Chapter V
Results and discussion of
\( \text{Co}_{1+y}\text{Sn}_y\text{Fe}_{2-2y-x}\text{Cr}_4\text{O}_4 \) system

5.1 Introduction

The polycrystalline ferrite with high resistivity, low current losses play an important role in many technological applications. They are widely used in electronic and computer industries. The properties like high electrical resistivity, high permeability and low losses can be achieved by careful control of composition and microstructure. The physical properties of ferrites depend on the method of preparation and the amount of the doping type. A study on the ferrite is important in view of their extensive applications in microwave devices like isolator, phase shifters, gyrators etc.

It is well known that when ferrites are sufficiently diluted with non magnetic atoms they can show wide spectrum of magnetic structure; ferrimagnetic order, cluster spin glass etc.[1]. Recently a tentative phase diagram has been proposed [1] to classify the different substituted ferrite compounds.

The knowledge of cation distribution and spin alignment is essential to understand the properties of spinel ferrite. The interesting physical and chemical properties of spinel ferrites
arise from their ability to distribute the cations among the available tetrahedral A and octahedral B-sites [2].

The magnetic structure of the spinel ferrites depend upon the type of ions residing on tetrahedral A and octahedral B-sites and the relative strength of the inter (J_{AB}) and intra sub-lattice interaction (J_{AA}, J_{BB}). When the A-B inter sub-lattice interactions are much stronger than the A-A and B-B intra sub-lattice interactions, the spins have a collinear spin structure in which the moments on the A-sites are anti parallel to the moments on the B-sites. When one of the intra sub-lattice interaction become comparable with the inter sub-lattice interaction it leads to a non-collinear spin structure [3]. Thus, J_{AB} renders the undiluted spin ferrimagnetic with all A-sites moment oriented anti-parallel to all B-site moments, but with B-B and A-A bonds remaining unsatisfied on dilution, frustration of certain moment should occur leading to collapse to the collinearity of the ferrimagnetic phase and the effective moments are created within the ferrimagnetic structure by local canting around the magnetic imperfection [4].

Cobalt ferrite possesses an incomplete inverse spinel structure and the degree of inversion depends on the heat treatment [5]. The addition of tetravalent ions like Ti^{4+}, Ge^{4+} and Si^{4+} influences the electrical and magnetic properties of the systems [6,7,8]. The addition of Cr^{3+} ions in the ferrite systems is
likely to increase the resistivity and decrease the saturation magnetization [9]. In the literature the studies on the substitution of divalent cations like Zn$^{2+}$ and Cd$^{2+}$ [10,11] and trivalent cations like Al$^{3+}$ and Cr$^{3+}$ in cobalt ferrite [12,13] have been appeared. Many workers have studied the substitution of Sn$^{4+}$ ions in nickel ferrite [14,15,16,17]. It has been reported that a smaller substitution of Sn$^{4+}$ ions in nickel ferrite increases the resistivity by segregating at grain boundaries and hence acts to decrease the electrical losses. A larger substitution of Sn$^{4+}$ ions however causes discontinuous grain growth, which decreases the initial permeability and increases the magnetic loss factor. The presence of Mn$^{3+}$, Fe$^{2+}$ or Co$^{2+}$ in the ferrite system introduces an additional factor (i.e. uniaxial anisotropy [18]) which increases the possible magnetic structure and may changes the phase diagram of the system.

The system under investigation, Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ ($y = 0.05$, $x = 0.0$ to 0.5) contains the anisotropic magnetic ion Co$^{2+}$, small amount of Sn$^{4+}$ and Cr$^{3+}$, which may lead to affect the magnetic and electrical properties of the system. In view of this the structural, electrical and magnetic properties of the Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ system ($y = 0.05$, $x = 0.0$ to 0.5) are investigated by means of X-ray diffraction, infrared, d.c. resistivity, thermoelectric power measurements, dielectric
properties. a.c. susceptibility and magnetization. No measurements have previously been reported in the literature.

5.2 Experimental

The polycrystalline samples of compositions Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ ($y = 0.05$, $x = 0.0$ to $0.5$) was prepared by well-known double sintering ceramic technique. The used pure oxides CoO, SnO$_2$, Cr$_2$O$_3$ and Fe$_2$O$_3$ (all AR-grade, supplied by E-Merck) were mixed according to the compositions Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ and ground in an agate pestle mortar in order to obtain a very fine powder. The mixture was dried and pressed into pellets. These pellets were pre-sintered at $900^\circ$C for 12hr. and then slowly cooled to room temperature. The samples were again powdered, pressed into pellets and sintered at $1100^\circ$C for 24 hr. and then slowly cooled to room temperature at the rate of $2^\circ$C/min Finally the pellets were polished to have uniform surfaces.

