Effect of Sn Substitution on Structural, Electrical and Magnetic Properties of Copper Ferrites Synthesized by Sol-gel auto Combustion Method.

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Absract:

The $Cu_{1-x}Sn_xFe_2O_4$ (X= 0, 0.25, 0.5, 0.75 and 1) were synthesized by using Sol-gel auto combustion method in order to obtain homogenous crystal structure. Thermal analysis techniques were used to decide sintering temperature of the ferrite. X-ray diffraction studies reveal that ferrites are polycrystalline with cubic spinel structure. Lattice constant (a), X-ray density (dx) & Porosity (P) are also calculated from XRD data. Micro grain size and compositional features of all samples were studied by scanning electron microscopy and energy dispersive X-ray analysis techniques respectively. The dc electrical resistivity of all the samples is measured in the temperature range of 323-673K. & it is found to decrease with increasing temperature indicating the semiconducting nature of the material. The magnetic properties were studied by using M-H hysteresis loop. The saturation magnetization (Ms) decreases with increase in Sn content.

Keywords: Sol-gel, Ferrite, Spinel, X ray diffraction, Electron microscopy, Semiconductor, Hysteresis loop.

1. Introduction:

Mixed metal oxides (ferrites) have been commercially used for many years, as a high frequency device such as radio frequency coils, rod antenas , transformer cores and magnetic cores of read write heads for high speed digital tapes [1,2]. Spinel ferrites, MFe_2O_4 (M= Mn, Zn, Co, Mg etc) are a family of oxide material with a great technological importance and can be used in the fabrication of magnetic, various microwave and radar devices [3-5].Among various oxides, transition metal oxides with iron oxides as their main component have attracted the attention of physicist & technologist, since these are magnetic semiconductors suitable for use in microwave device [6]. High electrical resistivity and relatively easy preparation make same materials widely useful for the cores of intermediate and high frequency electromagnetic device. Ferrites have vast applications from microwave to radiofrequency[7] .The physical and chemical properties of ferrites are dependent upon various factors such as sintering temperature, sintering time, rate of heating and rate of cooling etc. [8]. Copper ferrite ($CuFe_2O_4$) has mostly an inverse spinel structure [9].In order to improve electrical and magnetic properties, many researcher attempted several cations such as Co^{2+}, Zn^{2+}, Cu^{2+}, Ti^{4+} in to ferrites [10-16]. Ti^{4+} substitution at iron site in manganese ferrites is known to be effective in reducing magneto crystalline anisotropy and enhancing the electrical resistivity, these properties are suitable for wide range of industrial applications [17]. However, Ti^{4+} substitution in $MnFe_2O_4$ requires costly titanium salts for chemical synthesis and also needs higher heat treatment to obtain single phase [18].

Recently, considerable efforts have been made on the surface modification and the preparation of different types of mixed metal oxides. Various methods such as hydrothermal method [19], citrate method [20], ceramic method[21], solvent evaporation method [22], combustion method [23] and sol-gel method [24].The Sol-gel auto combustion method has various advantages such as simple, inexpensive, quick synthesis and does not required any vacuum process or sophisticated instrumentation.

The aim of present work is to synthesize nanocrystalline materials and to study electrical (dc resistivity), magnetic (saturation magnetization, remanence) properties and also to reduce the coercivity (Hc) to make this material suitable for recording media and microwave device.

2. Experimental.

2.1. Preparation.

Polycrystalline $Cu_{1-x}Sn_xFe_2O_4$ powders (X= 0,0.25,0.50,0.75 and 1)) were synthesized by sol–gel auto-combustion method with analytical grade Copper nitrate [$Cu(NO_3).3H_2O$],Tin chloride[($SnCl_2$).$2H_2O$] , Ferric nitrate [$Fe(NO_3)_3.9H_2O$] and Citric acid [$C_6H_8O_7$]. Metal nitrates and citric acid were dissolved in minimum quantity of deionised water with stoichiometric proportions and solutions were mixed. The pH of the solution was maintained to 9.0-9.5 using ammonia solution. The solution was transformed into dry gel on heating at 100^0C. On further heating the dried gel burnt in a self propagating combustion manner till whole quantity of gel get completely converted to a floppy loose powder. Later burnt precursor powder was sintered at 900^0C for 5 hours.

