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ELECTRICAL BEHAVIOUR OF W-TYPE $Ba_xCo_{3-x}Fe_{16}O_{27}$ HEXAGONAL FERRITES

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Abstract: A series of $Ba_xCo_{3-x}Fe_{16}O_{27}$ hexagonal ferrites with x = 0.5, 1.0, 1.5, 2.0 and 2.5, were prepared using co-precipitation method. The X-ray diffraction analysis of the samples reveals that the crystal structure is hexagonal. Electrical resistivity was measured by two-probe method. The results of temperature dependence on dc electrical resistivity measured in the temperature range 13 to 200°C indicate semi-conducting behaviour of these ferrites. The resistivity and activation energy both increase with the increasing Ba concentrations in all samples.

Keywords: Co-Precipitation, Hexa-ferrites, Electrical Resistivity

INTRODUCTION

Hexagonal ferrites have many technological applications at high frequencies ranging from microwave to radio frequencies due to their unique electrical and magnetic properties. The electrical properties of these ferrites are related to experimental conditions, such as method of preparation, sintering temperature, sintering atmosphere and chemical compositions [Ata *et al.*1999]. Several properties of the hexagonal ferrites such as electrical conductivity, dielectric behaviour, thermo-power, magnetic properties have been studied by many researchers [Verway and Boer 1936, Ram *et al.* 1989, Ismael *et al.* 1995, Ata *et al.* 1997, Ata1998, Ata *et al.* 1998, Ata *et al.* 1999, Ata *et al.* 1999, Hiti *et al.* 1999, Ata *et al.* 2000]. There are two well-known conduction mechanisms in hexagonal ferrites. At low temperature, the conduction takes place by hopping of electrons between equivalent octahedral sites, i.e. $Fe^{2+} \Leftrightarrow Fe^{3+}$, where at high temperatures, holes transfer between Co^{2+} and Co^{3+} ions [Ata 1998] or between Ni^{2+} and Ni^{3+} [Ata *et al*. 1999] take place. The purpose of this study is to understand the conductivity mechanism in $Ba_xCo_{3-x}Fe_{16}O_{27}$ by X-ray diffraction and electrical resistivity measurements.

MATERIALS AND METHODS

Polycrystalline samples with composition $Ba_xCo_{3-x}Fe_{16}O_{27}$ (w-type) were prepared by chemical co-precipitation technique. The precipitating agent was hydroxide-carbonate buffer solution with a ratio of 1:1 (NaOH: Na_2CO_3). The co-precipitation was achieved by adding aqueous solution of precipitating agent into aqueous solution containing $BaCl_2.H_2O$, $CoCl_2.6H_2O$ and $FeCl_3.H_2O$ in the stoichiometric ratio 1:2:16. The filtered solution was then tested using precipitating agent in order to check the complete precipitation of Ba^{2+}, Co^{2+}, and Fe^{3+} cations. Finally, the precipitates obtained were washed with cold distilled water until all the chloride ions were eliminated. This was tested with $AgNO_3$ solution. The precipitates were dried at 110°C (overnight) in an oven to obtain dry powders. These dried powders were pressed at 30KN to get pellets of 8mm diameter. The pellets were annealed at different temperatures to obtain equilibrium of cations.

The crystal structure was determined by XRD analysis. The XRD patterns were obtained on Schimadzu XD-5A X-ray diffractometer equipped with Cu-K_a radiation. The electrical resistivity was measured by two-probe method. Both sides of the samples were polished to remove oxide layers. In order to make good ohmic contacts silver paste was applied on both sides of the samples. A dc IP-2717 Heathkit power supply and a very sensitive 610-C Keithley Electrometer were used in the measurements. The resistivity was calculated using the following relation;

$$\rho = R A / t$$

Where R and t are the resistance and thickness of the sample respectively, A is the effective area of the electrode in contact with the sample. Temperature dependent electrical resistivity was measured in the temperature range 13-200°C in a furnace having an accuracy of ±2°C.

RESULTS AND DISCUSSION

STRUCTURAL ANALYSIS

Two representative XRD patterns of the samples are shown in Fig.1. The d-values and the corresponding *hkl* measured from these patterns are listed in Table 1. The phase is identified to be hexagonal.