The X-ray powder diffraction patterns were obtained for each sample using Cu K$\alpha$ radiation at room temperature. The analysis of X-ray diffraction pattern proved that the studied sample has single-phase cubic spinel structure.

The IR spectra in the 200 to 800 cm$^{-1}$ ranges were recorded at room temperature on the infrared spectrometer (Model 783, Perkin Elmer). For recording IR spectra, powders were mixed
with KBr in the ratio 1:250 by weight to ensure uniform
dispersion in the KBr pellet. The mixed powders were then
pressed in cylindrical die to obtain clean discs of approximately
1mm thickness.

The d.c. resistivity $\rho$ with temperature was measured using
two probe method in the temperature range 300-800K. The
electrical contacts were made ohmic using air-dried silver epoxy.
A calibrated chromel-alumel thermocouple was used to measure
the temperature. A typical sample holder was designed for the
measurements of d.c. electrical resistivity. The dielectric
measurements of all samples were measured as a function of
frequency at room temperature using LCR-meter (HP 4284 A).

The magnetization measurements of all the samples were
carried out using high field hysteresis loop technique [19] at
300K. The a.c. susceptibility measurements on powdered samples
were made in the temperature range 300-800K using a double coil
set up[20] operating at a frequency of 263 Hz and in rms field of
7 Oe.

5.3 Results and discussion

5.3.1 X-ray diffraction

The room temperature X-ray diffraction patterns of the
$\text{Co}_{1+y}\text{Sn}_y\text{Fe}_{2-2y-x}\text{Cr}_x\text{O}_4$ system ($y = 0.05$, $x = 0.0$ to 0.5) are shown
in Fig. 5.1(a,b,c). All the X-ray diffractogram are clean and
diffraction lines are found to be sharp corresponding to single-phase cubic spinel structure. No other phase has been detected for all the samples. The lines are indexed using a computer programme, which are consistent with face centred cubic spinel structure. The reflections observed are (111), (220), (311), (400), (422), (333), (511) and (440). These hkl values correspond to the allowed value of reflections for cubic spinel structure. The data on observed and calculated d-values and the Miller indices are presented in Table 5.1.

The values of the lattice constants 'a' determined from X-ray data analysis with an accuracy of ±0.002Å for x = 0.0 to 0.5 are shown in Fig.5.2 as a function of 'x'. It is observed from Fig.5.2 that the lattice constant slightly increases from x = 0.0 to 0.2 and thereafter it decreases as 'x' value increases. The slight increase in 'a' for x = 0.0 to 0.2 may be due to the fact that the addition of Cr³⁺ upto x = 0.2 does not affect the crystal lattice. However, the decrease in the lattice constant 'a' with increase in 'x', from x = 0.2 can be explained on the basis of difference in ionic radii of Fe³⁺ and Cr³⁺. In the present system larger crystal radius Fe³⁺(0.67Å) are replaced by the smaller ionic crystal radius of Cr³⁺(0.63Å), which results in decrease in 'a' with 'x' for x = 0.2 to 0.5.

Using the experimental values of lattice parameter 'a' and oxygen positional parameter 'u' of each samples in the equation,
\[ d_{AX} = a\sqrt{3} \left( u - \frac{1}{4} \right) \text{ tet. bond} \]  
(i)

\[ d_{BX} = a \left( 3u^2 - \frac{43}{4} u + \frac{63}{4} \right)^{1/2} \text{ oct. bond} \]  
(ii)

\[ d_{BX} = a\sqrt{2} \left( 2u - \frac{1}{2} \right) \text{ tet edge} \]  
(iii)

\[ d_{xx} = a\sqrt{2} \left( 1-2u \right) \text{ tet bond} \]  
(iv)

\[ d_{xx} = a \left( 4u^2 -3u + \frac{11}{16} \right)^{1/2} \text{ unshared oct. edge} \]  
(v)

we have calculated the selected interionic distances and the radius of the tetrahedral and octahedral interstices of all the samples from \( d_{AX} \) and \( d_{BX} \) by taking radius of the divalent oxygen ion to be 1.32A\(^0\). The oxygen positional parameter ‘u’, octa edge, radius of tetrahedral and octahedral interstices of the system Co\(_{1+y}\)Sn\(_y\)Fe\(_{2-2y}\)-xCr\(_x\)O\(_4\) are shown in Table 5.2. The oxygen positional parameter is taken as a constant value 0.375 A\(^0\) for all the values of ‘x’.