2.2. Characterization.

A computerized X-ray powder diffractometer (Siemens D-500 diffractometer) with Cu-Kα radiation (λ=1.5406 Å) was used to identify the crystalline nature of the samples and to calculate lattice parameter and crystallite size. The lattice parameters were calculated for the cubic phase using following relation.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \dots\dots\dots\dots [1]$$

Where a, b and c are lattice parameters, (hkl) is the Miller indices and d is the interplanar distance.
From the X-ray diffraction peaks, crystallite size was estimated using Debye Scherer's formula [25].

$$t = \frac{0.9\,\lambda}{\beta\cos\theta} \dots\dots\dots\dots [2]$$

Where, symbols have their usual meaning.

The X-ray density (dx) was calculated by using the relation,

$$dx = \frac{8M}{Na^3} \dots\dots\dots [3]$$

Where N= Avogadro's number (6.023×10^{23} atom/mol), M= molecular weight and a = lattice constant .

The percentage porosity of sample was calculated using the formula

$$P(\%) = \left(\frac{d_a - d_x}{d_a}\right) * 100 \dots\dots\dots [4]$$

Where d_a = actual density and d_x = theoretical density.

Formation temperature of samples was checked by taking TGA/DTA curves on the SDT Q600 V20.9 instrument by heating the powders at a rate of 10°C/min from room temperature to 1000°C in an air atmosphere. Scanning electron microscope (SEM) was used to study the morphology of the powders. The grain size of all the samples was calculated by Cottrell's method. An energy dispersive X-ray spectroscopy analyzer equipped with SEM was used for the compositional analysis.

The electrical resistivity measurements in the temperature range from 323 to 673 K were taken by two probe method. The electrical contacts were established by pasting silver paste on both surfaces of the pellet. The graphs of the logρ vs. 1000/T was plotted for all the samples under investigation and their energy of activation values (E_a) were calculated by using the equation:

$$E_a = 1.983 * 10^{-4} \left(\frac{\log\rho}{\frac{1}{T}} \right) \text{ev} \dots \dots \dots [5]$$

Where, symbols have their usual meaning.

A computerized high field hysteresis loop tracer was used to measure magnetic properties at room temperature for all compositions. The magnetic moment per formula unit in Bohr magnetron (μ_B) was calculated by using the relation [25].

$$\mu_B = \frac{MW * M_s}{5585} \dots \dots \dots [6]$$

Where, MW=molecular weight of composition (in grams); M_s = saturation magnetization (in emu/gm).

3. Result and discussion

3.1 Thermal Analysis:

TGA analysis of dried $Cu_{0.5}Sn_{0.5}Fe_2O_4$ powder was presented in fig.1. TGA curve show thermal decomposition process involving several steps that from room temperature to 1000^0C. The weight loss from room temperature to about 1000^0C was 32.23% .The weight loss below 200^0C is due to loss of water vapours of adsorbed water. The weight loss from 200 to 400^0C is due to loss of organic matter including citric acid.The weight loss above 400^0C is due to loss of unreacted nitrates. The TGA curve shows that formation of spinel ferrites is at about 550^0.

