Electrical, dielectricand permeability studies of Ba$_3$ Co$_{2-x}$Cd$_x$ Fe$_{24}$ O$_{41}$Hexaferrite

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Abstract

Co$_2$Z Hexaferrite a planar anisotropic iron oxide having chemical composition in M$_3$Co$_2$Fe$_{24}$O$_{41,}$ M is a divalent cation (Ba,Sr),which has much higher permeability and thermal stability. But the phase formation and sintering temperature is higher than1300^{0}C.In the present study the polycrystalline samples of Ba$_3$Co$_{2-x}$Cd$_x$Fe$_{24}$O$_{41}$ (x = 0.0, 0.1, 0.2, 0.4, 0.5, 0.6) were synthesized by the standard solid-state-reaction method. The addition of Cadmium lowered the sintering temperature to 1190^{0}C.The X- ray diffraction pattern of the samples confirms the formation of monophasic Z type phase. The surface morphology indicates that the samples are well formed with almost uniform well defined grains. The sample with Cd content x =0.1 have very much smaller grains with average grain size(d$_m$) of the order of 2µm. The grain size seems to grow with the increase in the concentration of Cd from x = 0.1 to x = 0.8.The resistivity of the undoped Co$_2$Z hexaferrite is of the order of 0.2x10^{8}Ωm. For x=0.1 the d.c. resistivity increases to the order of 17.8x10^{8}Ωm. For further addition of Cd from x=0.1 to x=0.8, resistivity is found to decrease. The dielectric properties of the silver pasted pelletized samples are studied as a function of frequency in the frequency range 100Hz - 1MHz at room temperature. The sample with Cd content x=0.1 possesses highest resistivity and lowest dielectric dispersion. The variation of dielectric constant with temperature shows ferroelectric behaviour. Curie temperature of the investigated samples is measured by an instrument developed in our laboratory based on Lauria technique.The compositional and temperature dependence of initial permeability of the investigated samples have been studied. The densification and microstructure are correlated to the magnetic and electric properties of the samples.

Keywords: Co$_2$Z Hexaferrite; Permeability and electrical properties; Microstructure

1. Introduction

Co2Z hexa ferrite is a planar anisotropic iron oxide which has a much higher permeability and ferromagnetic resonance up to 1.5–3.4GHz and a high thermal stability due to its high Curie point of 400^{0}C [1]. This makes it very useful in high frequency inductor and uhf communication applications [2].The structure of Co$_2$Z-hexaferrite is very complex since ionic radii of barium and strontium are comparable with that of oxygen ion and they prefer oxygen position over the interstitial sites. Co$_2^+$ ions will be locate in ten non-equivalent interstitial sites of which one is a trigonal bipyramid, three are in tetrahedrally and six are in octahedrally coordinated sites.Its special plain-hexagonal structure is very complicated and only formed at rather high temperature(1300-1400^{0}C) (3,4). Furthermore, the purity and stability ofZ-type phase during sintering at low

temperature is also a key problem.In the present study cadmium is substituted in Co_2Z hexaferrite as $Ba_3 Co_{2-x}Cd_x Fe_{24} O_{41}$ with x=0, 0.1,0.2, 0.4, 0.5, 0.6 and 0.8. An increase in resistivity is expected on the addition of cadmium which may cause low loss. Cadmium is a divalent nonmagnetic ion having ionic radius (1.03Å) which is substituted to replace Co^{2+}. However, the substitution of Cd in $Ba_3Co_2Fe_{24}O_{41}$lowers the sintering temperature to 1190°C and modifies the microstructure and hence influences the electric and permeability properties. The influences of Cd-substitution on phase formation,densification, microstructure and electromagneticproperties have been investigated.

2. Experimental

2.1 Sample preparation

Samples of $Ba_3Co_{2-x} Cd_xFe_{24}O_{41}$ with x = 0, 0.1, 0.2, 0.4, 0.6, 0.8 ferrites are prepared by a standard solid state reaction technique. The powders of $BaCO_3$, Co_3O_4, CdO, Fe_2O_3 are stoichiometrically weighed, mixed thoroughly and finely powdered. The powder is then calcinated at 800^0C for about 10 hours. The pressed pellets and toroids are obtained by sintering the green bodies at1190^0C for about 16 hours and then cooled in the furnace.

