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Influence of Cr^{3+} ions on Structural and magnetic properties of in Cu-Cd ferrites synthesis by Citrate Gel Method



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Abstract

Nano Size Cu-Cd ferrites of system $\text{Cu}_{0.7}\text{Cd}_{0.3}\text{Cr}_x\text{Fe}_{2-x}\text{O}_4$ for $x=0.0$ to $x=1.0$ prepared by citrate gel method. These samples were sintered at 750°C for 6 hours. The XRD data revealed that the all samples possess a single phase cubic spinel structure. The Lattice constant, X-ray density, determined from XRD data decreases with increase in Cr^{3+} . The saturation magnetization and magneton number both are decreasing with increase of chromium concentration x . The decrease in saturation magnetization and magneton number is attributed to the substitution of the Cr^{3+} ions. Curie temperature (T_c) from susceptibility plot is found to decrease with Cr concentration x .

Keywords: Cu-Cd ferrites, Lattice Constant, A.C. Susceptibility, Curie Temperature

Introduction

The spinel structure of these ferrites possesses the general formula of $(\text{A})[\text{B}_2]\text{O}_4$, where A represents cations in tetrahedral sites and B represents cations in the octahedral positions in a cubic structure. However, the formula $(\text{A}_{1-x}\text{B}_x)[\text{A}_1\text{B}_{2-x}]\text{O}_4$ represents many possible intermediary distributions that denote considerable cation disorder, indicating that this structure requires special attention in terms of magnetic characterization¹.

Review of Literature

Spinel type oxides (MFe_2O_4 ; where M divalent cations, e.g., Ni, Co, Mn), which include magnetic ferrites, are often denoted by the formula AB_2O_4 , where A and B refer to tetrahedral and octahedral sites, respectively, in the fcc oxygen lattice². The addition of impurities induces changes in the defect structure and texture of the crystal³, creating significant modifications in the magnetic and electrical properties of these materials. Chromium (Cr^{3+}) ions with antiferromagnetic nature are known for achieving control over magnetic parameters in developing technologically important materials. Copper substituted ferrites are a well-known as class of technologically important ferrites. This material enjoys special significance, particularly at high frequencies, because of its high resistivity and therefore low eddy current losses. This usual method of preparing ferrites is the conventional solid state method which apart from being cumbersome has some serious limitation^{4,6}. The spinel ferrites currently used as key materials for the advancements in information storage systems, ferrofluid technology, magnetic refrigeration, detoxification of biological fluids, magnetic resonance imaging (MRI) contrast enhancement, and magnetic cell separation^{7,8}. The polycrystalline ferrites such as Cu-Cd ferrites have very important structural properties dependent on several factors such as method of preparation, substitution of cations, sintering temperature, sintering time, sintering atmosphere, porosity and microstructure^{9,10}. while Cd ferrite (CdFe_2O_4) has a regular spinel structure in which Cd^{2+} ions occupy the tetrahedral A-sites and Fe^{3+} ions occupy the octahedral B-sites¹¹. The ferrite material used in different biomarkers, magnetic drug delivery systems, electrochemical energy storage, catalysis, and digital technology¹².

Aim of the Study

This paper therefore presents a study of nanosized Cu -Cd ferrite doped with Cr^{3+} produced by citrate gel method and its structural, magnetic and a.c. susceptibility characterization.

Experimental

$\text{Cu}_{0.7}\text{Cd}_{0.3}\text{Cr}_x\text{Fe}_{2-x}\text{O}_4$ was chosen to conduct this study. All reagents used were of AR grade. An aqueous solution of stoichiometric amount of copper nitrate, Cadmium nitrate, Chromium nitrate, iron II. Citrate were reacted with citric acid in 1: 1 molar ratio. The PH of the solution was increased to 7 the addition of ammonium hydroxide to complete the reaction of the Cu-Cd-Cr citrate precursor.

The solution was evaporated very slowly over a period of ten hours to dryness. Viscosity and color changed as the sol, turned into puffy, porous dry gel. As soon as the solvent removal was complete the dried. Precursor underwent a self ignition reaction to form a very fine powder known as synthesized powder.