The X-ray density \( d_x \) for each composition was calculated using the relation [21].

\[ d_x = \frac{Z \cdot M}{N \cdot V} \text{ gm/cm}^3 \]  
(5.1)

where,

- \( Z \) is the number of molecules per unit cell ( \( Z = 8 \) ),
- \( M \) is the molecular weight,
- \( N \) is Avogadro’s number and
$V$ is the value of unit cell volume.
The values of X-ray density for each composition are summarized in Table 5.3. It is evident from Table 5.3 that X-ray density decreases up to $x = 0.2$ and then increases which is attributed to the variation of ‘$a$’ with ‘$x$’.

The XRD line width and particle size are connected through the Scherrer equation [21].

$$t = \frac{0.9\lambda}{B \cdot \cos \theta_B} \quad (5.2)$$

where,
- $t$ is the particle diameter;
- $\lambda$ is the wavelength of the X-ray radiation and
- $B$ is a measure of the broadening of diffraction line due to size effect.
- $\theta_B$ is the Bragg angle.

The particle size estimated from Scherrer formula is summarized in Table 5.3.

The distribution of cations among the sites in spinel has been experimentally proved to be an equilibrium function of temperature, pressure and composition [22,23]. The cation distribution, which results in any given case, is the result of a fine balance of the respective octahedral, tetrahedral preferences of the ions concerned. Certain factors, which contribute to the octahedral and tetrahedral preferences of cations such as, effect
of ionic charge and ionic radius [24] are well known. There are other factors, however such as crystal and ligand field effects [25,26,2] and anion polarization [27].

In the present method, based on the X-ray diffractogram the ratio of intensities of reflections due to the planes (220) and (440), (400) and (440) has been chosen as a criterion to determine the cation distribution among the tetrahedral A-sites and octahedral B-sites. It has been reported that the absorption and temperature factor does not affect the relative intensity calculations for spinels at room temperature [28,29]. Therefore, in our calculation we have not taken into account the absorption and temperature factors.

Comparing the site preference energies of the constituent ions [30], the cation distribution $\text{Co}_{1.05}\text{Sn}_{0.05}\text{Fe}_{1.9}\text{O}_4$ has been accepted as,

$$(\text{Co}_{0.04}\text{Fe}_{0.96})^A \ [\text{Sn}_{0.05}\text{Co}_{1.01}\text{Fe}_{0.94}]^B \text{O}_4 \quad (5.3)$$

In order to determine the cation distribution of the present system, XRD intensities were calculated using the formula suggested by Buerger [31].

$$I_{hkl} = |F|_{hkl}^2 \cdot P \cdot L_P \quad (5.4)$$
where, notations have their usual meaning.

In the present Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ series of ferrites, variation of Cr$^{3+}$ concentration 'x' results in the replacement of Fe$^{3+}$ ions by Cr$^{3+}$ ions. In accordance with the site preference energies, Sn$^{4+}$ ions occupy the B-sites. Also, Cr$^{3+}$ ions occupy the B-sites, where as the Fe$^{3+}$ ions shows no definite site preference [30].

The distribution of divalent, trivalent and tetravalent cations amongst octahedral and tetrahedral sites in Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ was determined from the ratio of X-ray diffraction lines [Fig.5.3], $I_{220}$ / $I_{440}$ and $I_{400}$/$I_{440}$. The results of X-ray intensity calculations for various possible models have been tried for samples $x = 0.1$ to 0.5 and those which agree with the experimental intensity ratio are shown in Fig. 5.3. The cation distribution obtained in this manner is represented in the Table 5.4.

5.3.2 Infrared spectra

The infrared spectra of the system Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ ($y = 0.05$, $x = 0.0$ to 0.5) in the range 200-800 cm$^{-1}$ obtained at room temperature are shown in Fig. 5.4(a,b). A cursory inspection of spectra shows two absorption bands below 800 cm$^{-1}$ as a common feature of all the ferrites. The band arises from lattice vibrations of the oxide ions against the cations. The absorption bands in the region 200 – 800 cm$^{-1}$ can be assigned to the
vibration of ions in the crystal lattice. The classification of lattice vibrations of cubic spinel is given by Brabers [32]. For the normal vibrations of unit cell of the cubic spinel these only four bands appear to be IR active. In the normal spinel, four modes IR active are triply degenerate in inverse and partly inverse spinels. The local symmetry is distributed and each of the triply degenerate vibrations split into three vibrations. If the splitting is not too large and there is certain statistical distribution of various cations over the octahedral and tetrahedral, one cannot observe splitting but only a broadening of absorption. In the present IR spectra broad absorption bands are observed which may be because of the fact that the cobalt ferrite is a partially inverse spinel ferrite.

