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Fourier transform infrared spectroscopy study of Cr^{3+} ions substituted copper ferrite nanoparticles

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Abstract
A series of multi crystalline nano ferrites having the chemical formula $CuCr_xFe_{2-x}O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) were successfully synthesized by using self-propagating sol-gel auto combustion method. The X-ray diffraction patterns were recorded at room temperature. in 2θ range $20°$ to $80°$. The X-ray diffraction pattern confirms the formation of a single-phase cubic spinel structure of Cr^{3+} ions substituted copper ferrite. The Fourier transform infrared (FTIR) spectroscopy also shows two significant bands due to interatomic vibrations tetrahedral and octahedral coordination compound. The FTIR analysis explains the two absorption bands υ_1 and υ_2 assigned at tetrahedral (A) and octahedral (B) sites respectively. The values of υ_1 are lower as compared to υ_2, so there is an impact produced on force constant K_1 and K_2. The nature of absorption bands in the spectra depends on the distribution and type of cations among octahedral and tetrahedral sites.

Keywords: Copper ferrite, FTIR, absorption band, force constant

1. Introduction
Ferrites are important components in the latest electronic products, such as cell phones, computers, video cameras, memory devices, etc. They require small dimensions and all light weights and have better functions. The soft ferrites exhibit two antiferromagnetically coupled sub-lattices namely tetrahedral (A) and octahedral [B] sites [1, 2]. The properties of polycrystalline ferrite are dependent on several factors, such as the method of preparation and substitution of different ions. The usefulness of ferrites is influenced by the physical and chemical properties of the materials. The physical properties of polycrystalline ferrites are very sensitive to the microstructure. The bulk (Grain) and grain boundary are the two main components that determine the microstructure.

Soft ferrites remain of great interest because of their high initial permeability over a large frequency range leading to widespread applications e.g., inductor cores in RF systems, recording heads, and microwave devices. Soft ferrites are commercially important materials because of their excellent magnetic and electrical properties [3]. The frustrated magnetic structure in ferrite with the spinel structure can arise when there is a replacement of magnetic ions by non-magnetic ones [4, 5]. The frustration is a necessary condition for the appearance of a canted local state, which was first obtained by Rossnewaig [6]. Ferrite (MFe_2O_4, M=Co^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Cu^{2+}, etc.) nano-crystals attract great research interest due to their potential applications in ferrofluids [7-9], magnetic fluids [10], magnetic recording media [11], magnetic resonance image [12], remarkable chemical stability and a mechanical hardness, which make it possible material for high-density recording media [13].

The present work aims to study systematically the structural analysis by using Fourier-transform infrared spectroscopy (FTIR) study of chromium substituted copper ferrite prepared by the self-propagating sol-gel auto combustion method.

2. Material used and sample preparation
A series of multi crystalline nano ferrites having the chemical formula $CuCr_xFe_{2-x}O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) were synthesized by using self-propagating sol-gel auto combustion method. The initial materials copper nitrate (Cu $(NO_3)_2 \cdot 6H_2O$), ferric nitrate (Fe $(NO_3)_2 \cdot 9H_2O$), chromium nitrate (Cr $(NO_3)_2 \cdot 9H_2O$), citric acid ($C_6H_8O_7 \cdot H_2O$) and ammonia (NH_3) solution were taken in 99.9% AR grade.

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All materials were further used without further purification. Deionized distilled water was used throughout the complete experimental work.

The starting materials having high purity (99%, S. D. fine, India) were copper nitrate: $Cu(NO_3)_2 \cdot 6H_2O$, ferric nitrate: $Fe(NO_3)_2 \cdot 9H_2O$, chromium nitrate: $Cr(NO_3)2 \cdot 9H_2O$, citric acid: $C_6H_8O_7 \cdot H_2O$ and ammonia: NH_3 all of 99% pure AR grade. Calculated quantities of metal nitrates were dissolved together in 100ml of distilled water to get a clear solution. An aqueous solution of citric acid was then added to the metal nitrate solution. The molar ratio of citric acid to the total moles of nitrate ions was adjusted to 1:3. A small amount of NH_3 was added drop wise into the solution to adjust the pH value to about 7 so the sample becomes neutral. A continuous stirring and heating at 90 °C to a solution on a hot plate with a magnetic stirrer until it becomes a very viscous gel. The powder was annealed in air at a temperature of 500 °C for six hours with a heating rate of 50^0C per minute to obtain a spinel phase. The final product is then ground and subjected to further study.

3. Characterization

The X-ray powder diffraction patterns were recorded on a Philips X-ray diffractometer wavelength 1.5418 Å. The XRD patterns were in the 2θ range of 20^0 to 80^0 with a scanning rate of 1^0/min. All the structural parameters were calculated from the X-ray diffraction analysis. The XRD investigations confirm the single-phase formation of the spinel structure of prepared ferrite.

The FTIR spectra in the wave number range 4000-500 cm^{-1} were recorded at room temperature on the spectrometer. Obtained FTIR spectra are used to determine absorption band positions. FTIR spectra are analyzed to get structural information about the prepared ferrite systems.