The as-synthesized powder thus obtained was treated in furnace at 200° C for 6 hours followed by further heat treatment at 750° C for 6 hours to remove the residual carbon.

The structural characterization of all the prepared sample of the series

$\text{Cu}_{0.7}\text{Cd}_{0.3}\text{Cr}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5) was carried out by X-ray diffraction techniques (XRD). X-ray diffraction is considered as the most versatile non-destructive analytical tool for identifying the constituent of multiphase mixture qualitatively and quantitatively and also to determine the amorphous content of sample. The pattern helps to identify the structural phases present in the end product obtained by the method of preparation employed. The phase purity, unit cell parameter, particle size, X-ray density, Cation distribution etc. can be obtained from analysis of XRD data The saturation magnetization of the ferrite samples were measured with the help of high field hysteresis loop tracer. The a.c. susceptibility measurements of all the powdered samples were measure using the set up developed by Likhite et al. It consists of Helmholtz coil, two pick-up coils, and furnace and sample holder. The set up operates at frequency of 263 Hz and in the r.m.s. field of 7 Oe. The set up consists of two Helmholtz coil to produce uniform field at pick up coil. To heat the sample from room temperature to about 800 K, a furnace was fabricated by winding the platinum wire on silica tube. To avoid overheating of coil a glass jacket with water circulation was used. The furnace was inserted in the glass jacket and was placed at the center of pick up coil. The sample holder was made up of a quartz tube fused at one end.

Result

X-ray Diffraction

X-ray diffraction pattern were recorded using Philips X- ray diffractometer

(Model PW1710) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the range of 2θ of 22° to 70° They recorded X-ray diffraction pattern of typical samples are shown in fig. 1. The X- ray diffraction pattern shows the presence of signal phase spinel structure. There are no addition peaks corresponding to extra phases. The analysis of X-ray diffraction pattern indicates that the sample having cubic spinel

structure. The lattice constant 'a' of all the samples was determined by using the equation discussed elsewhere¹³. The value of lattice constant 'a' were determined with an accuracy of $\pm 0.002 \text{ \AA}$ using XRD data. The variation of lattice constant with Cr content 'x' is shown in the fig 2. From Fig 2 it is observed that the lattice constant is decreases with increase in concentration of chromium. This is due to replacement of larger Fe^{3+} ion (0.63 \AA) in the system. A similar nature was reported for other Cr substituted spinel ferrites¹⁴. The average crystallite size (t) was determined using the line broadening of the main reflection (3 1 1) and (4 4 0) diffraction peak using the Debye Scherrer formula¹⁵. The crystallite size is decreases from 40 nm to 25 nm with increasing Cr^{3+} content. The value of X- ray density dx was calculated by using for relation.

$$d_x = \frac{ZM}{NV} \quad (1)$$

Where,

Z is no of molecule per unit cell for cubic ferrites Z= 8

M is molecular weight.

N is Avogadro's no. (6.22×10^{23})

V is volume of unit cell.

The value of X-ray density is present in fig 2 From Fig 2 it is observed that the X- ray density is decreases with due to increase in molecular weight. Mass over takes the decrease in the unit cell volume¹⁶.

Magnetization

The magnetization magnetron number (n_B) of all the samples were carried out at room temperature using high field hysteresis loop technique. The value of saturation magnetization (σ_s) using these values to calculate magnetron number (n_B) (the saturation magnetization per formula unit in Bohr magneton) at room temperature was calculated using the formula.

$$n_B = \frac{\text{Molecular weight} \times \text{Saturation magnetization}}{5585} \quad (2)$$

The value saturation magnetization (σ_s) and magnetron number (n_B) are depicted in Fig 3. From Fig 3 it is clear both decreases with increases in Cr content x due Fe^{3+} ions replaced by Cr^{3+} ions. Thus, A-B interaction decreases in the system¹⁷

A. C. Susceptibility

The plots of a.c. Susceptibility χ_T/χ_{RT} against temperature for the the samples $x=0.0, 0.2$ and 0.6 composition are shown in fig 4. Which exhibit normal ferromagnetic behaviour which decreases with increase in Cr content 'x'. The Curie temperature determined from the Fig 4 (Where $\chi_{ac} = 0$). The value of Curie temperature is show in fig 5. It can be seen that there is decrease in Curie temperature with the addition of chromium. This is attributed to replacement of strong magnetic ion Fe by Cr ions¹⁸.

