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Mössbauer, X-ray near edge and X-ray diffraction studies on Cu-Ni ferrites

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In the present paper, the study on the $Cu_{1-x}Ni_x Fe_2O_4$ (x= 0.00, 0.05, 0.10) samples has been carried out. These samples were synthesized by the solid-state root method. The samples have been analyzed by X-ray diffraction (XRD), Mössbauer spectroscopy and X-ray absorption near edge spectroscopy (XANES). XRD analysis revealed single phase and tetragonal structure of samples, while Mössbauer spectroscopy showed how to determine the site preference of the substitution and their effect on the hyperfine magnetic field. The X-ray near edge (XANES) technique has been used to determine oxidation state of copper and it also gives very precise information about the parameters like chemical shift. The structural knowledge and magnetic properties of materials have also been interpreted using the two other techniques mentioned in the present paper. The XAFS spectra have been recorded at the Dispersive EXAFS beamline (BL-8) at Indus-2 synchrotron radiation source, RRCAT, Indore, India. The normalized μ (E) data is obtained for all samples at the K absorption edge of Cu-Ni ferrites.

Keywords: X- ray diffraction, Mössbauer, X-ray absorption near edge spectroscopy, K-edge, DEXAFS, Cu-Ni ferrites

1 Introduction

Ferrites are usually nonconductive ferromagnetic ceramic compounds derived from iron oxide such as hematite (Fe_2O_3) or magnetite (Fe_2O_4) as well as oxide of other metals. XRD is one of most powerful techniques for describing the perfect information about the chemical composition and crystallographic structure of natural and manufactured materials.

The study of magnetic properties of materials has been one of the most frequent applications of Mössbauer spectroscopy. The Mössbauer study gives unique information about the isomer shift, hyper fine structure and other magnetic properties. Most of the studies have utilized the 14.4 keV transition in ^{57}Fe. There are several reasons for the popularity of this isotope in the study of magnetic materials. The major reason is the presence of iron as a constituent in most of the scientifically and technologically important materials. Even other materials not containing iron can be studied by the introduction of very small amount of ^{57}Fe as a substitutional doping. The iron isotope has also nuclear properties that facilitate the measurements: low energy, long life-time, adequate nuclear moments and usually strong lattice bonding (high Debye temperature) and long lived parent activity[1] ^{57}Co.

X-ray absorption spectroscopy (XAS) is a direct probe of oxidation state and of the local structure and electronic environment of the atom. In the process, the X-ray beam passes through the sample and after absorption, the material gives very good spectra to understood the local and surrounding metal ligand information of the studied samples. In the present paper, X-ray near edge study technique has been used to determine the oxidation state of iron in ferrite sample. The recorded XAFS spectra have been analyzed using the Demeter program. This is open source program for flexible data reduction/fitting engine that can be used directly in command line mode or called by external programs. Athena has nine integrated graphical interfaces that has been used for most of the numerical calculations.

2 Experimetal Details

The Cu-Ni ferrites were prepared by solid-state root method using CuO, NiO, Fe_2O_4 (pure 99.9% Merck grade). The compositions are taken in stoichiometric proportion and mixed in the agate mortar for 8 h and acetone was added at each time to achieve the homogeneity of the mixture. The samples were heated up to 1000°C in the high temperature furnace for 12 h then it was cooled to room temperature[2]. The powdered samples were prepared for the study. The prepared three samples for these studies are:

(1) Cu Fe_2O_4
(2) $Cu_{.95}Ni_{.05}Fe_2O_4$
(3) $Cu_{.90}Ni_{.10}Fe_2O_4$.

