

TRANSPORT AND MAGNETIC PROPERTIES OF Cu-Co FERRITES DOPED WITH GALLATE ION

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Abstract

The effect of gallium substitution on conduction mechanism and the magnetic properties of $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$ ferrites have been studied. It was found that the value of the DC electrical conductivity decreased with the increasing of Ga^{3+} concentration. The thermoelectric power φ is negative, which indicates *n*-type semiconductor behavior for all samples. The hysteresis curve recorded at room temperature shows that the samples are ferrimagnetic at room temperature. The coercive field (H_c) decreases with increasing Ga^{3+} content in the samples, indicating that the loss of magneto crystalline anisotropy. The initial permeability (μ_i) is steadily decreased with the increasing temperature and becomes constant at a very small value of (μ_i). The Curie temperature decreases with increasing Ga^{3+} concentration.

1. Introduction

Spinel ferrite, MFe_2O_4 ($M = \text{Mn, Mg, Zn, Ni, Co, Cu}$ etc.), has a face-centered cubic lattice with a large unit cell containing eight formula

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units. They have two kinds of lattice sites for cation to occupy *A* and *B* sites having tetrahedral and octahedral coordination, respectively. Commonly, the M^{2+} and Fe^{3+} cations are distributed at both the sites. The addition of different metal cations of different valence states can lead to variety of tetrahedral (*A*) and octahedral (*B*) sites distribution. Changes in distribution of cations between the two sites (*A* and *B*) are believed to affect the electrical and magnetic properties of spinel ferrites.

Cobalt ferrite, owing to its strong ferromagnetism and high Curie temperature, is used in electronic appliances, as it causes the materials to stay magnetized, even when the applied magnetic field is turned off, leading to a useful way of storing information. Substitution of Al^{3+} [16], Cr^{3+} [14], Nd^{3+} [20], Ni^{2+} [15], and Zr-Mg [7] decreases the saturation magnetization in cobalt ferrite, while Zn^{2+} [2, 3], Cu^{2+} [18], and Cr^{3+} [14] decrease the Curie temperature (T_c). High electrical resistivity is an important property for the materials to be used in data storage devices. Little attention has been given to the study of electrical properties of the substituted cobalt ferrite.

The goal of the present work is focus the light on the effect of gallium doping on the electrical conduction mechanism, and magnetic properties of the composition are expressed by a molecular formula of $Cu_{0.5}Co_{0.5}Fe_{2-x}Ga_xO_4$ with ($0.0 \leq x \leq 0.5$).

2. Experimental

The DC-electric conductivity of the synthesized samples measured at 293K by two prop method with silver past used as a contact material, taking into consideration that, the current passing through the sample does not exceed 10mA to avoid the Joule heating effect.

The thermoelectric power or Seeback coefficient ϕ was measured by sandwiching the sample between two copper electrodes, where a small heating coil used to raise up the temperature of one surface of the sample to make a temperature gradient (differential method). The sample was on disk shaped with the surfaces coated by silver past. The optimum temperature difference ΔT between two ends of the sample was kept at 10K. The potential difference ΔV between the two sample surfaces is read

by a digital voltmeter (FLUKE 189) with accuracy 0.025%V. To eliminate the effects of the reference leads, the absolute potential difference of copper electrodes was subtracted from the measured thermoelectric voltage for each temperature. The sign of the thermoelectric power is taken as the sign of the cold electrode, where the charge diffuses from the hot to the cold part of the specimen. The Seebeck coefficient measurements (ϕ) was calculated by using the relation; $\phi = \lim_{\Delta T \rightarrow 0} \Delta V / \Delta T \approx \Delta V / \Delta T$, where (ΔT) is small as compared to the absolute temperature. The Seebeck coefficient was taken over a wide range of temperature starting from room temperature up to 850K.

Digital AC hysteresis loops of the samples were observed by inductive method from 0 to 16 Tesla using equipment model 9600-1 VSM. The values of the saturation magnetization (M_s), remanence (M_r), and coercivity (H_c) are calculated from the loops.