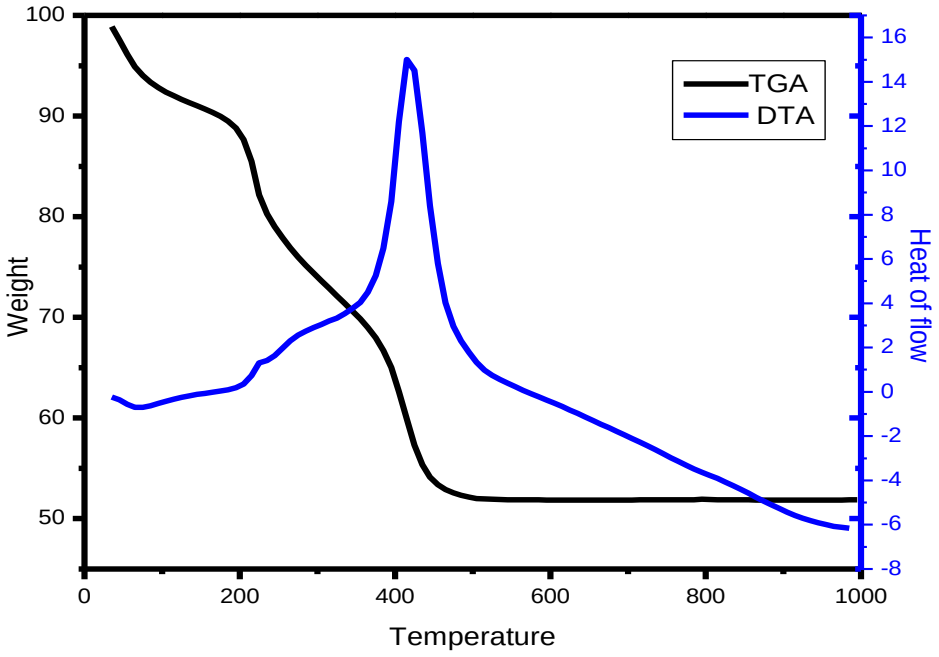


Fig. No. 1 Thermal Analysis of $Cu_{0.5}Sn_{0.5}Fe_2O_4$

3.2. X-Ray Diffraction study.

The structure and phase purity of the product were confirmed by analyzing the observed powder X-ray diffraction patterns. Fig. 2 depicts the observed powder XRD patterns of the synthesized $Cu_{1-x}Sn_xFe_2O_4$

compositions. All observed reflections of the Sn substituted Cu ferrite samples could be assigned to cubic spinel lattice indicating their single phase nature. Lattice constant (a) varies between 8.327 to 8.3844 A^0. The crystallite size was in the range of 23.2 to 34.96 nm. It was observed that theoretical density increases with increase in Sn substitution. The theoretical density of the ferrites was determined accurately by the hydrostatic method. Plot of theoretical density vs. Sn content is shown in Fig.3. It is also observed from the figure that theoretical density increases up to X=0.75 thereafter decreases for X=1. Theoretical density, lattice constant (a), crystallite size (t), X-ray density (d_x), actual density (d_a), porosity (%P) and average grain size are summarized in Table 1.

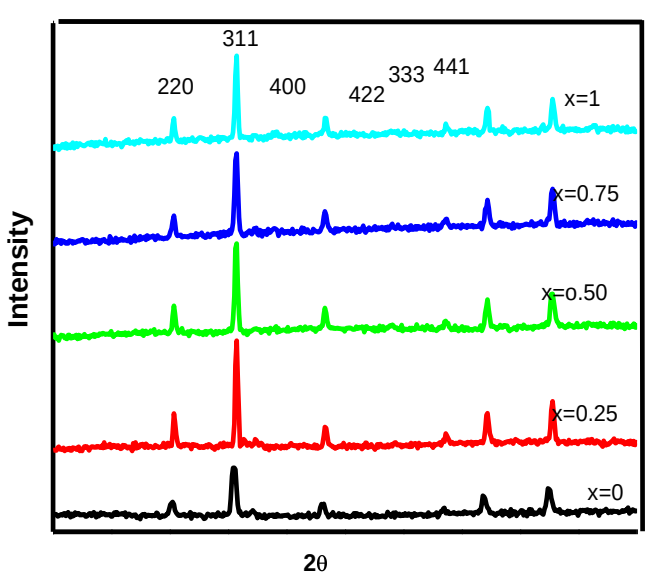


Fig. No. 2 XRD of $Cu_{1-x}Sn_x Fe_2O_4$ (X= 0, 0.25, 0.50, 0.75 & 1)