2.2 Characterization

The phase identification of the sample is carried out by X- ray diffraction studies. The X-ray diffraction pattern of the samples is obtained using Philips PW-1710 diffractometer with Cu- K alpha 1 radiation. The micrographs of the fracture surface of the sintered samples are carried out using scanning electron microscope (SEM). The bulk density of these samples is also determined.

2.3 Property measurements

Two probe set up is employed to study the d.c. resistivity of the samples in pellet form.

The dielectric properties of the silver pasted pelletised samples are studied as a function of frequency in the frequency range 100Hz-1MHz at room temperature using complex impedance analyser. Using high temperature assembly, dielectric constant of the samples at different temperatures is measured at 1 KHz. Cavity resonator technique is used to measure the dielectric constant in GHz region.

For initial permeability, the inductance of sintered toroid samples is measured using a standard LCR meter at 1kHz. The inductance (L) of the samples in the form of toroids is measured with 50 turns winding (N) at a frequency of 1kHz in the temperature range 303-573K.Their initial permeability $μ_i$ is calculated using the relation

$$\mu_i = \frac{L}{0.0004606N^2t\log{d_2}/{d_1}}$$

where d_1 is the inner radius, d_2 is the outer radius and t the thickness of the of the toroid.

Variation of initial permeability as a function of temperature is studied in the temperature range 303K- 600K.

Curie temperature of the investigated samples is measured by an instrument developed in our laboratory based on Lauria technique.

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3. Results and discussion

3.1 X-ray Diffraction Data

X- ray diffraction pattern of the samples confirms the formation of monophasic Z type phase according to JCPDS file 19–97.
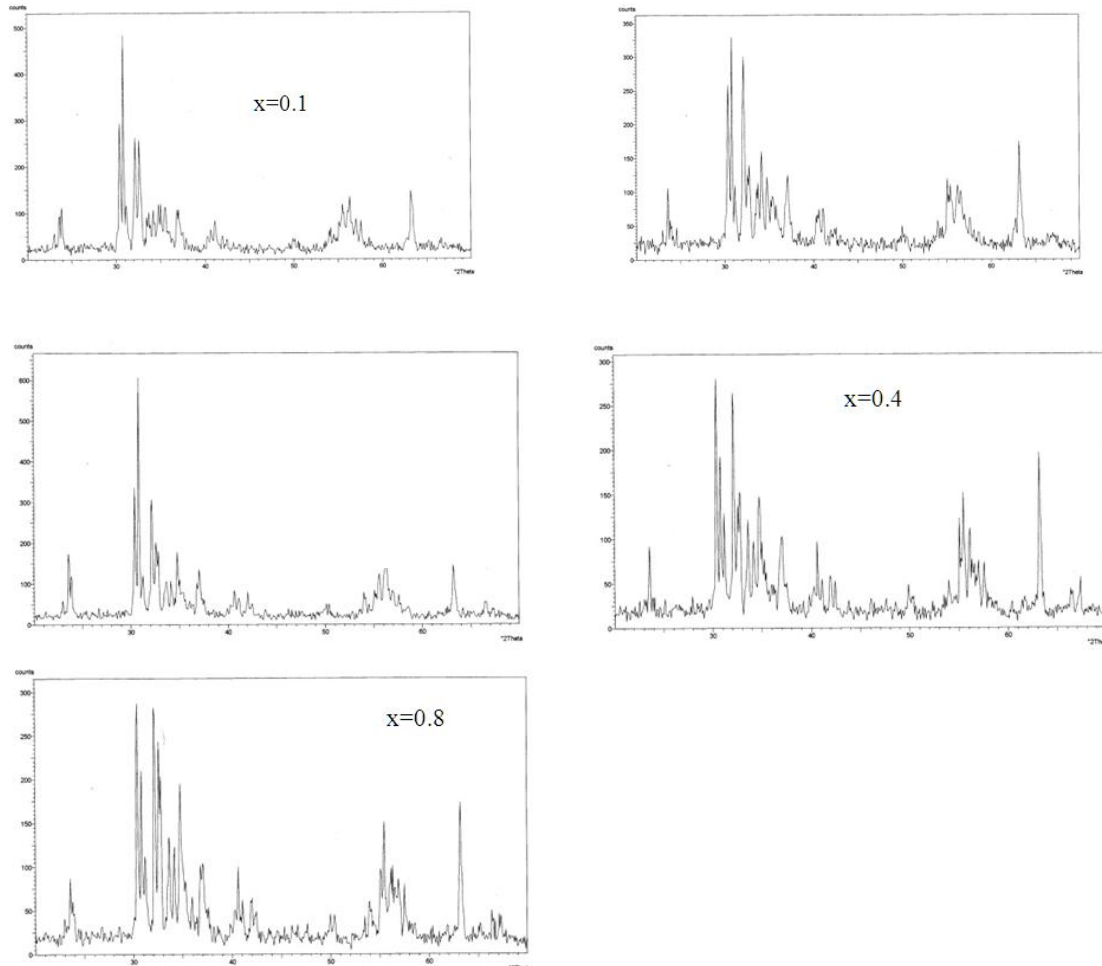