Conclusion

1. X- ray diffraction patterns revealed the formation of single phase cubic spinel structure.
2. The variation of lattice constant with content x exhibits linear behaviour.

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- The magnetization data shows the structure is collinear.
- Curie temperature determines from a.c. susceptibility data decreases with increases in Cr ions.

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Figure 1
X - Ray Diffraction Pattern of $\text{Cu}_{0.7}\text{Cd}_{0.3}\text{Cr}_x\text{Fe}_{2-x}\text{O}_4$ for $x=0.0$, $x=0.2$ and $x=0.4$.

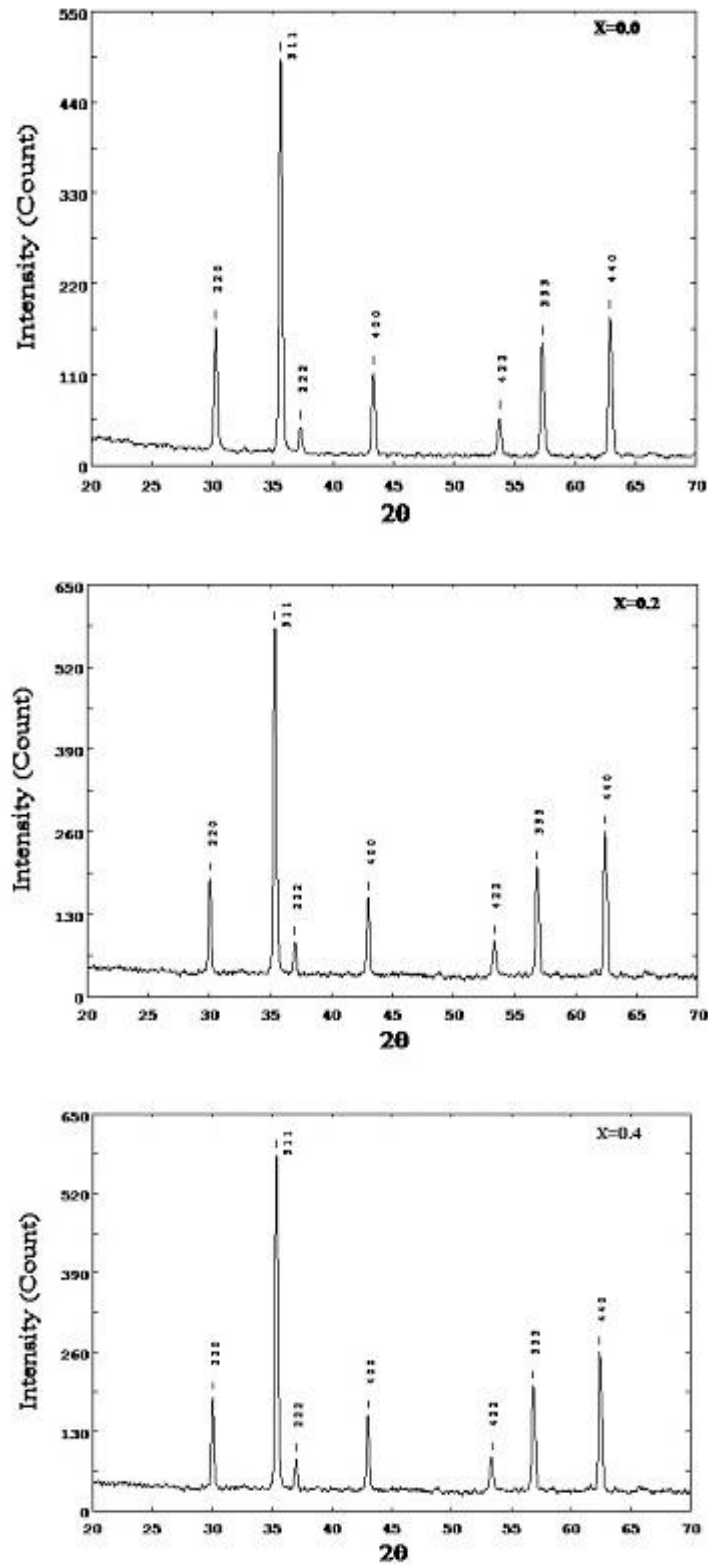


Fig-2 Variation of Lattice Constant (a) and X- ray density with Cr content x.