In the present study, the absorption bands of the \( \text{Co}_{1+y}\text{Sn}_{y}\text{Fe}_{2-2y-x}\text{Cr}_x\text{O}_4 \) ferrite are seen to be for higher frequency \( (v_1) \) near 600 cm\(^{-1}\) and for lower frequency \( (v_2) \) near 400 cm\(^{-1}\). The values of \( v_1 \) and \( v_2 \) are listed in Table 5.5. The vibrational frequency depends on the cation mass, cation oxygen distance and bonding force.

According to classification of lattice vibration into species of point group \( (T_d) \), four active infrared bands are observed in the range 100 – 1000 cm\(^{-1}\). The high frequency band \( v_1 \) is caused by the stretching of the tetrahedral metal oxygen bonds and absorption band \( v_2 \) is caused by oxygen vibrations in a direction perpendicular to the tetrahedral ion oxygen axis. The two
absorption bands $v_3$ and $v_4$ are associated with the vibrations of the metal ions in the isotropic force fields of their octahedral and tetrahedral environments [33]. The modes $v_3$ and $v_4$ are located in the far infrared region [34].

Waldron [35] observed two bands in various ferrites in the region of $200\text{cm}^{-1}$ to $1000\text{cm}^{-1}$. Similar observations have been made by Srinivasan et.al [36]. The high frequency band $v_1$ is related to tetrahedral complexes and low frequency band $v_2$ to octahedral complexes. In the present study the absorption bands of the ferrites are found to be in the range reported by many workers [37,38,39]. The difference in the band positions is expected because of the difference in the $\text{Fe}^{3+}-\text{O}^{2-}$ distance for the octahedral and tetrahedral complexes.

The force constants have been obtained from infrared absorption data using the analysis of Waldron [35]. The bond lengths $R_A$ and $R_B$ have also been calculated. The values of force constant $K_1$ and $K_0$, $R_A$ and $R_B$ are given in Table 5.5. The molecular weights of tetrahedral ($M_t$) and octahedral ($M_o$) sites have been calculated by using the cation distribution of $\text{Co}_{1+y}\text{Sn}_y\text{Fe}_{2-2y-x}\text{Cr}_x\text{O}_4$ as given in Table 5.4 Srivastava et al. [40] has stated that the bond stretching for tetrahedral site would led to higher force constants than that for octahedral sites. Our results are analogous with the result of Srivastava et.al.

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5.3.3 Magnetization

The values of saturation magnetization and magneton number $n_B$ (saturation magnetization per formula unit in Bohr magneton) for the samples with $x = 0.0$ to $0.5$ at room temperature are listed in Table 5.6. It is evident from table 5.6 that all sample shows ferrimagnetic behaviour which decreases with increasing ‘$x$’. The variation of magneton number $n_B$ with $\text{Cr}^{3+}$ concentration ‘$x$’ is shown in Fig. 5.5. It can be seen from Fig. 5.5 that $n_B$ decreases with increase of $\text{Cr}^{3+}$ concentration ‘$x$’. This behaviour can be explained on the basis of changes in the magnetization $M_A$ and $M_B$ of tetrahedral A and octahedral B sub-lattices respectively. In the present system, according to cation distribution data $\text{Cr}^{3+}$ ions having $3\mu_B$ magnetic moment replaces $\text{Fe}^{3+}$ ions of $5\mu_B$ magnetic moment, thereby lowering the values of $M_B$ and $M_A$. The decrease in $M_B$, predominant over the decrease in $M_A$, which results in decrease in net magnetization of the system.

According to Neel’s two sub-lattice model of ferrimagnetism [41]. Neel’s magnetic moment per formula unit in $\mu_B$, $n^N_B$ is expressed as,

$$n^N_B (x) = M_B(x) - M_A(x) \quad (5.5)$$

where,

$M_B$ and $M_A$ are the B and A sub-lattice magnetic moment in $\mu_B$
The $n_{B}$ ($\mu_{B}$) values for the present system were calculated using Neel's equation (5.5) and taking ionic magnetic moments of Fe$^{3+}$, Co$^{2+}$, Cr$^{3+}$ and Sn$^{4+}$ as $5\mu_{B}$, $3\mu_{B}$, $3\mu_{B}$ and $0\mu_{B}$ respectively. The variation of calculated values of $n_{B}$ with Cr$^{3+}$ concentration 'x' is depicted in Fig.5.5. It is observed from Fig.5.5 that the calculated $n_{B}$ value fairly agrees with the experimental values. This indicates that structure is collinear over the range of composition studied.

The cation distribution obtained from X-ray diffraction intensity calculations is very well supported by cation distribution obtained from magnetization data.