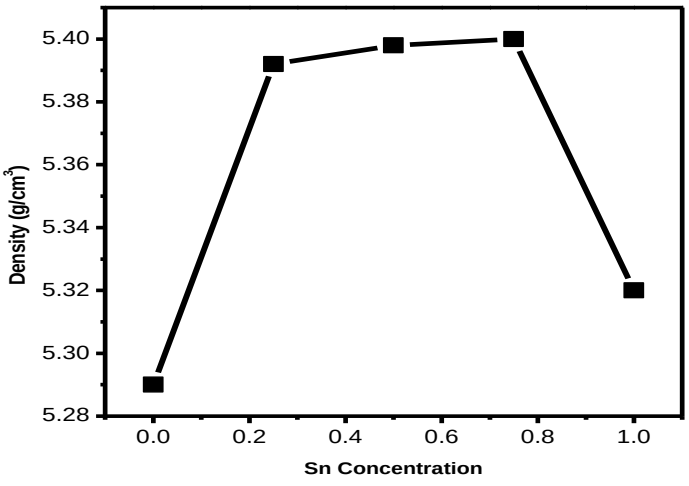


Fig. No.3. Density Vs Sn Content.

3.3. Scanning Electron Microscopy

SEM micrographs of the samples are displayed in the Fig.4. These figures indicate that samples obtained by this method are uniform in both morphology and crystallite size, but having agglomeration to

some extent, due to the relative higher annealing temperature and interaction between magnetic particles. The agglomeration is due to the Van-der Waal forces between the particles [26]. Present study reveals that, all samples were of fine grains. The average grain size was calculated by Cottrell's method [27] and it remains in the range of 0.68 to 1.97µm. Average grain size of ferrites increases with increase in Sn content. Also it was observed that the porosity decreases with increasing grain size which is summarized in Table 1.