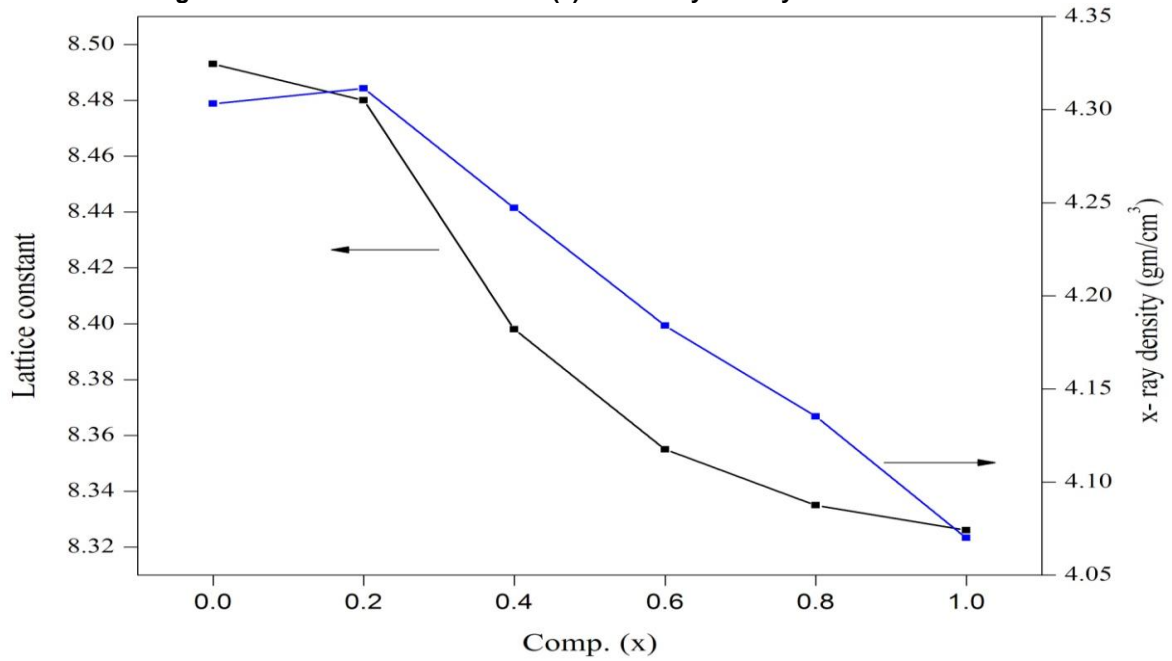


Fig-3 Variation of saturation Magnetization (σ) and Magnetron number (nB) with Cr content x.