The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The X-rays were produced using a sealed tube and the wavelength of X-ray was 0.154 nm (Cu-Kα radiations). The X-ray diffraction pattern of prepared samples was obtained by varying the scattering angle 2θ from 10° to 80° and the same has been indexed using JCPDS software[3]. The crystalline sizes were calculated using Scherrer equation[4] ^{57}Fe Mössbauer measurements were carried out using a Janis superconducting magnet, analysis of the spectra was performed using the Normos least squares fitting programs[5]. XAS spectra were recorded at Dispersive EXAFS beam line (BL-8) at INDUS-2 synchrotron source (2.5 GeV, 100 mA) at Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. The beamline uses a 460-mm long Si (111) crystal having 2d value equal to 6.2709Å mounted on an elliptical bender, which can bend the crystal to take the shape of an ellipse. A position sensitive detector (CCD) is used to record XAFS spectra of the sample in transmission mode. Athena[6] (a subroutine of Demeter software package) has been used for processing the X-ray absorption data.

3 Results and Discussion

X-ray diffraction technique is useful for the structural analysis. The single phases XRD pattern of the samples for without doped Ni and with doped Ni in percentage are shown in Fig. 1. Table 1 presents the particle size (in nm) and lattice parameter (in Å) for the all samples. The particle sizes and lattice parameters indicate that the samples after indexing the pattern, are found to be the tetragonal in structures. The X-ray diffraction pattern of prepared samples was obtained by varying the scattering angle 2θ from 10° to 80° in step size of 0.01°. The X-ray diffraction patterns shows that the substitutions of cations (Cu^{2+}and Ni^{4+}) are fully methodical and found correct in their substituted sites. The pattern has been indexed using JCPDF software and lattice parameters have been determined by using the Braggs relation $n\lambda=2d \sin\theta$. In the present study, the tetragonal structures have been found and reported sides as $a=b\neq c$, and angles $\alpha=\beta=\gamma=90$. The particle sizes of these samples have been calculated by using Debye Sherrar formula $t=0.9\lambda/(\beta \cos\theta)$, where, λ =1.54Å, β=full width half maxima (FWHM).

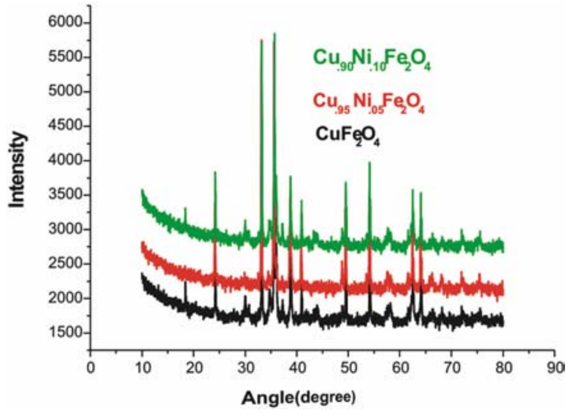

Fig. 1 — XRD pattern of Cu-Ni ferrites.

Mössbauer spectroscopy is a spectroscopic technique based on the Mössbauer effect which was discovered by Rudolf Mössbauer in 1957, observed in the recoil-free, resonant absorption and emission of gamma rays in solids. Mössbauer spectroscopy probes tiny changes in the energy levels of an atomic nucleus in response to its environment. Typically, three types of nuclear interaction may be observed: an isomer shift, also known as a chemical shift; quadrupole splitting; and, magnetic or hyperfine splitting. Due to the high energy and extremely narrow line widths of gamma rays, Mössbauer spectroscopy is one of the most sensitive techniques in terms of energy (and hence frequency) resolution, capable of detecting change in just a few parts per 10^{11}. In its most common form, Mössbauer absorption spectroscopy, a solid sample is exposed to a beam of gamma radiation, and a detector measures the intensity of the beam transmitted through the sample. The atoms in the source emitting the gamma rays must be of the same isotope as the atoms in the sample absorbing them. In the resulting spectra, gamma ray intensity is plotted as a function of the source velocity. At velocities corresponding to the resonant energy levels of the sample, a fraction of the gamma rays is absorbed, resulting in a drop in the measured intensity and a corresponding dip in the spectrum. The number, positions, and intensities of the dips (also called peaks; dips in transmitted intensity are peaks in