4. Results and discussion

The X-ray diffraction (XRD) patterns of the $CuCr_xFe_{2-x}O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) nano-particles show the reflections belonging to cubic spinel structure; no extra peaks have been observed in the XRD patterns. The single-phase formations of compounds under investigation were confirmed from the analysis of the XRD pattern.

Table 1: Absorption bands υ_1 and force constant K_1 at (A)-site and Absorptions bands υ_2 and force constant K_2 at [B]-site, and average force constant K_{av} of Cr^{3+} ions content $CuCr_xFe_{2-x}O_4$ (0.0 ≤ x ≤ 1.0) ferrite

Cr content x	Frequency (cm^{-1})		Force constant (N/m)		
	ν_1	ν_2	$K_1 \times 10^5$	$K_2 \times 10^5$	$K_{av} \times 10^5$
0.0	567.81	407.02	2.977	1.529	2.253
0.2	577.20	412.64	3.076	1.572	2.324
0.4	577.73	425.94	3.081	1.675	2.378
0.6	582.44	460.49	3.132	1.958	2.545
0.8	586.57	492.06	3.176	2.235	2.706
1.0	605.73	494.61	3.387	2.259	2.823
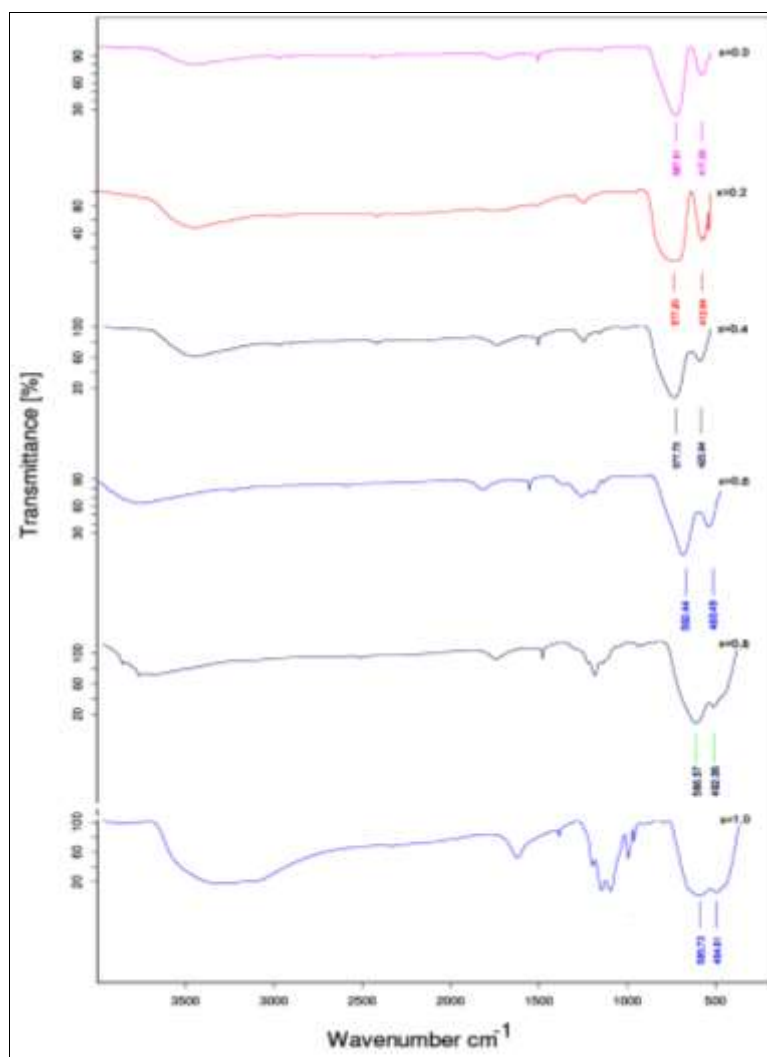
Fig 1: FTIR spectra of Cr^{3+} ions content $CuCr_xFe_{2-x}O_4$ (0.0 ≤ x ≤ 1.0) ferrite system