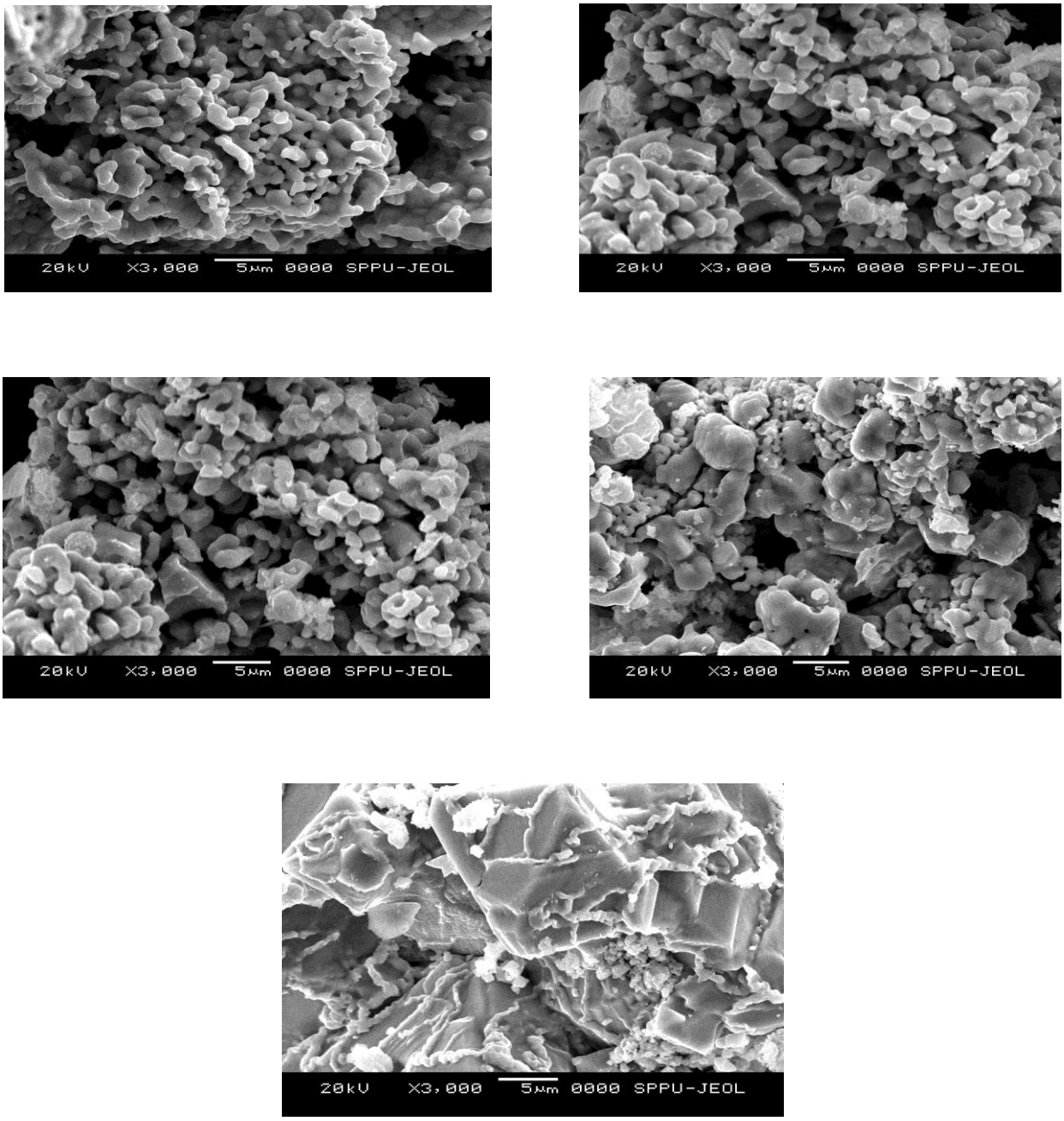


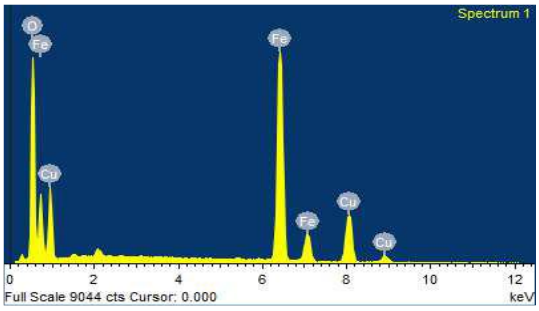
Fig. No. 4. SEM Images of $Cu_{1-x}Sn_xFe_2O_4$ (X= 0, 0.25, 0.50, 0.75 & 1)

Table 1– Lattice constant (a), Crystallite size (t), Theoretical /X-ray density (d_X), Actual density (d_a), Porosity (%P) and Average grain size from SEM

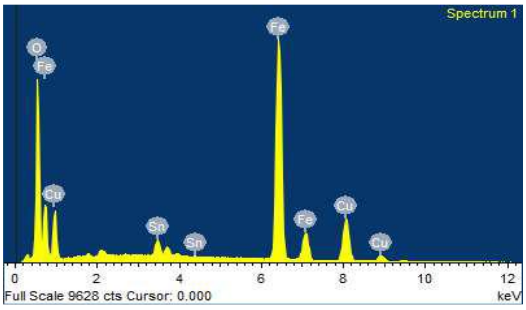
Sr.No	Composition	Lattice Constant a (A^0)	Crystallite size t (nm)	X-ray density dx g/cm^3	Observed density da. g/cm^3	Porosity P (%)	Average Grain size (μm)
1	0	8.3276	34.96	5.290	6.76	21.6	0.68
2	0.25	8.3394	33.12	5.392	6.35	15.03	1.12
3	0.50	8.3436	30.77	5.398	6.43	15.87	1.34
4	0.75	8.3460	26.44	5.40	6.56	17.23	1.59
5	1	8.3844	23.27	5.32	6.08	12.45	1.97

