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Structural and magnetic investigation on Cr^{3+} substituted $Mn_{0.25}Cu_{0.25}Zn_{0.5}Fe_2O_4$ nano ferrites by co-precipitation route

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Abstract A low-temperature co-precipitation approach was used to prepare $Mn_{0.25}Cu_{0.25}Zn_{0.5}Fe_{2-x}Cr_xO_4$ (x=0.0, 0.4). The X-ray diffraction with most intense (311) peak and crystallite size in the range 25-29 nm confirms the formation of spinel nano ferrites. The transmittance within 400-600 cm^{-1} for all samples confirms Fe-O bond at tetrahedral and octahedral sites of prepared spinel nano ferrites demonstrated by FTIR. The soft magnetic nature of prepared material was recorded by VSM. The small Coercivity (16.6032 &20.9224 Oe), retentivity (1.4588 &1.5617 emu/g) and magnetic saturation (23.83 &31.8169 emu/g) demonstrates superparamagnetic, pseudo single domain and randomly oriented multi-domain nature of the nano ferrites. The produced superparamagnetic nano ferrites advantageous in high frequency and biomedical applications.

1. Introduction

A soft magnetic nanosized material with cubic structure (space group Fd-3m) and chemical composition MFe_2O_4 (M is divalent Mn, Zn, Ni, Cu, Mg etc.) known as spinel ferrites have attracted a lot of interest among the many sorts of nanomaterials because of their prospective applications in MRI, magnetic drug delivery, wastewater treatment, catalysis, biomedical applications, gas sensors, memory chip of computers, and various magnetic applications [1-4]. Manganese-copper-zinc (MnCuZn), one of the several combinations of divalent metal ions in spinel ferrites, has particular significance because of their low losses and high permeability values at lower frequencies [5].

In present research work, $Mn_{0.25}Cu_{0.25}Zn_{0.5}Fe_2O_4$ and $Mn_{0.25}Cu_{0.25}Zn_{0.5}Fe_{1.6}Cr_{0.4}O_4$ have been prepared using a low-temperature co-precipitation route in order to obtain pure form of spinel ferrite samples for systematical structural, spectroscopic and magnetic investigation.

2. Experimental Details

$Mn_{0.25}Cu_{0.25}Zn_{0.5}Fe_{2-x}Cr_xO_4$ (x=0.0, 0.4) were synthesized using a co-precipitation approach. Manganese chloride ($MnCl_2.4H_2O$), cupric chloride ($CuCl_2.2H_2O$) , zinc chloride ($ZnCl_2$), and iron chloride ($FeCl_3$) were used as precursors. Each precursor dissolved in the appropriate stoichiometric ratio of 1:2 in de-ionized water. Solutions were stirred 20 mins separately for homogeneous mixing of metal salts in aqueous medium under constant magnetic stirring. Reaction temperature was maintained at 80°C with continuous stirring on magnetic stirrer. Once the desired reaction temperature reached, NaOH(4M) solution added dropwise to maintain the pH-12. At about constant reaction temperature (80°C) solution was heated for 2 hrs. The precipitate washed with distilled water & acetone after cooling to room temperature. Filtered precipitate then dried at 100°C for 2 hours. The resulting sample grounded for 2 hours using mortar & pestle. Ferrite powder now calcinated at 800°C indicated as MCZF@Cr0.0 and MCZF@Cr0.4 respectively. Both samples after calcination were grinded for 2 H and processed further for crystallographic, spectroscopic and magnetic study.

2.1 Characterization Techniques

X-ray diffraction pattern of prepared sample was recorded by X-Ray diffractometer (Rigaku Mini-Flex 600 Rigaku Japan). The functional group and nature of their bonds were studied within the absorption scale 0.4K cm^{-1} to 4K cm^{-1} with Fourier Transform Infrared Spectroscopy (FTIR) (Model: IR Affinity–1Shimadzu, Japan). Magnetic parameters of synthesized nano-ferrite were investigated using a Vibrating Sample Magnetometer (VSM) (series 7400 Lakeshore).