Fig.1. X-ray diffraction pattern for $Ba_3Co_{2-x}Cd_xFe_{24}O_{41}$

3.2 SEM micrograph

The surface morphology indicates that the samples are well formed with almost uniform well defined grains(fig.2). The average grain size of the undoped sample is found to be of the order of 16µm. The sample with Cd content x =0.1 have very much smaller grains with average grain size (d_m) of the order of 2µm and the grains are also more well packed and uniformly distributed compared to that of the other samples. It is also noted that the grain size seems to grow with the increase in the concentration of Cd from x = 0.1 to x = 0.8. As Cd content increases the micrographs consist of more number of pores and voids which may be due to the volatisation of cadmium from the outer surfaces of the ferrite pieces due to the increased sintering time. The rate of Cd volatisation increases as the concentration of Cd content increases. The average grain size is about 8µm, 10µm and 12µm for samples with x =0.2, x =0.4 and x =0.8 respectively across the

hexagonal plane. Fig.3 shows the variation of bulk density as a function of Cd content. Density of the sampleincreases with the small addition of Cd content and attains its maximum value at x=0.2. It then decreases with further addition of Cd.
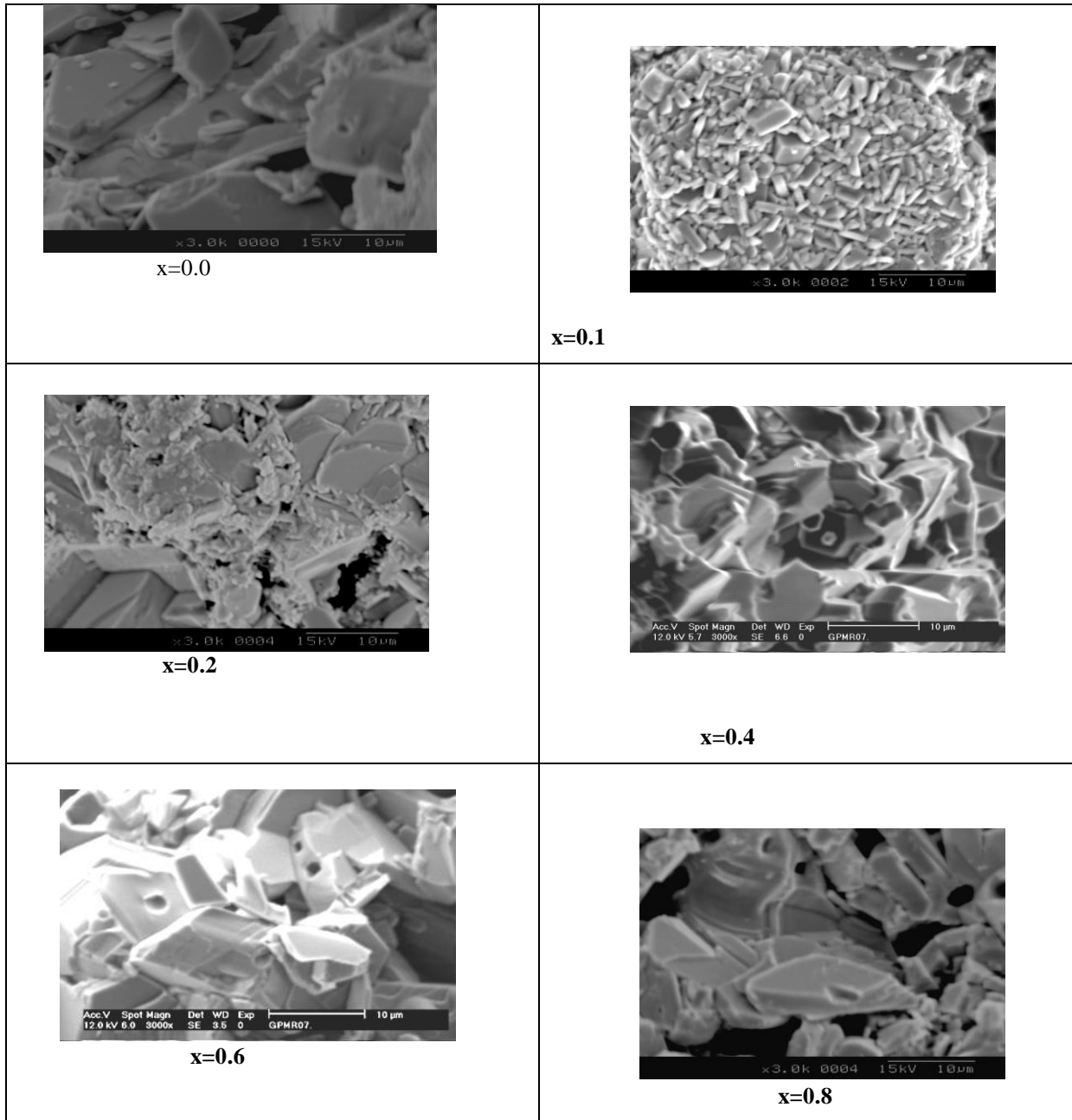
 x=0.0	 **x=0.1**
 x=0.2	 **x=0.4**
