM (bottom inset of Figure 10) and the loops did not saturate but were found to show hysteresis at room temperature when annealed at 900 °C/2h. Hence, after annealing at 900 °C in air, the magnetization curve becomes smooth and the corresponding SEM micrograph also presented only platelet-like particles (not shown here). The $M_{max}$ values were found to increase with increasing refluxing hour (top inset of Figure 10) and also found to increase with increasing “Fe%” in nanocrystalline CuO samples refluxed for 50 hour and annealed at 900 °C/2h in air (Figure 11). Inset of Figure 11 shows the comparison of the magnetization data of all the samples with pure copper ferrite; note the large difference in magnetization. This may be presumably due to increasing volume fraction of CuFe$_2$O$_4$ within the samples. The non-saturation of loops may be due to the following reasons: (a) presence of clusters of undoped paramagnetic CuO (at 300 K), and (b) incomplete formation of ferrite secondary phases, which are responsible for the observed dominant magnetic behaviour.

In our case of “Fe”-doped CuO, ferrimagnetic correlations among “Fe$^{2+}$” atoms substituting the “Cu” site may lead to an ordered spin configuration enhancing the magnetic susceptibility. But this effect is masked by the dominant ferromagnetic signal from the CuFe$_2$O$_4$ phase, at 300 K. Though the observed magnetic behavior at 300 K is dominated by the CuFe$_2$O$_4$ phase, other plausible contribution comes from the “Fe$^{2+}$” substituted in “Cu” site of CuO. The dominant ferromagnetic signal from CuFe$_2$O$_4$ masks magnetic contribution from “Fe$^{2+}$” substituted in CuO and pertains from reaching a conclusive hypothesis. One has to
temperature is well below the Neel temperature ($T_N$) of "Fe" in CuO at 300 K for the 50-hour refluxed nanocrystalline hysteresis loops (Figure 12). This is because the measurement 2% Fe-doped CuO performed at 77 K showed distorted ferromagnetic transition occurring in CuO in which spins orates. At 77 K, the sample becomes an antiferromagnetic-ferromagnetic (AFM-FM) type compounds [46]. Susceptibility observations also show three dimensional AFM behavior below 212 K [47].

The magnetization measurements on bulk 1% and 2% Fe-doped CuO performed at 77 K showed distorted hysteresis loops (Figure 12). This is because the measurement temperature is well below the Neel temperature ($T_N$) of CuO. The noncollinear spin arrangement due to partial Fe substitution at the Cu site now weakens and the spin alignment tend towards (perfect anticollinear) antiferromagnetic arrangement. The distorted hysteresis (Figure 12) showed a loop shift away from the $M = 0$ (inset of Figure 12) which is known as exchange bias [45]. Exchange bias is commonly observed in a mixture of antiferromagnetic (AFM) and ferromagnetic (FM) type compounds [46]. Susceptibility studies also show three dimensional AFM behavior below 212 K [47].

The 1% "Fe"-doped CuO showing ferrimagnetic behavior at 300 K is found to present distorted signal at 77 K. At 77 K, CuO is antiferromagnetic; hence the spins tend towards antiferromagnetic arrangement leading to decrease in magnetization. However, if reasonable quantity of CuFe$_2$O$_4$ is present, then, an increase in magnetization at 77 K should have been observed, but, to the contrary it deteriorates. At 77 K, the sample becomes an antiferromagnetic-ferrimagnetic composite mixture, whereas at 300 K, it is a paramagnetic-ferrimagnetic mixture. At 77 K, the loss of hysteresis behavior could be explained based on the antiferromagnetic transition occurring in CuO in which spins do more work to explain from the standpoint of "Fe$^{2+}$" substituting the "Cu" site by delineating the contribution from the segregated CuFe$_2$O$_4$ phase.

The magnetization measurements on CuO, with CuFe$_2$O$_4$ oxide Fe$_3$O$_4$/Mg$_2$TiO$_4$ (MTO)/LSMO structure, Alldredge et al. [54] reported minimal mismatch due to similar oxide layers. MTJs using Al$_2$O$_3$ barrier and an Fe-oxide layer converted to ferromagnetic Fe$_3$O$_4$ by annealing have also been demonstrated [48]. Heterostructures MTJ device using Ti$_{1−x}$Co$_x$O$_2$ DMS as the spin injection electrode and Fe$_3$O$_4$/MgO/Fe$_3$O$_4$, Fe$_3$O$_4$/CoCr$_2$O$_4$/La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) have also been reported [50]. In the case of all oxide Sr$_2$FeMoO$_6$/SrTiO$_3$/CoFe$_2$O$_4$ MTJ, Alldredge et al. [54] reported minimal mismatch due to similar spinel structure at the Fe$_3$O$_4$/MTO interface. They have also reported coercive fields of about 200 and 600 Oe for the LSMO and Fe$_3$O$_4$ layers, respectively. Diode effect has been observed in all oxide Sr$_2$FeMoO$_6$/SrTiO$_3$/CoFe$_2$O$_4$ MTJ by Fix et al. [55]. The coercive field of the two magnetic electrodes in an MTJ should be well separated and the...