5.3.4 A. C. Susceptibility

The variation of low field a.c. susceptibility with temperature ($\chi \rightarrow T$) for the samples with $x = 0.0$ to 0.5 within the temperature range 300 K – 800 K are shown in Fig. 5.6(a,b). which exhibit normal ferrimagnetic behaviour.

The values of Curie temperature determined through a.c. susceptibility curves are given in Table 5.6 and variation of Curie temperature ($T_{C}$) with Cr$^{3+}$ concentration 'x' is shown in Fig. 5.7. It is observed from figure 5.7 that, $T_{C}$ decreases as 'x' increases. According to Neel's model, the A-B interaction is most dominant in ferrites and therefore the Curie temperature of the ferrite can be determined from the overall strength of A-B interaction [42]. The strength of a A-B interaction is a function of number of
Fe$^{3+}_{(A)}$ -O$^{2-}$ - Fe$^{3+}_{(B)}$ linkage [43], which in turn depends upon the number of Fe$^{3+}$ ions in the formula unit and their distribution among tetrahedral A and octahedral B-sites.

In the present system of ferrites $\text{Co}_{1+y}\text{Sn}_y\text{Fe}_{2-2y-x}\text{Cr}_x\text{O}_4$, the chromium (Cr$^{3+}$) ions (3$\mu_B$) replace Fe$^{3+}$ ions (5$\mu_B$) on the octahedral B-sites. This results in decreasing the strength of A-B interactions, which leads to decrease in Curie temperature of the samples as observed experimentally (Fig. 5.7).

### 5.3.5 D.C. resistivity

The electrical conductivity measurements are carried out by the two-probe method on compressed sintered pellets of about 1cm diameter and 3mm thickness. The measurements were carried out in the temperature range 300 – 800K. A typical sample holder was designed to measure the electrical conductivity of $\text{Co}_{1+y}\text{Sn}_y\text{Fe}_{2-2y-x}\text{Cr}_x\text{O}_4$ system. The variation of log$\rho$ versus reciprocal of temperature for the $\text{Co}_{1+y}\text{Sn}_y\text{Fe}_{2-2y-x}\text{Cr}_x\text{O}_4$ system is shown in Fig.5.8 (a,b). From the plots it is observed that all the samples show two regions corresponding to paramagnetic region and ferrimagnetic region. Since these ferrites behave as semiconductor, their resistivity should decrease with increase in temperature according to relation,
\[ \rho = \rho_0 \exp \left( \frac{E_g}{KT} \right) \]  

(5.6)

where,

- \( E_g \) represents activation energy
- \( \rho \) represents the resistivity at temperature \( T \) and
- \( \rho_0 \) is a temperature independent constant and
- \( K \) is the Boltzmann’s constant.

From Fig.5.8 (a,b) it is observed that the curve breaks into two regions at a point which may corresponds to Curie temperature of the sample. The two regions are ferrimagnetic and paramagnetic. The values of activation energy in ferri and para magnetic regions have been calculated from the plots of \( \log \rho \) versus temperature (Fig. 5.8) and using the equation 5.6.

The values of activation energies for ferri and para region are given in Table 5.7. It is clear from Table 5.7 that the values of activation energy are lower in ferrimagnetic region than that in paramagnetic region. The lower activation energy values in ferrimagnetic region is attributed to the magnetic ordering due to decrease in concentration of current carriers [44] while the change in the activation energy is attributed to the change in the conduction mechanism [45]. The conduction in \( \text{Co}_{1+y}\text{Sn}_y\text{Fe}_{2-2y-x}\text{Cr}_x\text{O}_4 \) ferrite results mainly from the hopping of electrons between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) ions present at octahedral
B-sites. Also, the presence of Co\(^{2+}\) ions at octahedral B-site may contribute to conduction process in these ferrites. The Sn\(^{4+}\) ions present at octahedral B-sites may not take part in conduction process, they only replaces Fe\(^{3+}\) ions from B-sites to A-site thereby increasing the resistivity.

### 5.3.6 Dielectric properties

The measurements of the real dielectric constant (\(\varepsilon'\)) dielectric loss (\(\varepsilon''\)) and dielectric loss tangent (\(\tan\delta\)) were carried out by two-probe method on the pellets of 10mm. diameter and 3mm. thickness. Two surfaces of the pellets were polished well and silver paste was applied for good ohmic contact. The measurements were carried out at room temperature in the frequency range 100Hz to 1MHz using HP-LCR bridge (Model 4284A). The effect of frequency on each of the real dielectric constant and dielectric loss factor (\(\tan\delta\)) is illustrated in Fig. 5.9(a,b) and 5.10(a,b) respectively. It is observed from Fig. 5.9 and 5.10 that both \(\varepsilon'\) and \(\tan\delta\) decreases as the frequency increases; this is the normal dielectric behaviour of ferrites. The decrease is rapid at lower frequency and becomes slow, almost constant at higher frequencies. The decrease in \(\varepsilon'\) and \(\tan\delta\) takes place when the jumping frequency of electric charge carriers cannot follow the alternation of applied a.c. electric field beyond a certain critical frequency [46]. Our results are similar with
those previously reported by others [47,9,48]. In the present study, the variation of $\varepsilon'$ and $\tan\delta$ with frequency clearly shows the normal dielectric behaviour.