3.4. Energy dispersive X-ray analysis

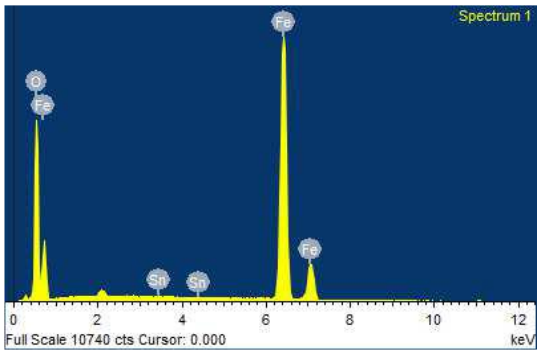
The composition of the metal oxides had been determined by using the energy dispersive X-ray analysis (EDAX) [28]. X-ray analysis spectrum $Cu_{1-x}Sn_xFe_2O_4$ (X=0 to 1) is shown in Fig. 5. The presence of Cu, Sn, Fe and O are confirmed in all samples from EDAX spectrum. Spectrum analysis proved the stoichiometries of $Cu_{1x}Sn_xFe_2O_4$ (X=0 to 1) ferrites synthesized by sol gel auto combustion method. Analysis did not indicate the presence of any foreign elements in it. This confirms the purity and the composition of the material.



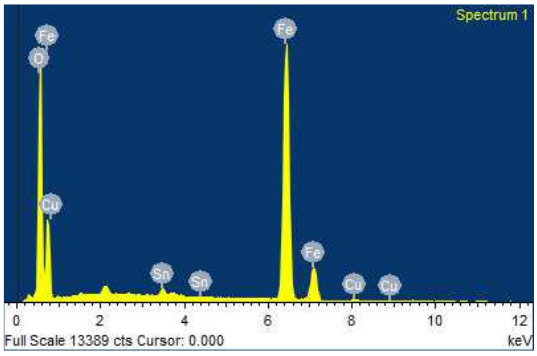
X= 0.0



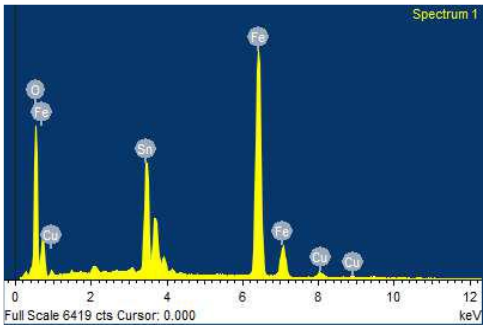
X= 0.25



X= 0.50



X= 0.75



X= 1.0

Fig. No.5. EDAX Images of $Cu_{1-x}Sn_xFe_2O_4$ (X= 0, 0.25, 0.50, 0.75 & 1)

3.5 DC Electrical Resistivity

The electrical resistivity of the synthesized samples were measured by two probe method. Temperature dependent DC electrical resistivity of the $Cu_{1-x}Sn_xFe_2O_4$ is shown in Fig. 6. Linear decrease in resistivity with increasing temperature reflects semiconducting nature of material [29]. The conduction mechanism in ferrites is explained on the basis of Verwey De Boer mechanism that involves exchange of electrons between the ions of the same elements present in more than one valence state and distributed randomly over equivalent crystallographic lattice sites. The decrease in resistivity with increase in temperature is attributed to increase in drift mobility of the charge carriers. Activation energy of all samples varies in range of 0.2946 to 0.8635 eV.