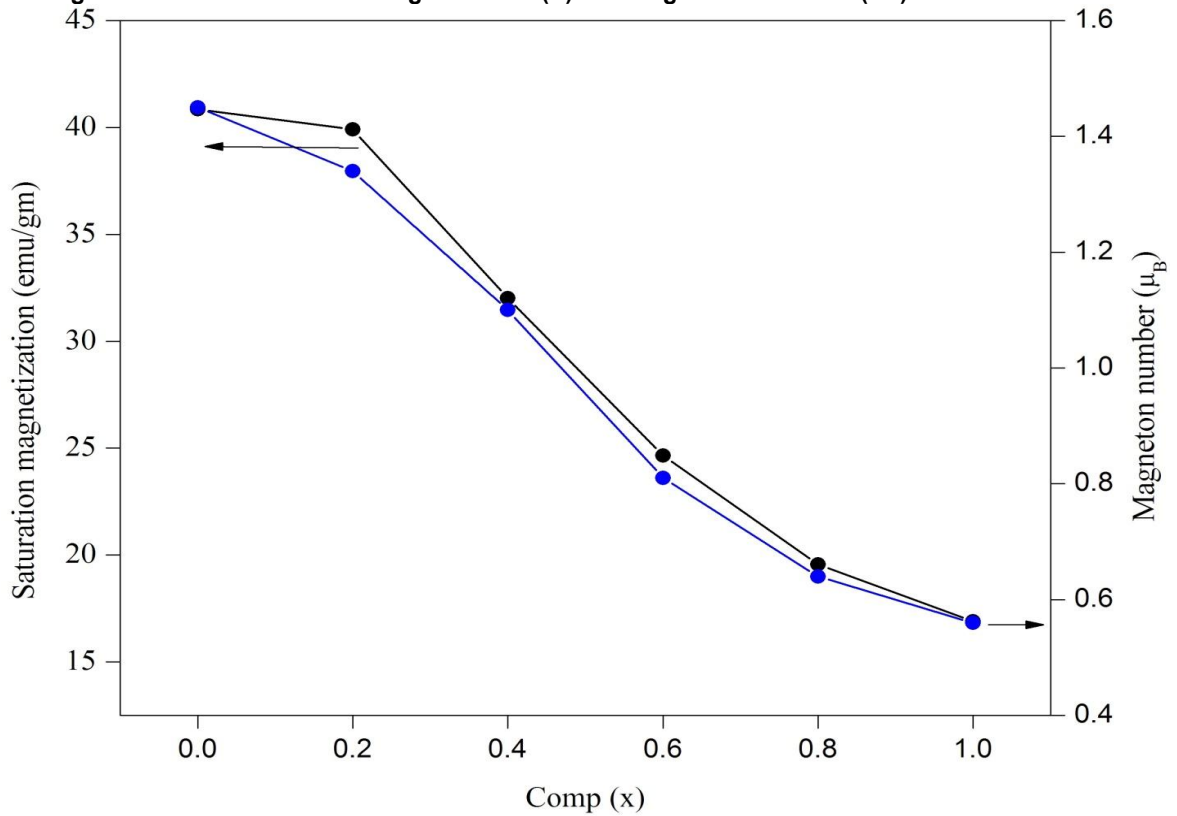


Fig-4 Variation of $\chi T / \chi RT$ versus temperature of $\text{Cu}_{0.7}\text{Cd}_{0.3}\text{Cr}_x\text{Fe}_{2-x}\text{O}_4$ for $x=0.0$, $x=0.2$ and $x=0.6$.

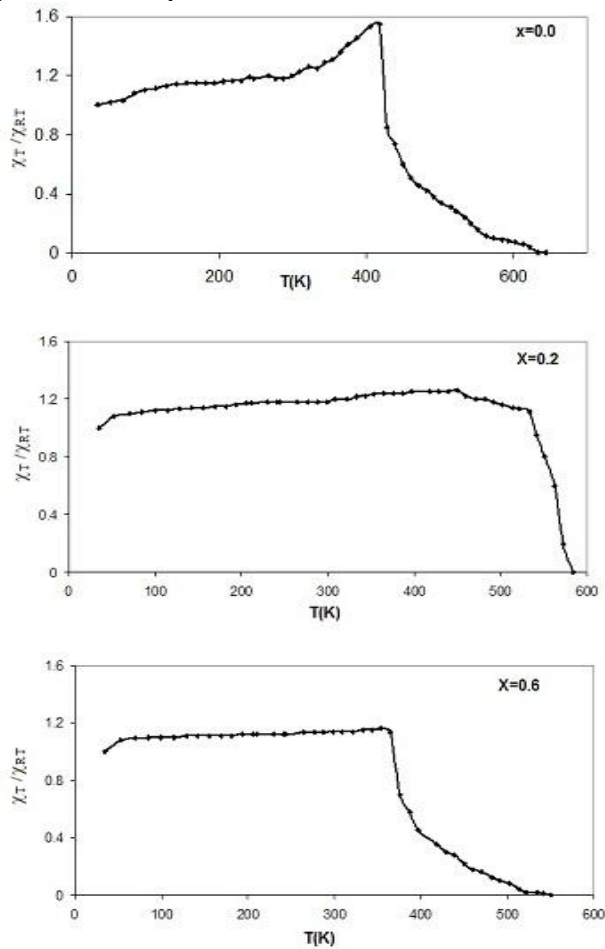


Figure 5
Variation of Curie temperature with Cr Content x