The high values of $\varepsilon'$ could be explained on the basis of Maxwell-Wagner theory [49,50], which is a result of the inhomogeneous nature of dielectric structure, and increase of $'x'$ decreases Fe$^{3+}$ ions concentrations thereby decrease in dielectric relaxation intensity. No relaxation peaks are observed in $\varepsilon'$ and $\tan\delta$ curves.

### 5.4 Conclusion

The experimental results of the Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ $(y = 0.05, x = 0.0$ to $0.5)$ ferrite system lead us to conclude the following,

Analysis of X-ray diffraction pattern reveals that the studied samples are single phase cubic structured. XRD data has been used to find lattice parameter X-ray density and other structural parameters. The lattice constant initially increases up to $x = 0.2$ and then after it decreases as Cr$^{3+}$ content increases. The X-ray intensity calculations suggest that Cr$^{3+}$ and Sn$^{4+}$ ions occupy B-sites. Cation distribution has been calculated from X-ray intensity ratio calculations.

Infrared spectra of all the samples exhibit two absorption bands, which are in the reported range. The values of force
constant $K_t$ and $K_0$ have been obtained by using Waldron’s analysis.

The plots of log of resistivity versus reciprocal of temperature indicate two regions corresponding to ferrimagnetic and paramagnetic. Curie temperature deduced from resistivity plots are in good agreement with those obtained from other methods. The activation energy in paramagnetic region is found to be greater than in ferrimagnetic region.

The dielectric constants, dielectric loss and dielectric loss tangents decreases as frequency increases. The decrease is fast at lower frequency. This behaviour of dielectric is similar to that of other ferrites.

The saturation magnetization $\sigma_s$ and magneton number (the saturation magnetization per formula unit) measured at room temperature decreases as $\text{Cr}^{3+}$ content increases. The magneton number obtained by using Neel’s model is fairly agrees with the observed magneton number. This indicates that the structure is collinear for $x = 0.0$ to $0.5$.

The plots of a.c susceptibility exhibit normal ferrimagnetic behaviour, which decreases as $\text{Cr}^{3+}$ content increases. Curie temperature ($T_C$) obtained from a.c susceptibility data decreases as $\text{Cr}^{3+}$ content increases.
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Table 5.1

Miller Indices hkl and interplaner spacing (d) for \( \text{Co}_{1+y} \text{Sn}_y \text{Fe}_{2-2y} \text{Cr}_x \text{O}_4 \) (y = 0.05) system.

<table>
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<th>Sr. No.</th>
<th>Plane (hkl)</th>
<th>( x = 0.0 ) a = 8.352 Å d(Å)</th>
<th>( x = 0.1 ) a = 8.355 Å d(Å)</th>
<th>( x = 0.2 ) a = 8.358 Å d(Å)</th>
<th>( x = 0.3 ) a = 8.345 Å d(Å)</th>
<th>( x = 0.4 ) a = 8.340 Å d(Å)</th>
<th>( x = 0.5 ) a = 8.337 Å d(Å)</th>
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<td>-</td>
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<td>-</td>
<td>2.4079</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>400</td>
<td>2.0992</td>
<td>2.0886</td>
<td>2.0916</td>
<td>2.0874</td>
<td>2.0844</td>
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</tr>
<tr>
<td>6</td>
<td>422</td>
<td>-</td>
<td>1.7061</td>
<td>-</td>
<td>1.7036</td>
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</tr>
<tr>
<td>7</td>
<td>333</td>
<td>1.6137</td>
<td>1.6097</td>
<td>1.6083</td>
<td>1.6065</td>
<td>1.6056</td>
<td>1.6035</td>
</tr>
<tr>
<td>8</td>
<td>440</td>
<td>1.4835</td>
<td>1.4789</td>
<td>1.4796</td>
<td>1.4755</td>
<td>1.4765</td>
<td>1.4731</td>
</tr>
</tbody>
</table>
Table 5.2

Tet edge, Octa edge, radius of tetrahedral and octahedral interstices for Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ ($y = 0.05$) system.