Table 1 — Calculated lattice parameter and particle size of Cu-Ni ferrites

S.No.	Compound name	Lattice parameter a(A^0)	Particle size t (nm)
1	Cu Fe_2O_4	a=7.099,c=7.401	56.36
2	$Cu_{.95}Ni_{.05}Fe_2O_4$	a=7.071,c=8.242	53.3
3	$Cu_{.90}Ni_{.10}Fe_2O_4$	a=7.142,c=7.808	54.4

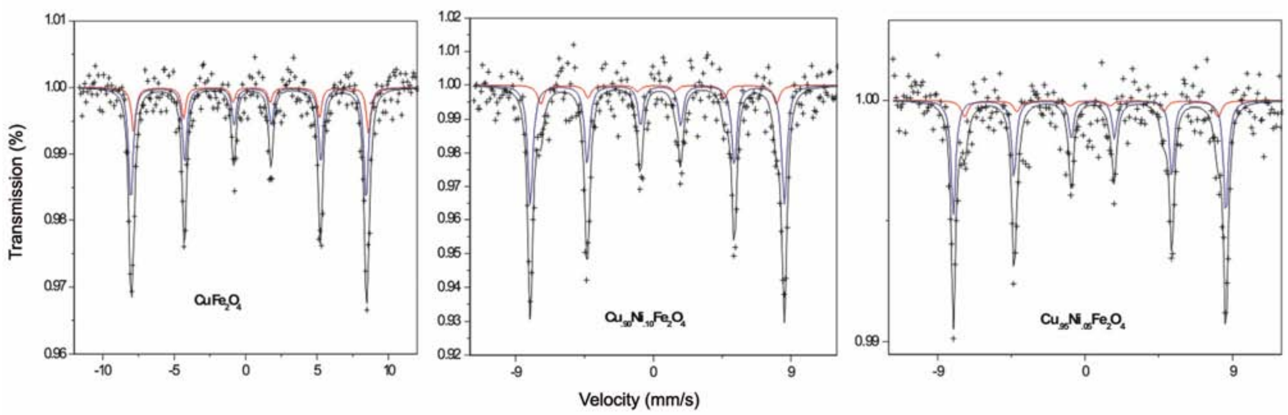

Fig. 2 — Mössbauer spectra of Cu-Ni ferrites

Table 2 — Mössbauer parameter of Cu-Ni ferrites

Sample	Width (mm/s)	Isomer shift (mm/s)	Q.S (mm/s)	BHF (Tesla)	Area (%)
Cu Fe_2O_4	0.37 ±0.03	0.40 ±0.03	-0.02 ± 0.08	51.1 ± 0.12	28.6
	0.37 ±0.03	0.35 ±0.01	-0.28 ±0.04	51.1 ±0.05	71.4
$Cu_{0.95}Ni_{0.05}Fe_2O_4$	0.52 ±0.16	0.34 ±0.04	0.06 ± 0.08	47.9 ± 0.36	24
	0.34 ±0.03	0.38 ±0.01	-0.19 ±0.01	51.6 ±0.05	76
$Cu_{0.90}Ni_{0.10}Fe_2O_4$	0.49 ±0.14	0.27 ±0.04	0.15 ± 0.08	47.7 ± 0.31	18.5
	0.42 ±0.02	0.38 ±0.01	-0.21 ±0.01	51.5 ±0.05	81.5