The toroidal samples with outer diameter 1.7cm and inner diameter 0.9cm were used as transformer cores for measuring initial permeability (μ_i). The initial permeability (μ_i) was measured as function of temperature at constant magnetizing current and a constant frequency. The value of (μ_i) was calculated by using Poltinnikov's formula [11], which is given by $V_s = K \mu_i$, where V_s is the induced voltage in the secondary coil and K is a constant, which depends on the magnetizing current, frequency, number of turns of the primary and secondary coils, and the dimensions of the sample.

3. Results and Discussion

3.1. Conduction mechanism

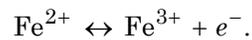
The X-ray diffraction pattern for the $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$ samples with ($0.0 \leq x \leq 0.5$) shows that, the nominal compositions with different concentration are single phase cubic spinel with no additional to any other phases [9]. The DC electrical conductivity of the synthesized samples $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$ measured at 293K is found to decrease with increasing of Ga^{3+} concentration. As Ga^{3+} content increases ($x > 0.3$), the DC-electrical conductivity is increased as given in Table 1. This change in values is based on the change in the cation distribution according to Mössbauer effect [1].

Table 1. DC (σ) conductivity, Seebeck coefficient (φ) values at 300K, Curie temperature T_c , and thermoelectric power transition temperature T_s for $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$ ferrites

Composition (X)	0.0	0.1	0.2	0.3	0.4	0.5
$\sigma(E^{-8})(\Omega^{-1}\text{cm}^{-1})$	5.08	4.54	0.246	0.191	2.25	3.52
φ	- 9.3	- 3.7	- 1.2	- 29.58	- 10.8	- 3.9
$T_c(\text{K})$	501	455	416	396	369	343
$T_s(\text{K})$	508	448	418	398	368	348

Figure 1 shows the variation of thermoelectric power with temperature for all compositions. It is clear that, the thermoelectric power φ is negative, indicating n -type semiconductor behavior for all samples. This means that, the conduction mechanism in these ferrites is predominantly due to electron hopping process only. The nature of the centers responsible for the hopping transport can be interpreted by the most general form of the cation distribution of the investigated samples. Cobalt ferrite is an inverse spinel ferrite [8], on doping cobalt ferrite with Cu-Ga; the cation distribution according to Mössbauer effect [1] with $x \leq 0.3$, the Ga^{3+} replaces Fe^{3+} at A -site, which has the formula $(\text{Co}^{2+}_{0.18}\text{Ga}^{3+}_x\text{Fe}^{3+}_{0.82-x}) [\text{Cu}^{2+}_{0.5}\text{Co}^{2+}_{0.32}\text{Fe}^{3+}_{1.18}]\text{O}^{-2}_4$. As Ga^{3+} content increases ($x > 0.3$), the Ga^{3+} replaces Fe^{3+} at B -site. The presence of diamagnetic Ga^{3+} ions with a closed 3d shell ($3d^{10}$) indicated that the gallium ions do not participate in the conduction mechanism. Also, the Cu^{2+} ions do not participate in the conduction mechanism, according to the sign of the thermoelectric power φ , which is negative. Therefore, the other two transition elements with open 3d shells, Co^{2+} ($3d^7$) and Fe^{3+} ($3d^6$) may be making the conduction mechanism. The conduction mechanism of Co^{2+} is according to; $\text{Co}^{2+} \leftrightarrow \text{Co}^{3+} + e^-$. But, the ratio of Fe^{3+} to Co^{2+} ions in the octahedral site is very high (fourth times) according to Mössbauer effect [1]. Thus, the participation of Co^{2+} ion in the conduction mechanism may be neglected. So, the conduction mechanism in ferrites under investigation is due to the exchange of

electrons between Fe^{2+} and Fe^{3+} ions, that results in local displacement of charges causing polarization of the lattice. The magnitude of this exchange depends on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ion pairs present on octahedral (B) sites. As the distance between the two ions (Fe^{3+} and Fe^{2+}) present at the octahedral site is minimal, hopping mechanism could be responsible for the electrical conduction. Thus, the substitution of Ga^{3+} would increase the number of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ion pairs present at the octahedral (B) sites, consequently, increasing the room temperature DC-electrical conductivity; from $x = 0.0$ to $x = 0.3$. As Ga content increases ($x > 0.3$), the room temperature DC-electrical conductivity decreases according to Ga^{3+} substitutes for Fe^{3+} ions at the octahedral B -site. Therefore, the conduction mechanism in these ferrites is predominantly due to hopping process between Fe^{2+} and Fe^{3+} at B -site:



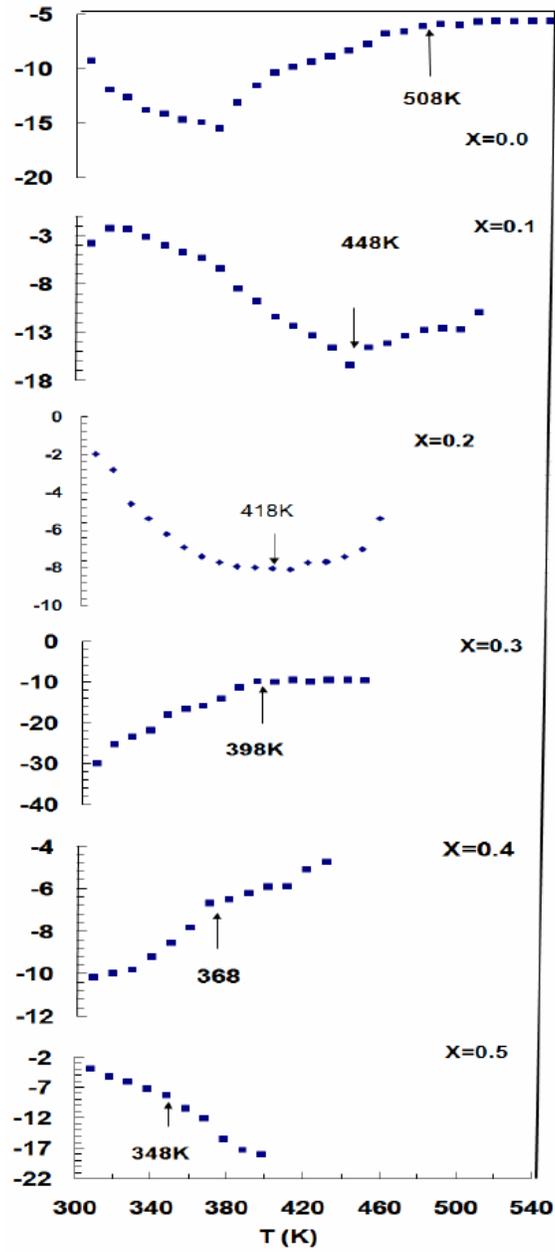


Figure 1. Variation of thermoelectric power with temperature for $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$ with $(0.0 \leq x \leq 0.5)$.

The values of thermoelectric power for all samples is low, close to that of metals and degenerate semiconductors, which varies very little with temperature, and correlate with the sample composition.

The thermoelectric power ϕ is change in behavior with the temperature from go down to up. This means that, the substitution of Ga ions in $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$ may be making blockade on Fe^{3+} .

It is clear from Figure 1, for all compositions, that the slope value of thermoelectric power ϕ is changing with the increasing of temperature to a certain temperature T_s (K). A similar behavior of thermoelectric power with temperature was observed for the compounds ferrites [4, 12, 13]. The values of T_s for all samples are tabulated in Table 1, which shows good agreement with T_c values obtained from dielectric measurements [1]. This indicating that; the change in behavior of the thermoelectric power with temperature could be due to magnetic transition from the order (magnetic) state to the disorder (paramagnetic) state. Therefore, the value of thermoelectric power, which shows upper or lower values at T_s (K) indicates that the magnetic ordering has a marked influence on the thermoelectric property of our spinel ferrite system.

3.2. Magnetic properties

The hysteresis loops shape for $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$ ferrite recorded at room temperature is shown in Figure 2. The hysteresis curve shows that, the samples are ferrimagnetic at room temperature similar to many ferrite systems. The changes in the magnetization with the concentration of gallium substitution are given in Table 2. From this table, it can be seen that, the variation in the saturation magnetization (M_s) may be due to the presence of the ferrimagnetic behavior of particles [19].