<table>
<thead>
<tr>
<th>Composition $x$</th>
<th>Tet. edge (Å)</th>
<th>Octa edge</th>
<th>$r_{\text{tet.}}$ (Å)</th>
<th>$r_{\text{Oct.}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.9528</td>
<td>2.9528</td>
<td>2.9528</td>
<td>1.8082</td>
</tr>
<tr>
<td>0.1</td>
<td>2.9539</td>
<td>2.9539</td>
<td>2.9539</td>
<td>1.8089</td>
</tr>
<tr>
<td>0.2</td>
<td>2.9546</td>
<td>2.9546</td>
<td>2.9546</td>
<td>1.8093</td>
</tr>
<tr>
<td>0.3</td>
<td>2.9503</td>
<td>2.9503</td>
<td>2.9503</td>
<td>1.8066</td>
</tr>
<tr>
<td>0.4</td>
<td>2.9486</td>
<td>2.9486</td>
<td>2.9486</td>
<td>1.8056</td>
</tr>
<tr>
<td>0.5</td>
<td>2.9475</td>
<td>2.9475</td>
<td>2.9475</td>
<td>1.8049</td>
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</tbody>
</table>
Table 5.3

Lattice constant, X-ray density and particle size for Co_{1+y}Sn_yFe_{2-2y-x}Cr_xO_4 (y = 0.05) system.

<table>
<thead>
<tr>
<th>Composition x</th>
<th>Lattice Constant 'a' (Å)</th>
<th>Particle Size 'l' (Å)</th>
<th>X-ray density 'd_x' (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.352</td>
<td>301</td>
<td>5.425</td>
</tr>
<tr>
<td>0.1</td>
<td>8.355</td>
<td>460</td>
<td>5.410</td>
</tr>
<tr>
<td>0.2</td>
<td>8.358</td>
<td>460</td>
<td>5.398</td>
</tr>
<tr>
<td>0.3</td>
<td>8.345</td>
<td>230</td>
<td>5.412</td>
</tr>
<tr>
<td>0.4</td>
<td>8.340</td>
<td>229</td>
<td>5.414</td>
</tr>
<tr>
<td>0.5</td>
<td>8.337</td>
<td>228</td>
<td>5.411</td>
</tr>
<tr>
<td>Composition (x)</td>
<td>Cation Distribution</td>
<td>Cation Distribution</td>
<td>Cation Distribution</td>
</tr>
<tr>
<td>----------------</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4

Cation distribution and X-ray intensity ratios for Co_{1+y}, Sn_{y}, Fe_{2-2y}, Cr_{x}, O_{4+y} (y = 0.05) system.
Table 5.5

Vibrational Bands ($v_1, v_2$), Force Constant ($K_t, K_o$) and Bond length ($R_A, R_B$) for $Co_{1+y}Sn_yFe_{2-2y-x}Cr_xO_4$ ($y = 0.05$) system.

<table>
<thead>
<tr>
<th>Composition x</th>
<th>Wave number</th>
<th>Force Constant</th>
<th>Bond Length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v_1(cm^{-1})$</td>
<td>$v_2(cm^{-1})$</td>
<td>Tetrahedral $K_t$ dyne/cm</td>
</tr>
<tr>
<td>0.0</td>
<td>605</td>
<td>390</td>
<td>246151.5</td>
</tr>
<tr>
<td>0.1</td>
<td>590</td>
<td>390</td>
<td>234065.8</td>
</tr>
<tr>
<td>0.2</td>
<td>620</td>
<td>400</td>
<td>258817.8</td>
</tr>
<tr>
<td>0.3</td>
<td>610</td>
<td>380</td>
<td>250933.1</td>
</tr>
<tr>
<td>0.4</td>
<td>620</td>
<td>395</td>
<td>259224.3</td>
</tr>
<tr>
<td>0.5</td>
<td>615</td>
<td>410</td>
<td>254872.4</td>
</tr>
</tbody>
</table>
Table 5.6

Curie temperature ($T_C$) Saturation magnetization ($\sigma_s$) and Magneton number ($n_H$) for $\text{Co}_{1+y}\text{Sn}_y\text{Fe}_{2-2y-x}\text{Cr}_x\text{O}_4$ ($y = 0.05$) system.