3. Results and Discussion

Based on the above given experimental observations, formation of cubic CuFe$_2$O$_4$ is confirmed. However one could not discard the candidature of CuO to be an efficient material from applications point of view. This is because, even if CuFe$_2$O$_4$ phase persists in CuO, the material can be utilized for the fabrication of magnetic tunnel junction (MTJ-) like structures and also there may be an intrinsic magnetic behaviour due to "Fe" substitution in the "Cu" site. The magnetization measurements on CuO, with CuFe$_2$O$_4$ as an impurity, show large variation in $M_{max}$ and $H_C$ as observed from the magnetization experiments which are essential criteria for an MTJ. There are a reasonable number of literature reports on MTJs composed of partly or all oxide layers. MTJs using Al$_2$O$_3$ barrier and an Fe-oxide layer converted to ferromagnetic Fe$_3$O$_4$ by annealing have also been demonstrated [48]. Heterostructures MTJ device using Ti$_{1−x}$Co$_x$O$_2$ DMS as the spin injection electrode and Fe$_3$O$_4$/MgO/Fe$_3$O$_4$, Fe$_3$O$_4$/CoCr$_2$O$_4$/La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) have also been reported [50]. In the case of all oxide Sr$_2$FeMoO$_6$/SrTiO$_3$/CoFe$_2$O$_4$ MTJ, Alldredge et al. [54] reported minimal mismatch due to similar spinel structure at the Fe$_3$O$_4$/MTO interface. They have also reported coercive fields of about 200 and 600 Oe for the LSMO and Fe$_3$O$_4$ layers, respectively. Diode effect has been observed in all oxide Sr$_2$FeMoO$_6$/SrTiO$_3$/CoFe$_2$O$_4$ MTJ by Fix et al. [55]. The coercive field of the two magnetic electrodes in an MTJ should be well separated and the...
magnetization reversal of these layers should be abrupt. Hence without attaining single phase one may try to use this material for multilayer switching applications considering it as a composite material of “pinned” type magnetization; the discussion in this point of view is given in this section.

3.1. Pinned Type Composite Magnetic Material. The VSM measurements on CuO doped with varying “Fe%” show the $M_{\text{max}}$ value to increase. Since CuFe$_2$O$_4$ present in the sample is mainly responsible for the observed magnetic behavior, then with increasing “Fe%” in CuO, the volume fraction of CuFe$_2$O$_4$ has to increase; that is, the samples should tend towards more soft nature, with high $M_{\text{max}}$ and low $H_C$. Instead, we observe a linear increase in $M_{\text{max}}$ and an increase in $H_C$ with increasing “Fe%” instead of decrease in $H_C$ (Figure 13) for 1, 4, and 7% “Fe”-doped CuO, which may be due to domain wall pinning effects. The spontaneous magnetic moment per “Fe” atom in CuO for 1, 4, and 7% are 0.0057 $\mu_B$, 0.0168 $\mu_B$, and 0.0276 $\mu_B$, respectively. Besides the enhancement of $H_C$, the squareness ratio, $M_S/M_S$ also increases with “Fe%” in CuO. The value of squareness ratio of 1, 4 and 7% “Fe” doped CuO is 0.249, 0.448, and 0.519, respectively. This is an indication that the “Fe”-doped CuO tend towards “hard” nature in spite of the presence of soft magnetic CuFe$_2$O$_4$.

The $H_C$ value of 7% “Fe”-doped bulk CuO (620 Oe) is three times greater than the value of 1% “Fe”-doped bulk CuO (202 Oe) (Figure 13 inset) indicating that the layer of “Fe” composition-varied CuO thin films may show exchange coupling. High $H_C$ CuO layer may be used as a “pinned” layer in MTJ structures. The $H_C$ of bulk and nanocrystalline Cu$_{0.95}$Fe$_{0.05}$O was found to be 236 Oe and 1225 Oe, respectively. The $H_C$ increased five times in magnitude in the nanocrystalline sample (Figure 14). The $M_{\text{max}}$ value of nanocrystalline CuO:Fe (1% to 5%) is found to increase with “Fe” concentration (Figure 14 inset). These effects could induce exchange coupling which is desirable for device fabrication if one could stabilize a single phase Cu–Fe–O solid solution without any ferrite formation by adopting different preparation techniques or by preparing a sample with homogenously dispersed CuFe$_2$O$_4$ in CuO.