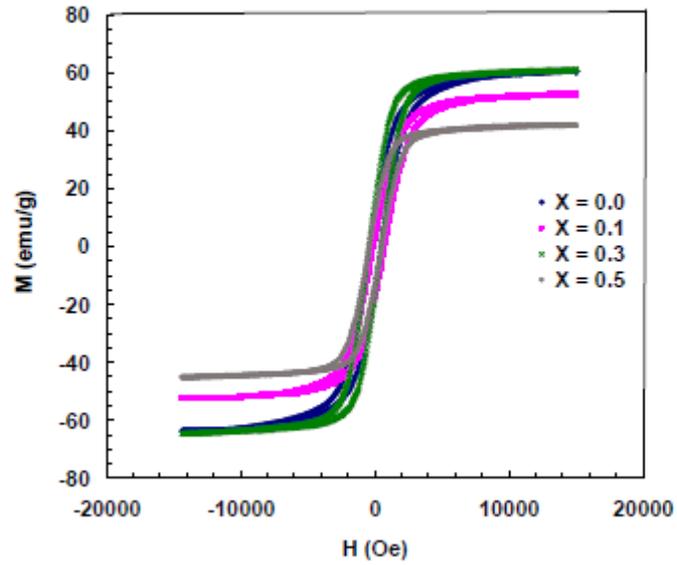


Figure 2. Magnetic hysteresis loops at room temperature for $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$.

Table 2. Saturation magnetization M_s , remanence M_r , coercivity H_c , grain size D , and magnetic transition temperature T_m for $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$ ferrites

Composition	0.0	0.1	0.2	0.3	0.4	0.5
M_s (emu/g)	63.06	53.45	66.53	63.48	26.74	44.18
M_r (emu/g)	4.81	2.81	4.63	3.99	1.34	1.77
H_c (Oe)	148.5	119.2	107.6	74	70	60
D (nm)	7.9	7	7.1	6.9	7.1	7.8
T_m (K)	-	448	-	398	-	340

The ferrites are considered to possess collinear ferrimagnetic structure in which, the magnetization of the tetrahedral sub-lattice is found to be anti-parallel to that of the octahedral (B) sub-lattice. Thus, the magnetic order causes super exchange interaction mechanism occurring between the metal ions in the A and B sub-lattices. When Ga^{3+} is substituted in $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$ ferrite system, at $x \leq 0.2$, the saturation magnetization (M_s) increases, but at $x \geq 0.3$, the (M_s) decreases as given in Table 2. The initial increase in (M_s) due to the migration of some Fe^{3+} ions to octahedral site (B) with Ga substitution, which have a preferential A -site occupancy. For $x \geq 0.3$, the concentration of Fe^{3+} ions at octahedral site (B) decreases due to entrance of Ga^{3+} ions on B -sites. Therefore, the magnetic structure causes the decrease in (M_s) values. This is due to the fact that, the magnetic moment of Ga^{3+} ($0\mu_B$) and the magnetic moment of Fe^{3+} ($5\mu_B$). Hence, by varying the degree of gallium substitution, it is possible to vary magnetic properties of the samples.

The coercive field strength (H_c) of magnetic materials is the opposing magnetic field strength required to reduce remanent flux density (M_r) to zero. Figure 3 shows the variation in coercivity (H_c) and porosity with Ga content of the ferrite system $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$. It is well shown that Ga^{3+} substitution apparently decreases coercive force (H_c) from 148(Oe) at $x = 0.0$, then reaches to the lowest point with 60(Oe) at $x = 0.5$. Low (H_c) value in a magnetic material arises from the lower pinning forces between the magnetic domain walls [17]. Hemeda and Hemeda [6] are reported that in soft magnetic ferrites, the coercivity was independent of the density and depended highly on the porosity. From microstructural analysis [1], our results show the slightly increase of the porosity with the increase of Ga content. The decrease of (H_c) with the increase of porosity means that, a less demagnetizing field is required to vanish the magnetization, due to the presence of pores.

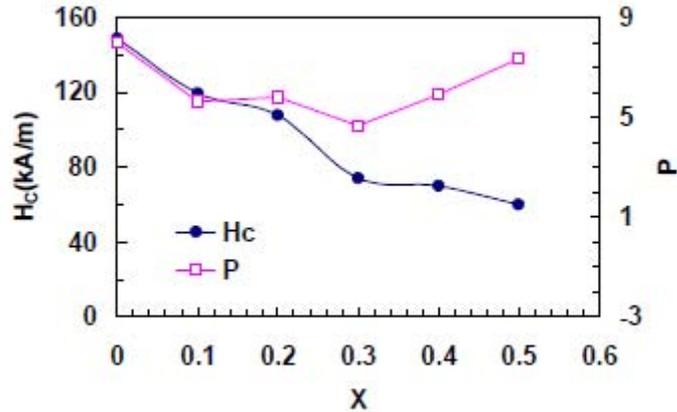


Figure 3. Dependence of coercive field H_c and porosity on gallium content x .