<table>
<thead>
<tr>
<th>Composition $x$</th>
<th>$T_C$ (K)</th>
<th>$\sigma_s$ (emu/gm)</th>
<th>$n_H$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Observ.</td>
</tr>
<tr>
<td>0.1</td>
<td>759</td>
<td>65.83</td>
<td>2.80</td>
</tr>
<tr>
<td>0.2</td>
<td>740</td>
<td>64.52</td>
<td>2.74</td>
</tr>
<tr>
<td>0.3</td>
<td>720</td>
<td>63.21</td>
<td>2.68</td>
</tr>
<tr>
<td>0.4</td>
<td>700</td>
<td>61.42</td>
<td>2.60</td>
</tr>
<tr>
<td>0.5</td>
<td>680</td>
<td>60.11</td>
<td>2.54</td>
</tr>
</tbody>
</table>
Table 5.7

Curie temperature, Activation energy $E_g$ for $\text{Co}_{1+y}\text{Sn}_y\text{Fe}_{2-2y-x}\text{Cr}_x\text{O}_4$ ($y = 0.05$) system.

<table>
<thead>
<tr>
<th>Composition $x$</th>
<th>Curie temperature $T_C$ (K)</th>
<th>Activation energy $E$ (eV)</th>
<th>$\Delta E = E_p - E_f$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>782</td>
<td>0.537</td>
<td>0.029</td>
</tr>
<tr>
<td>0.1</td>
<td>759</td>
<td>0.553</td>
<td>0.021</td>
</tr>
<tr>
<td>0.2</td>
<td>740</td>
<td>0.552</td>
<td>-0.180</td>
</tr>
<tr>
<td>0.3</td>
<td>720</td>
<td>0.675</td>
<td>0.057</td>
</tr>
<tr>
<td>0.4</td>
<td>700</td>
<td>0.710</td>
<td>0.073</td>
</tr>
<tr>
<td>0.5</td>
<td>680</td>
<td>0.687</td>
<td>0.042</td>
</tr>
</tbody>
</table>
Fig. 5.1 aXRD pattern of $\text{Co}_{1+y} \text{Sn}_y \text{Fe}_{2-2y-x} \text{Cr}_x \text{O}_4$ system.
Fig. 5.1b XRD pattern of Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ system.
Fig. 5. XRD pattern of $\text{Co}_{1+y}\text{Sn}_y\text{Fe}_{2-2y-x}\text{Cr}_x\text{O}_4$ system.
Fig. 5.2 Variation of lattice constant (a) with composition 'x' for Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ system
Fig. 53 Variation of intensity ratio with composition $x$ for $Co_{1+y}Sn_{x}Fe_{2-2y-x}CrO_4$ system
Fig. 5.4 a Infra red spectra for \( \text{Co}_{1+y} \text{Sn}_{1-y} \text{Fe}_{2.2+y-x} \text{Cr}_x \text{O}_4 \) system.
Fig. 5.4  Infrared spectra for \( \text{Co}_{1-x}\text{Sn}_x\text{Fe}_{2-2x}\text{Cr}_x\text{O}_4 \) system.
Fig. 5.5 Variation of magnetization $n_B (\mu_B)$ with composition 'x' for Co$_{1-y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ System.
Fig 5.6 a Thermal Variation of a.c. susceptibility with composition 'x' for Co_{1+y}Sn_{y}Fe_{2-2y-x}Cr_{x}O_{4} system.
Fig. 5.6b Thermal Variation of a.c. susceptibility with composition 'x' for $\text{Co}_{1+y} \text{Sn}_y \text{Fe}_{2-2y-x} \text{Cr}_x \text{O}_4$ system.
Fig. 5.7 Variation of Curie temperature ($T_c$) with composition 'x' for $\text{Co}_{1+2x} \text{Sn}_x \text{Fe}_{2-2y-x} \text{Cr}_y \text{O}_4$ System
Fig. 5.8 a Variation of resistivity (log ρ) as a function of temperature (10^3/T) K^{-1} for Co_{1+y}Sn_{3}Fe_{2-2y}Cr_{x}O_{4} system.
Fig. 5.8b Variation of resistivity (log\(\rho\)) as a function of temperature (10^3/T) K\(^{-1}\) for Co\(_{1+y}\)Sn\(_y\)Fe\(_{2-2p-x}\)Cr\(_x\)O\(_4\) system.
Fig. 5.9a Variation of dielectric constant ($\varepsilon'$) versus \( \log F \) for \( \text{Co}_{1+y}\text{Sn}_y\text{Fe}_{2-2y-x}\text{Cr}_x\text{O}_4 \) system.
Fig. 5.9 b  Variation of dielectric constant ($\varepsilon'$) versus 
Log F for $\text{Co}_{1+y}\text{Sn}_y\text{Fe}_{2-2y-x}\text{Cr}_x\text{O}_4$ system.
Fig. 5.10a Variation of dielectric loss tangent (tan δ) versus Log F for Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ system.
Fig. 5.10b Variation of dielectric loss tangent (tan δ) versus Log F for Co$_{1+y}$Sn$_y$Fe$_{2-2y-x}$Cr$_x$O$_4$ system.