absorbance) provide information about the chemical environment of the absorbing nuclei and can be used to characterize the sample. Mössbauer spectroscopy is an impressive technique to probe the magnetic phases as well to identify the magnetic ordering present in the structure. It can also give very precise information about the chemical, structural and magnetic properties of a material. Mössbauer measurements of iron complexes were carried out using standard PC-based spectrometer equipped with Weissel velocity drive operating in the constant acceleration mode. The room temperature Mössbauer spectra are fitted with NORMOS-SITE program and all samples show strong magnetic ordering. The ^{57}Fe Mossbauer spectrum of $FeCrO_3$ has been recorded at 300 K and shown in Fig. 2. It shows the clear sextet pattern and a broad doublet. This doublet component reports the values of isomer shift (*d*) in mms-1 and quadrupole (DEQ) in mms-1 at 300 K as the magnetic field splits the nuclear levels. The measured effective hyperfine field, Bhf, in applied external magnetic field is observed and as regards the effect of the substitution of Ni on the magnetic field *Bhf*, does affect. The other Mössbauer parameters BHF (in Tesla) and area (in %) are reported in Table 2.

The intensities I_0 and I_t, are obtained as the CCD outputs without and with the sample, respectively. Using the relation, $I_t = I_0 e^{-\mu x}$, where μ is the absorption coefficient and *x* is the thickness of the absorber, the absorption μ (*E*) corresponding to the photon energy (*E*) are obtained. When the absorption is plotted as a function of *E*, the experimental spectra show three features: (1) a decrease in X-ray absorption with increasing energy in the pre-edge region, (2) a sharp rise at certain energy called edge and (3) a series of wiggles or oscillatory structure that modulate the absorption in the post-edge region. The experimental data has been analyzed using the available computer software package Athena.

The shifts of the K-absorption edge of doping copper in the samples with respect to iron that of metal have been determined according to the Chemical shift $\Delta E_K = E_K$ (complex)-E_K (metal). In the present studies, the K absorption edge of copper was found to shift to the higher energy side in all nine complexes, which means that the chemical shift ΔE_K is positive.

For computing the chemical shift the value of E_K (Cu metal edge K-edge) has been taken at 8980.5 eV. In Fig. 3 shows X-ray absorption edge spectra for all

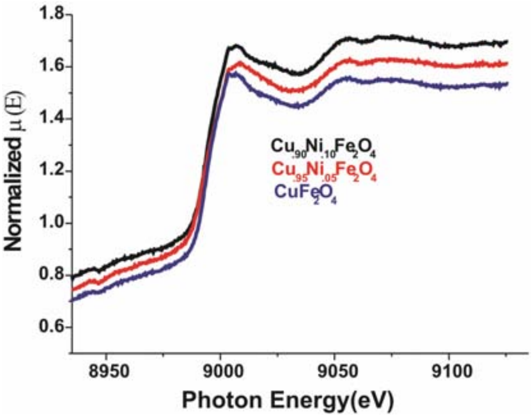

Fig. 3 — Normalized XANES spectra of Cu-Ni ferrites

the reported samples. It is reported that the copper compounds or complexes having oxidation state of +1(Cu^+) shows a chemical shift[7] of less than 10 eV, while those having oxidation state of +2(Cu^{2+}) shows chemical shift of more than 10 eV. The chemical shift values (ΔE_K) obtained from the absorption spectra of ferrites samples are 10.5, 11.0 and 11.7eV, which suggest that copper is in +2 oxidation state in these types of ferrites. The position of the X-ray absorption edge depends on the valence of the absorbing ion, the effective charge on the central atom and the geometry of the complex.. According to Agarwal and Verma[8], the chemical shift is towards the higher energy side of the metal edge and it increases progressively with increase in the valence of the cations, unless the shift is either suppressed by the covalent character of the bond or enhanced by the formation of metal-metal bonding. In the present work, the K-absorption edge of all the complexes was found to be shifted to the higher energy side of the metal edge.

4 Conclusions

The XRD analysis of Cu-Ni ferrites shows that cations (Cu^{2+} and Ni^{4+}) are substituted in the lattice. The Mössbauer spectroscopy of doped ferrites probes the site preference of the cation doping and their effect on the hyperfine magnetic fields. The chemical shift values obtained from XANES data suggest that copper is present in +2 oxidation state in the Cu-Ni ferrite samples.

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