3. Results and Discussion

3.1 XRD Studies

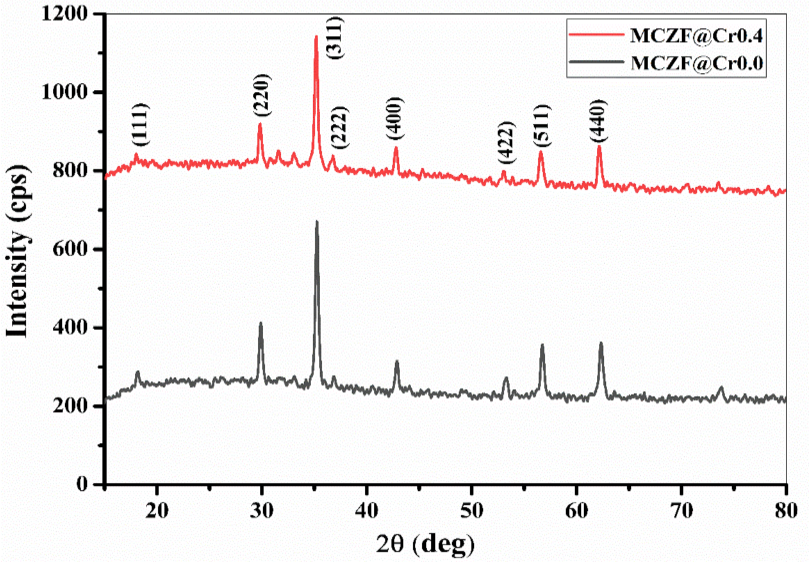

Figure 1. XRD spectra of MCZF@Cr0.0 and MCZF@Cr0.4 nano ferrite

XRD spectra of prepared MCZF@Cr0.0 and MCZF@Cr0.4 is shown in Figure 1. The expected Bragg peaks of (111), (220), (311), (222), (400), (422), (511) and (440) for the cubic spinel type structure (space group Fd-3m) are visible in these patterns, which are Miller indices of recognized reflections **[6]**. As shown in Fig 1, slight shift of **2θ** position and FWHM(β**)** of (311) corresponds to modification of spinel structure with Cr^{3+} substitution. The effect of chromium (Cr^{3+}) substitution on various crystallo-structural parameters like crystallite size (***D***), lattice parameter (***a***), dislocation density(**δ**), strain(ε) bond lengths (d_{AX} and d_{BX}) and hopping lengths (d_A and d_B) are calculated for (311) and estimated in Table 1 & Table 2 **[7]**.

Table 1. *2θ,* FWHM*(β),* d-spacing, crystallite Size*(D)*, lattice dimension*(a)* and volume*(V)* of prepared MCZF@Cr0.0 MCZF@Cr0.4 nano ferrite.

Sample	*2θ* (deg)	*β* (deg)	*d*-spacing (Å)	*D* (nm)	*a* (Å)	*V* (cm^3)
MCZF@Cr0.0	35.12	0.286	2.5531	29.150	8.467	607.12
MCZF@Cr0.4	35.18	0.285	2.5489	28.573	8.453	604.14

Table 2. Dislocation density*(δ),* strain*(ε),* X-ray density(ρX-ray), bond length on A site and B sites *(dAX* and *dBX*), hopping length on tetrahedral and octahedral sites (*dA* and *dB*) of prepared MCZF@Cr0.0 MCZF@Cr0.4 nano ferrite.

Sample	δ ($10^{15} 1/m^2$)	ε (10^{-3})	$\rho_{X\text{-}ray}$ (g/cm^3)	d_{AX} (Å)	d_{BX} (Å)	d_A (Å)	d_B (Å)
MCZF@Cr0.0	1.17683	3.9406	5.2066	1.8332	2.1169	3.6665	2.9937
MCZF@Cr0.4	1.22486	3.9205	5.1985	1.8302	2.1134	3.6605	2.9888

From Table 1 & 2, obtained crystallite size *(D)* and other structural parameter (d_{AX},d_{BX},d_A and d_B*)* decreases with Cr^{3+} due to dislocation length per unit volume (***δ***) of the crystal structure and induced microstrain(**ε**). The lattice parameter (*a*) is slightly higher for MCZF @Cr0.0 than MCZF@Cr0.4 because another larger radius ion has replaced (Fe^{3+} 0.064 nm) by smaller radius ion (Cr^{3+} 0.063nm) and induced microstrain due to dislocation in the sample (See Table 2) [8,9].