By comparing the virgin magnetization curve in the hysteresis loop, one recognizes two qualitatively different kinds of behavior: (i) nucleation type and (ii) pinning type [56]. In a nucleation type magnet, the virgin curve is steep and saturation is reached under fields much lower than the saturation loop coercive field. Domain walls are present in the virgin state and the fact that the material can be easily saturated shows that walls are free to move and do not experience any important pinning effects. Once the virgin domain structure has been swept away, the formation of reversed domains becomes a difficult process, and the demagnetization curve is characterized by a substantial coercivity.

In a pinning type magnet, fields of the order of the saturation loop coercive field are required to saturate the material even when one starts from the virgin state. This indicates that domain wall pinning is the main mechanism responsible for coercivity. Domain wall motion is the dominant mechanism and the loop width is mainly determined by wall pinning effects [56]. The impediments to wall motion will determine the coercive field. The physical picture summarized by the term wall pinning is one where the impediments to wall motion arise from some form of structural disorder; dispersed phases with magnetic properties different from those of the matrix, as well as nonmagnetic inclusions or cavities, may also be important sources of pinning. The strength of the pinning effect may critically depend on the dimensionality of the pinning sources. The strength, density, and dimensionality of pinning centers can affect the value of $H_C$. Though the solubility of “Fe” in CuO is very much limited, a very small quantity of any immiscible component will always dissolve in another component, as this increases the configurational entropy and lowers the free energy of the crystal [57]. Hence, though the formation of CuFe$_2$O$_4$ is more favorable while trying to dope “Fe” in CuO, a fraction of “Fe” also enters into the Cu$^{2+}$ site as substitutional impurity. Hence contribution from intrinsic magnetization from the fraction of Cu–Fe–O substitutional solid solution formed within the sample apart from the composite like behavior of paramagnetic CuO dispersed with CuFe$_2$O$_4$ particles cannot be disregarded. Hence, one has to really ascertain its effect delineating the major magnetic contribution from the segregated CuFe$_2$O$_4$ phase. The intrinsic magnetic behavior could result from the spin alignment induced by the fraction of “Fe” substituting the “Cu” site. One could also argue that as the “Fe%” in CuO increases, the fraction of “Fe” substituting the cationic site also increases reasonably. However to cross check this argument, neutron diffraction measurements at ambient and at high-pressures are necessary.

3.2. Comparison of 1% Fe Doped CuO and Cu$_2$O. The results of 1% “Fe”-doped Cu$_2$O imply us to elucidate the role of
Figure 14: Room temperature hysteresis loops of bulk and nanocrystalline (50 hour refluxed, annealed at 900°C) Cu_{0.95}Fe_{0.05}O showing five-fold increase in coercivity. Inset shows the increase in $M_{\text{max}}$ value with increasing “Fe” concentration in nanocrystalline samples.

Figure 15: XRD patterns of pure Cu$_2$O, 1% “Fe”-doped single phase Cu$_2$O, and 2% “Fe”-doped Cu$_2$O with impurity peaks of Fe$_3$O$_4$.

Figure 16: Paramagnetic behavior of 1% Fe-doped Cu$_2$O at 300 K. Inset shows the same for 2% “Fe”-doped Cu$_2$O.

substitutional “Fe” in CuO. The non-observation of room temperature ferromagnetic behaviour in diamagnetic Cu$_2$O doped with 1% of “Fe” is another indirect support for the plausible intrinsic magnetization of “Fe”-doped CuO. The XRD pattern of pure Cu$_2$O ($a = 4.253$ Å) confirmed the cubic structure of Cu$_2$O and is shown in comparison with 1% and 2% “Fe”-doped Cu$_2$O in Figure 15. Single phase 1% “Fe”-doped Cu$_2$O was achieved by optimizing the concentration of N$_2$H$_4$ and the stirring duration. The XRD pattern of 2% “Fe”-doped Cu$_2$O showed secondary phases of Fe$_3$O$_4$ which is shown in comparison with pure Cu$_2$O in Figure 15. The compositional analysis by EDAX confirmed the near stoichiometry of 1% and 2% “Fe”-doped Cu$_2$O as it is a random alloy. Reproducibility was confirmed by numerous trials because formation of Cu$_2$O by wet chemistry method fairly has a chance of formation of CuFe$_2$O$_4$ and metallic “Fe” on over reduction with N$_2$H$_4$. Moreover the as-prepared samples were crystalline in nature due to preparation by reducing with N$_2$H$_4$. Hence annealing was not performed for any of the samples. Moreover, copper (I) oxide, being a meta stable phase, turns into a stable copper (II) oxide when heated above 160°C in air. The magnetization measurements on 1% “Fe”-doped Cu$_2$O at 300 K showed paramagnetic behavior (Figure 16) [30]. Pure Cu$_2$O is diamagnetic, but on doping with “Fe”, the material exhibits paramagnetic behavior. The low temperature measurements at 77 K show clear diamagnetic behavior (not shown here) indicating the non-ferromagnetic role played by impurities present, if any. The magnetization measurements on 2% “Fe”-doped Cu$_2$O sample, though having Fe$_3$O$_4$ phase, did not show clear room temperature ferromagnetism (Inset of Figure 16), whereas 1% and 2% “Fe”-doped CuO presents clear ferromagnetic hysteresis behavior which suggests possible contribution from Cu–Fe–O in addition to that from cubic CuFe$_2$O$_4$. Neutron diffraction measurements at ambient and at high pressures are necessary on both the Fe-doped CuO and Cu$_2$O samples to shed more light in this aspect.