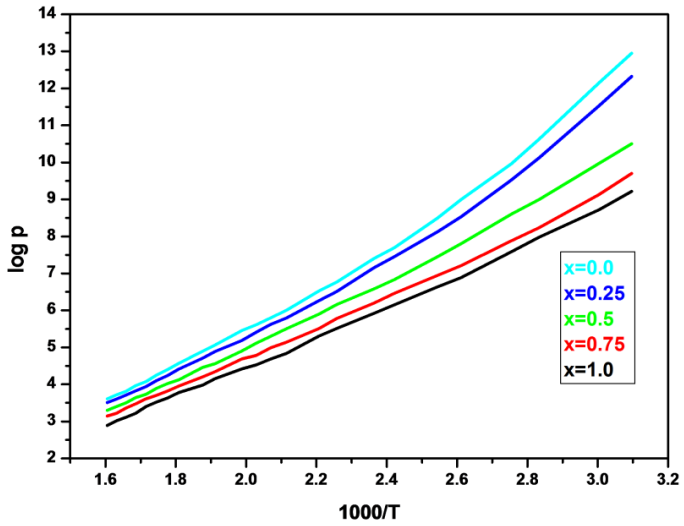


Fig.No.6 DC Electrical Resistivity of $Cu_{1-x}Sn_x Fe_2O_4$ (X= 0, 0.25, 0.50, 0.75 & 1)

3.6 Magnetic Properties:

In spinel ferrites magnetic properties depend on the sum of the magnetic moments at tetrahedral -A site and octahedral -B site [30]. The magnetic properties of sintered material have been determined at room temperature using vibrating sample magnetometer (VSM**)**. Hysteresis loops at room temperature (25^0c) $Cu_{1-X}Sn_xFe2O4$ (X= 0, 0.50 and 1) are shown in fig. 7. The values of saturation magnetization (M_s), Coercivity (H_c) and magnetic moment (μ_B) measurements are listed in Table 2. Saturation magnetization (Ms) of the synthesized samples varies from 27.313 to 37.39emu/g. Coercivity (Hc) increase with increase in Sn substitution from 95.59 - 216.46 Oe. The magnetic moment value in terms of Bohr magnetron varies in the range of 1.60 to 1.96 emu/g with Sn substitution.

Saturation Magnetization (Ms) decreases with addition of Sn that is mostly due to Yafet and Kittel spin arrangement [31, 32].