Fourier-transform infrared spectroscopy (FTIR) spectroscopic analysis is an additional tool for structural characterization. In the present investigation, the absorption spectra show two major absorption bands i.e., the higher absorption band (υ_1) lies in the range of 567.81 to 605.73 cm^{-1}, and the lower absorption band (υ_2) in the range 407.02 to 494.61 cm^{-1} are assigned to the tetrahedral (A) and octahedral [B] sites respectively. The values of absorption bands (υ_1 and υ_2) are presented in Table 1 and absorption bands are shown in Fig.1. The difference in frequencies of υ_1 and υ_2 is due to changes in the bond length Fe^{3+}-O^{2-} at tetrahedral and octahedral sites [14]. The remaining bands are probably due to combinational frequencies or overtones. The nature of absorption bands in the FTIR spectra depends on the distribution and type of cations among octahedral and tetrahedral sites [15].
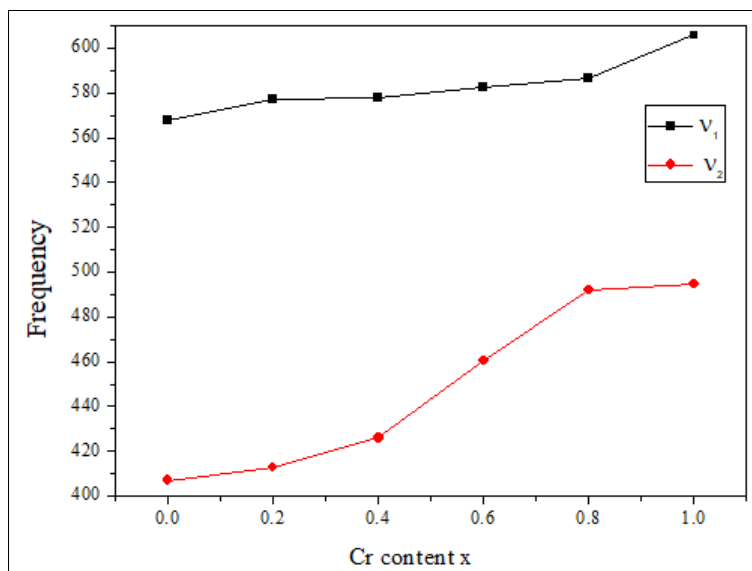
The force constant for the tetrahedral site (K_1), octahedral site (K_2), and average force constant K_{av} was calculated employing the relation where symbol have their usual meaning,

$$K_1 = 7.62 \times M_1 \times \nu_1^2 \times 10^{27} \text{ (N/m)}$$

$$K_2 = 10.62 \times 1.5\, M_2 \times \nu_2^2 \times 10^{27} \text{ (N/m)}$$

$$K_{av} = \frac{K_1 + K_2}{2} \text{ (N/m)}$$

The values of υ_1 and υ_2 are calculated from FTIR spectra of Cr^{3+} ions content $CuCr_xFe_{2-x}O_4$ ($0.0 \leq x \leq 1.0$) ferrite system shows in Table 1 and presented graphically in Fig.2, it is observed that, that υ_1 and υ_2 goes on increasing with increase in Cr^{3+} ions content means as the concentration of Cr^{3+} ions content increases automatically the frequencies of υ_1 and υ_2 increases. It is observed that the values of the force constant for the octahedral site are greater as compared to the values of the force constant of the tetrahedral site. The values of the force constant for tetrahedral site (K_1) and octahedral site (K_2) are shown in Table 1 and represented graphically in Fig.3.

Fig 2: Absorption bands at (A) and [B] site of Cr^{3+} ions content $CuCr_xFe_{2-x}O_4 \leq x \leq 1.0$) ferrite system
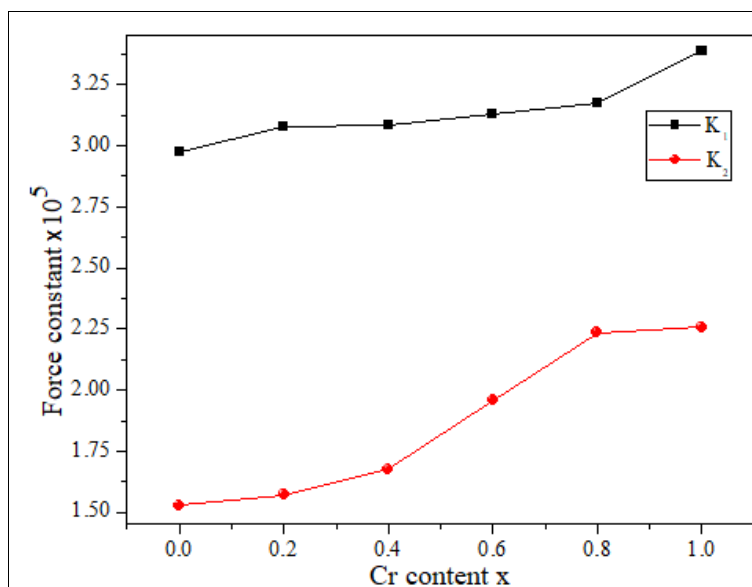
Fig 3: Force content K_1 and K_2 at (A) and [B] site of Cr^{3+} ions content $CuCr_xFe_{2-x}O_4$ ($0.0 \leq x \leq 1.0$) ferrite system

The force constant of the tetrahedral site (K_1) and octahedral site (K_2) both increase as an increase in Cr^{3+} ions content x. This behavior can be attributed to the variation in cation oxygen bond length [16]. Since the bond length (A-O) increased with an increase in Cr^{3+} ions content x, the energy required to break longer bonds is less, and this supports a decrease in the force constant of the sites.

5. Conclusions

The chromium-substituted copper ferrite system is successfully prepared by sol-gel auto combustion technique. The prepared chromium-substituted copper ferrite system shows a single-phase cubic spinel structure. Room temperature FTIR absorption spectra showed the main two absorption bands explaining the Waldron model used to calculate the force constant for both sites. Infrared spectra showed two prominent absorption peaks near 600 cm^{-1} and 400 cm^{-1} indicating the characteristic features of cubic spinel ferrite. It is observed that the values of the force constant for the octahedral site are greater as compared to the values of the force constant of the tetrahedral site.

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