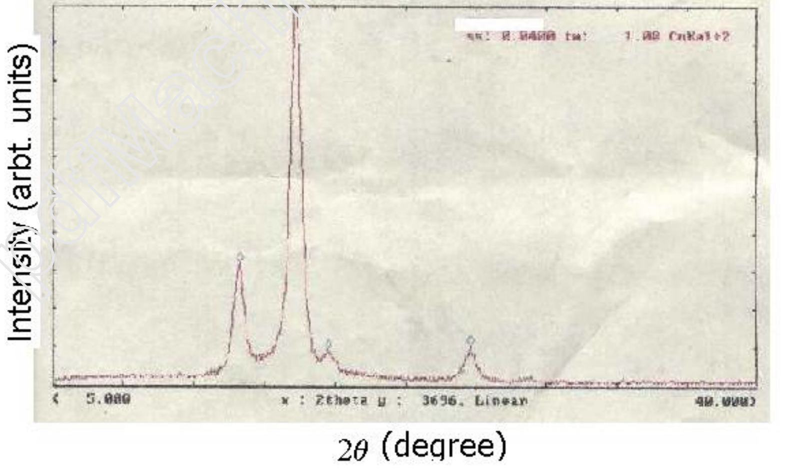

Fig. 1a: Representative XRD pattern of $Ba_xCo_{3-x}Fe_{16}O_{27}$ ferrites for x = 1.5.

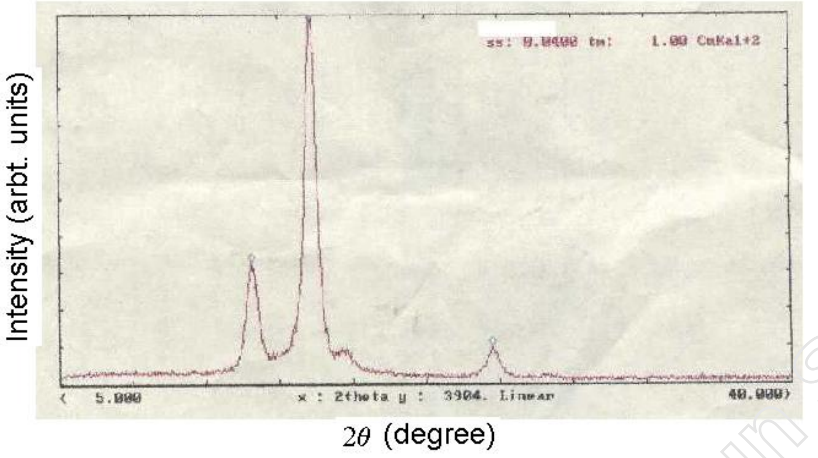

Fig. 1b: Representative XRD pattern of $Ba_xCo_{3-x}Fe_{16}O_{27}$ ferrites for x = 2.5.

COMPOSITION DEPENDENCE OF RESISTIVITY

The effect of Ba^{2+}substitution on Co^{2+} in the crystal on the dc electrical resistivity is shown in Fig. 2. The corresponding values are listed in Table 2. It can be seen that dc resistivity increases with increasing Ba^{2+}. Two regions of conduction were identified, a low conductivity region ($1.5 \leq x \leq 2.5$) and a high conductivity region ($0.5 \leq x \leq 1.5$). It is well known that Co^{2+} and Fe^{3+} ions can be distributed in both tetrahedral (A-sites) and octahedral (B-sites) [Yamazsaki and Satau 1973, Mazen and Zaki 1995].

Table 1: XRD analysis of representative $Ba_xCo_{3-x}Fe_{16}O_{27}$ (x = 1.5, 2.5) ferrites.

2θ	d (Å)	*hkl*
	X = 1.5	
14.26	6.20	100
17.06	5.20	101
18.68	4.75	002
25.77	3.45	110
28.71	3.10	103
33.12	2.70	404
	X = 2.5	
14.15	6.24	100
17.06	5.20	101
18.80	4.71	002
25.70	3.46	110
35.60	2.52	404

Table. 2: Values of resistivity and activation energies for $Ba_xCo_{3-x}Fe_{16}O_{27}$ ferrites.