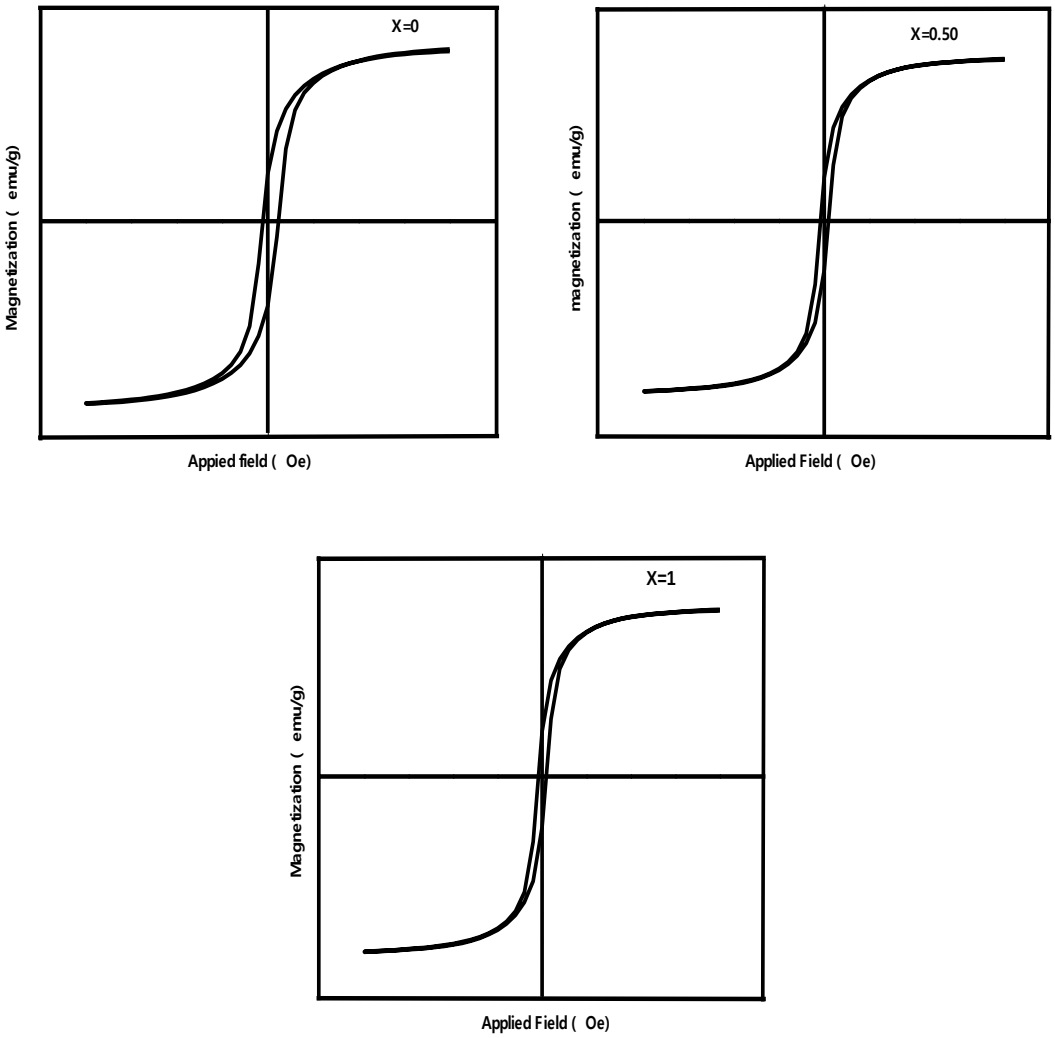


Fig. Hysteresis loop of $Cu_{1-x}Sn_xFe_2O_4$ (X= 0, 0.50 & 1)

Table 2- Data on magnetic hysteresis for $Cu_{1-}Sn_{x.}Fe_2O_4$ system (X= 0, 0.50 & 1)

Sr,No	Composition	Saturation Magnetization (Ms) Emu/g	Coercivity. Hc (Oe)	Magnetic Moment (μB) Bohr magnetron
1	$CuFe_2O_4$	37.39	95.59	1.60
2	$Cu_{0.50}Sn_{0.50}$ Fe_2O_4	33.003	185.14	1.57
3	Sn Fe_2O_4	27.313	216.46	1.96

Conclusion:

Spinel $Cu_{1-X}Sn_xFe_2O_4$ (X=0 to 1) has been successfully synthesized and characterized by sol-gel auto combustion method, for their structural, electrical and magnetic properties. The Substitution of Sn in $Cu_{1-X}Sn_xFe_2O_4$ ferrites causes appreciable changes in its structural and electrical properties. All samples have existence of single phase cubic spinel structure with increase of X-ray density whereas decrease of bulk density. Experimental results revealed that, the lattice constant increases and decrease in crystallite size with the increase of Sn content. Thermal analysis shows that ferrites are formed above 520^0C. Morphology studies shows that, average grain size increases from 0.68 to1.97 µm with addition of Sn content and elemental analysis of metals in the samples are in their stoichiometric proportions as expected. Electrical resistivity plot shows that nature of all samples is semiconducting. Activation energy varies in the range 0.2946 to 0.8635 eV. The magnetic moment in terms of Bohr magnetron varies in the range of 1.60 to1.96 emu/g with Sn substitution. The saturation magnetization decreases from 37.39 to 27.31 with increase in Sn content.

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