3.2 FTIR Analysis

FT-IR is regarded as one of the prominent methods for identifying the structural and chemical changes taking place in various materials observed due to the vibration of ions in the crystal lattice. Fig.2 exhibited FT-IR spectra recorded for MCZF@Cr0.0 and MCZF@Cr0.4. The spectra showed two principal absorption bands (v_A and v_B) around frequency range 600 $cm^{-1}$and 400cm^{-1}. The occurrence of such bands in these ranges provided confirmation that the spinel structure had formed. Higher absorption band (v_A) is assigned to the intrinsic lattice vibration of the tetrahedral complexes Fe^{3+}-O^{2-} whereas, the lower absorption band (v_B) is corresponding to the vibration of octahedral complexes [10]. In the present investigation, the shift in the v_A and v_B is observed among concentration of Cr^{3+} which attributed to lower d_{AX} and d_{BX} for MCZF@Cr0.4 than MCZF@Cr0.0 (Table 2). The strength of the bond i.e., Force constant *(K)* on tetrahedral A site and octahedral B site is calculated and estimated in Table 3.

Table 3. Tetrahedral vibration(v_1), Octahedral vibration(v_2), Force constant at A and B positions (K_1 and K_2) of prepared MCZF@Cr0.0 and MCZF@Cr0.4 nano ferrite nano ferrite

Sr. No.	Sample	v_A (cm^{-1})	v_B (cm^{-1})	K_A (N/m)	K_B (N/m)
1	MCZF@Cr0.0	573.639	461.20	2.4118×10^2	1.55905×10^2
2	MCZF@Cr0.4	588.680	476.239	2.5400×10^2	1.66238×10^2

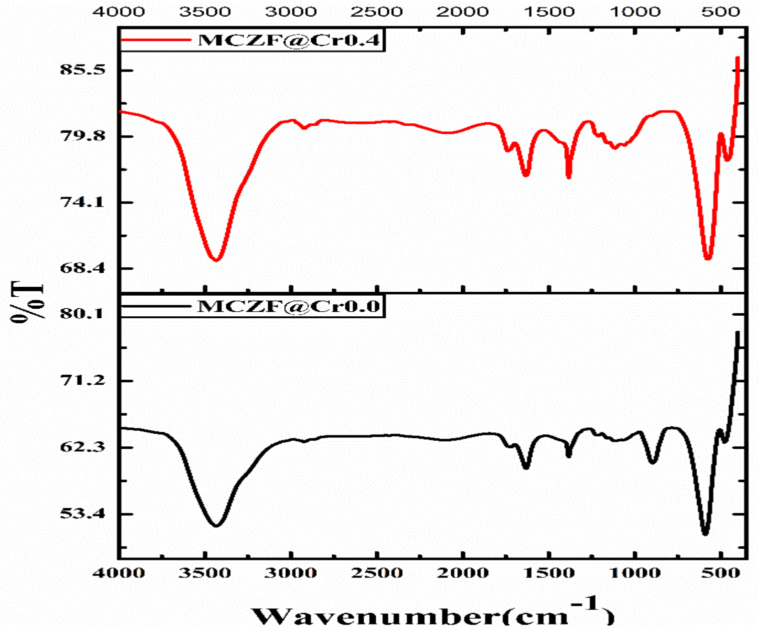

Figure 2. FTIR of MCZF@Cr0.0 and MCZF@Cr0.4 nano ferrite

$$K = 4\pi^2 \upsilon^2 C^2 m'$$

Where, *K* gives force constant, *ν* gives wavenumber, *C* gives velocity of light and *m'* is reduced mass of metal-oxygen bond. From Table 3. the force constant on respective sites found to be slightly greater as compared to x=0. This variation arises due to modification in the positioning band and produced stresses in samples [11].