Sr. No.	Ba Conc. (x)	log ρ (ohm-cm)	E (eV)
1	0.5	9.02	0.14
2	1.0	9.76	0.30
3	1.5	9.87	0.31
4	2.5	9.90	0.32

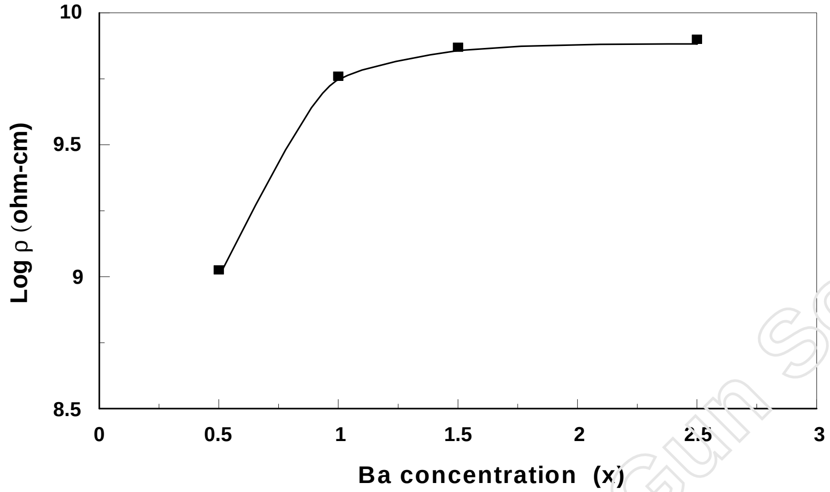

Fig. 2: Room temperature resistivity vs. Ba concentration for $Ba_xCo_{3-x}Fe_{16}O_{27}$ ferrites.

It is also suggested that partial conversion of Fe^{3+} ions in ferrites can take place upon firing at elevated temperature [Uitert 1957]. Also Fe^{2+} ions prefer B-sites, so that the conduction takes place by electron exchange between Fe^{2+} and Fe^{3+} ions in the B-sites i.e. hopping conduction as proposed by Verway and Heilmann [1947], where the conduction occurs by thermally activated jumps of electrons between equivalent sites in the lattice. In our case, the conduction mainly occurs by hole (p-type) exchange between Co^{2+} and Co^{3+} ions in low conductivity region and in high conductivity region in which the conduction occurs by electron exchange between Fe^{2+} and Fe^{3+} ions. It can be concluded that as Ba concentration increases or Co decreases, in $Ba_xCo_{3-x}Fe_{16}O_{27,}$ the change of charge species from n- to p-type takes place, which is consistent with the results reported in [Na *et al.* 1992, Abbas *et al.* 1995].

TEMPERATURE DEPENDENT DC RESISTIVITY

Fig. 3 shows the variation of Logρ vs 1000/T for all the samples. It can be seen that as the temperature increases the resistivity decreases verifying the equation $\rho = \rho_o \exp(E / k_B T)$, where E is activation energy, k_B is Boltzmann's constant, and T is absolute temperature. This shows that the present samples behave as semiconductors. In ferrites, cations are surrounded by closed pack oxygen anions and as a first approximation, can well be treated as isolated from each other. There will be a little direct overlap of the anion charge clouds. Therefore the electrons associated with particular ion will largely remain isolated and hence a localized electron model is more appropriate in the case of ferrites rather than the collective electron (band) model. Small polaron formation can take place