For the formation of AB$_2$O$_4$ spinel structure, A is required to be a dipositive ion, but in Cu$_2$O, “Cu” is in +1 oxidation state and hence formation of spinel CuFe$_2$O$_4$ is not favored. Due to the absence of this spinel impurity phase, “Fe” doped Cu$_2$O does not show a dominant ferromagnetic property as it is observed in the case of 1% Fe-doped CuO.

The coordination number between Cu and O atoms in tenorite CuO (2+) and cuprite Cu$_2$O (1+) is believed to play a crucial role in the observed difference in their magnetic properties with “Fe” doping. In monoclinic CuO, the Cu atoms are coordinated to four coplanar oxygen situated at the corners of an almost rectangular parallelogram [17] with two more distant apical “O” atoms. A distorted octahedron is formed because of large Jahn-teller effect. Depending on the valence state (1+, 2+ or 3+), a “Fe” ion has up to 5, 4...
and “3d” electrons with a total spin of $s = 2 \frac{1}{2}$, $s = 2$ and $s = 1 \frac{1}{2}$, respectively, due to Hund’s rule. A Cu ion has a total spin of 1/2 and hence “Fe” ions doped into CuO have extra moments which are coupled to the lattice of Cu spins via superexchange. CuO at 300 K is paramagnetic and has one unpaired spin due to the 3d9 electronic configuration. The fraction of Fe3+ ions substituted at the “Cu” sites in CuO has 5 unpaired electrons, which might also contribute to the observed magnetic property of “Fe”-doped CuO by forcing the “Fe” magnetic dipoles to align ferromagnetically by interacting with the unpaired spins of the CuO which is at paramagnetic state at 300 K. Extending the analogy in CuO: Mn [22], we suppose that a fraction of “d” electron states are available for hopping between the “Fe” sites and hence mediating ferromagnetism through the Hund’s rule coupling. Hence we attribute the observed magnetic behavior of CuO: Fe to have a dominant hidden intrinsic nature apart from the segregated CuFe2O4 phase whereas this is not in the case of Cu2O, where we have Cu+ ions coordinated linearly to two “O” ions, due to its 3d10 configuration. There are no unpaired spins and the spin value is $s = 0$. Hence on substituting with 1% Fe, irrespective of the charge state of “Fe”, the Cu2O matrix could not mediate a ferromagnetic ordering through the substituted “Fe” ions. Hence, the spin configuration of the host matrix into which “Fe” is doped is also responsible for the observed magnetic behavior.

4. Conclusion

The XRD, TEM, and TGA results imply that the observed magnetic properties of “Fe”-doped CuO have contribution from the impurity phases, the nature of variation of $H_{C}$ and $M_{\text{max}}$ with increasing “Fe%”, and the role of substitutional “Fe” and non-observation of ferromagnetic behavior in “Fe”-doped Cu2O invites exclusive investigation on CuO. Achieving ferromagnetic behavior from a paramagnetic/antiferromagnetic host by creating a spin imbalance seems to be relatively easier and advantageous than achieving it from diamagnetic oxides like ZnO, TiO2, and so on. The size dependent magnetic properties of “Fe”-doped CuO with controlled formation of CuFe2O4 are another interesting aspect of this material which could be exploited for applications by suitably varying the size of the particles. The above said properties could be exploited for device applications provided if the “Fe” composition in CuO and the preparatory method and processing conditions are stabilized so as to result in a good single phase Cu–Fe–O solid solution with intrinsic magnetization and high reproducibility. Variation of $H_{C}$ in “Fe”-doped CuO, though CuFe2O4 phases are present, extends from “soft” magnetic behaviour to “hard” variation with $H_{C}$ in the samples studied. This wide variation in $H_{C}$ of such a DMS-like composite material could be thought of for fabricating MTJs with low $H_{C}$-“free” layer and high $H_{C}$-“pinned” layer separated by a thin insulating layer. The advantage of MTJ’s made up of such all oxide DMS like layers with high $M_{\text{max}}$, $N_{T}$, and $H_{C}$ over the metallic Fe/AlOx/NiFe and CoFeB/AlOx/CoFeB type of MTJs is that these are less complicated and cheap and will have very good lattice matching and least strain between the “pinned” and “free” layers.

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