3.3 Magnetic Analysis

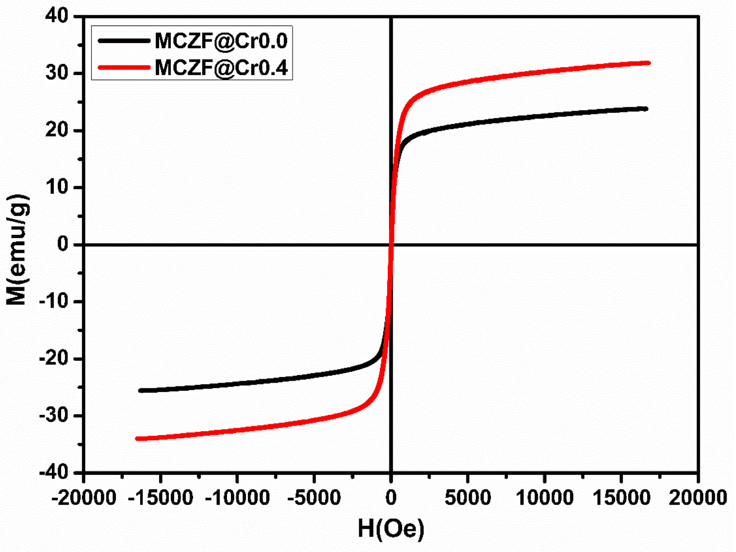

Figure 3. M-H loop of prepared MCZF@Cr0.0 and MCZF@Cr0.4 nano ferrite

As shown in Figure 3, a typical hysteresis M-H loop with minimum area for MCZF@Cr0.0 and MCZF@Cr0.4 related to soft ferrimagnetic nature of the synthesized material. The observed coercivity (*Hc*), retentivity *(Mr)* and magnetic saturation (*Ms)* in minimum range signifies superparamagnetic nature of prepared samples (Table 4). The prepared MCZF@ Cr 0.4 shows higher *Ms* than MCZF@Cr0.0 may be the results of cation distribution at tetrahedral and octahedral sites [12]. The obtain *Hc* found to be higher for MCZF@Cr0.4 than MCZF@Cr0.0 is mainly due to the exchange anisotropy caused by the spin canting effect, spin disorder and elevated surface barrier potential in surface layers correspond to distorted atoms from their usual position, resulting in distorted crystal lattice substituted sample, which leads to variation in *Hc* [13]. The computed magneto crystalline anisotropy (K), squareness ratio and magnetic moment (η_B) are calculated and estimated in Table 3 [14].

The obtained *K* for MCZF@Cr0.4 is higher compared to MCZF@Cr0.0 is mainly due to the surface effect as the main reason of anisotropy in ferrites is related to the presence of Fe^{3+} ions.

The magnetic hardness of the prepared samples are described by squareness ratio (*Mr/Ms*). As per earlier report [15], the computed *Mr/Ms* for MCZF@Cr0.0 (0.06) and MCZF@Cr0.4 (0.04) signifies pseudo single domain and multi-domain nature of prepared nano ferrites.

Table 4. Coercivity *(Hc*), Retentivity *(Mr),* Magnetic Saturation *(Ms*), crystalline anisotropy (K), Bohr's magneton and squareness ratio *(Mr/Ms)* of prepared nano ferrite.

Sr. No.	Sample	*Hc* (Oe)	*Mr* (emu/g)	*Ms* (emu/g)	*K* (erg/cm^3)	$\eta_B(\mu_B)$	*Mr/Ms*
1	MCZF@Cr0.0	16.60	1.45	23.83	412.13	1.015	0.06
2	MCZF@Cr0.4	20.92	1.56	31.81	693.42	1.346	0.04

4. Conclusions

$Mn_{0.25}Cu_{0.25}Zn_{0.5}Fe_{2-x}Cr_xO_4$(x=0.0, 0.4) spinel nano ferrite were successfully synthesised by co-precipitation route. XRD, FTIR, VSM characterization tools have been used to study the structural, spectroscopic and magnetic behaviour of prepared samples. The crystallite size and other structural characteristics such as bond length, hopping length, and lattice dimension are estimated using XRD and found to be decreased with Cr^{3+} substitution. FTIR is used to investigate the vibrational spectroscopic features of synthesized samples. The presence of two distinct bands around 600 cm^{-1} and 400 cm^{-1} is evidence for the formation of spinel ferrite. The M-H loop with small *Ms*, *Mr* and *Hc* exhibits superparamagnetic behaviour of the synthesized material. The observed and estimated parameter firmly suggests that these materials could be used in high frequency devices and biomedical applications.

5. References

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