Figure 4 shows that the variation of the initial permeability (μ_i) with the temperature at different doping of Ga^{3+} ($x = 0.1, 0.3, \text{ and } 0.5$) in the composition $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$. It can be seen that the sample $x = 0.1$ exhibits a continuous decrease of initial permeability (μ_i) up to near the Curie point. For higher additive concentrations, the initial permeability (μ_i) exhibits a maximum, and then sharply decreases with increasing the temperature to value near Curie temperature. It is well known that, the permeability of polycrystalline ferrite is related to two magnetizing mechanisms: spin rotation and domain wall motion. According to Globus et al. [5], the domain walls normally remain pinned to the grain boundary and bulge, when subjected to a small magnetic field. He assumed that, the permeability due to the wall motion is likely to be linearly dependent on the grain size, while the permeability contribution due to spin rotation was assumed to be independent of grain size. Kakatkar et al. [10] studied the effect of grain size on the initial permeability and found that the initial permeability (μ_i) is proportional to

the grain size (D). Thus, the domain wall motion is greatly affected by the grain size and enhanced with the increase of grain size. This is because, bigger grains tend to contain more number of domain walls and initial permeability being a result of the easy reversal of domain wall displacement in the direction of the applied magnetic field. The greater the number of domain walls, the higher is the initial permeability.

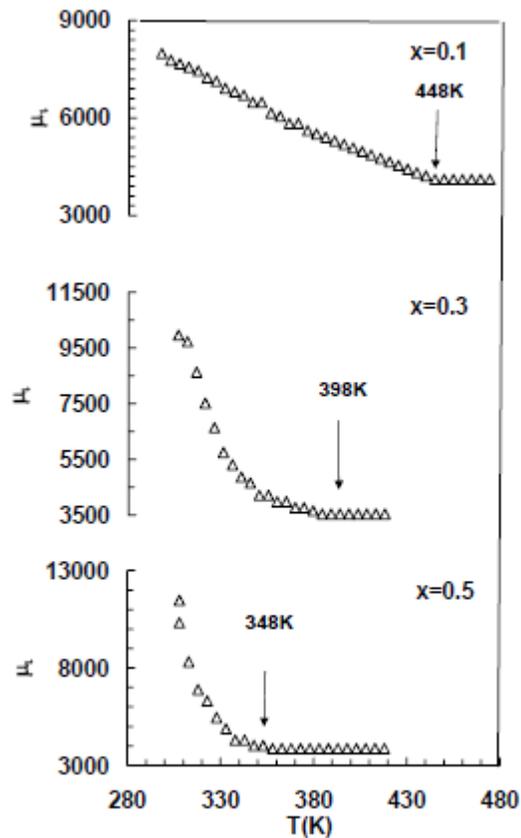


Figure 4. Variation of initial permeability with temperature for $x = 0.1$, 0.3 , and 0.5 for $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$.

4. Conclusion

The conduction mechanism is predominantly due to the hopping process between Fe^{2+} and Fe^{3+} at *B*-site according to $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + e^-$. The system of $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ga}_x\text{O}_4$ ferrites showed ferrimagnetic behavior, which was documented by hysteresis loop, measured at room temperature. The increase in Ga content tending to reduction of the *A-B* interaction and decrease the saturation magnetization. The decrease of H_c with the increase of porosity means that a less demagnetizing field is required to vanish the magnetization, due to the presence of pores. The increase in permeability can be attributed to the presence of Ga ions and leading to increase in grain size. The transition temperature determined from thermoelectric power is close to that from the initial permeability measurements. The determined transition temperature is found to decrease with increasing Ga content. These results agree with that obtained from the electrical conductivity measurements, and confirm that some correlation must exist between electrical and magnetic properties of the magnetic materials.

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