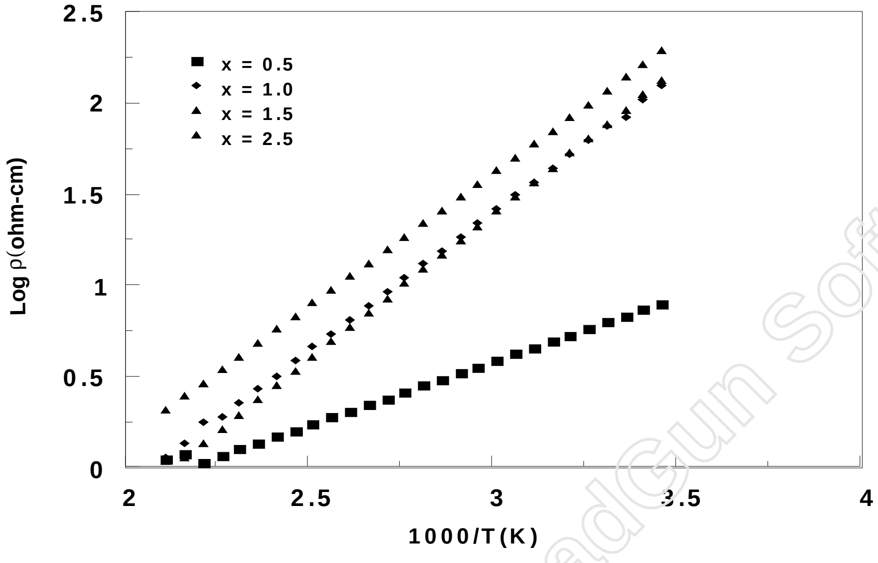

Fig. 3: Arrhenius plots of $Ba_xCo_{3-x}Fe_{16}O_{27}$ ferrites.

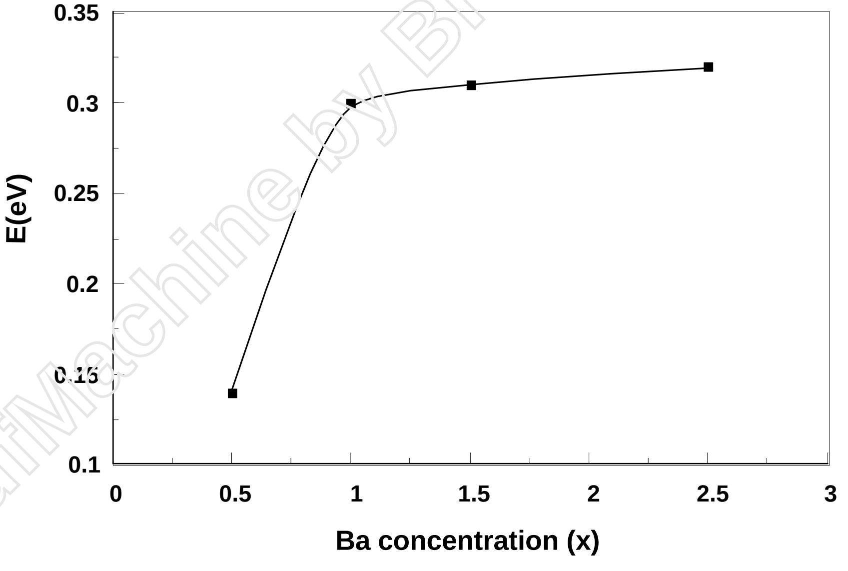

Fig. 4: Plot of activation energies vs. Ba concentration for $Ba_xCo_{3-x}Fe_{16}O_{27}$ ferrites.

in materials whose conduction electrons belong to incomplete inner (d or f) shells which is due to small electron overlap, tend to form extremely narrow bands. Based on small polaron model [Bhise *et al.* 1995] the conduction phenomena at low temperature are attributed to the presence of impurities, vacancies and defects, while at higher temperatures to the small polaron hopping mechanism.

Fig. 4 shows the variation of activation energies vs. Ba concentration and the corresponding values are tabulated in Table. 2. The behaviour of the activation energies seems to be similar to that of the room temperature resistivity vs. concentration. It can be seen from Fig. 4 that the samples having low resistivity have small activation energy and vice versa [Gill and Puri 1985].

CONCLUSIONS

From electrical resistivity measurements of $Ba_xCo_{3-x}Fe_{16}O_{27}$ ferrites with varying concentrations of Ba, it is concluded that all the samples behave like semiconductors. It is also concluded that the samples having low resistivity have small activation energy and vice versa. Moreover, the high value of resistivity shows that these samples are hard ferrites.

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