 x=0.6	 **x=0.8**

Fig.2 SEM micrographs of $Ba_3Co_{2-x}Cd_xFe_{24}O_{41}$ hexaferrite

$Dx10^{3} Kg/m^{3}$
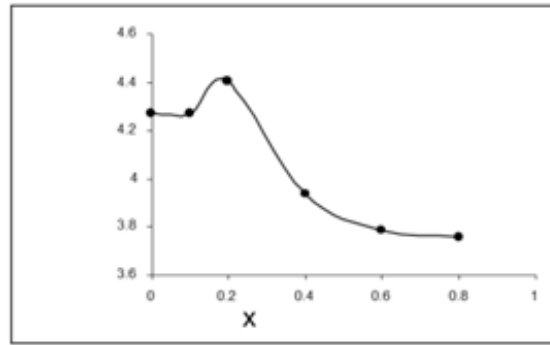
Fig.3 Variation of Bulk Density with Cd in $Ba_3Co_{2-x}Cd_xFe_{24}O_{41}$ **Hexaferrite**

4. Measurement of conductivity and dielectric properties.

4.1 Compositional variation of D.C Resistivity.

The values of average grain size and dc resistivity for different concentrations of Cd at room temperature are listed in table1

The resistivity of the undoped Co_2Z hexaferrite is of the order of $0.2x10^{8}\Omega m$. When a small concentration x=0.1 of Cd is substituted in the above ferrite system, it results in a considerable increase in the d.c. resistivity. Now the resistivity is of the order of $17.8x10^{8}\Omega m$. For further addition of Cd from x=0.1 to x=0.8, resistivity is found to decrease (fig.4).

On examining the microstructure and resistivity data, it is obvious that the sample with x=0.1 offers the minimum grain size and maximum resistivity. It has been reported (5, 6) that resistivity of a polycrystalline material, in general, increases with decreasing grain size. Smaller grains imply larger number of insulating grain boundaries which act as barriers to the flow of electrons. Smaller grains also imply smaller grain to grain surface contact area and reduce the electron flow.
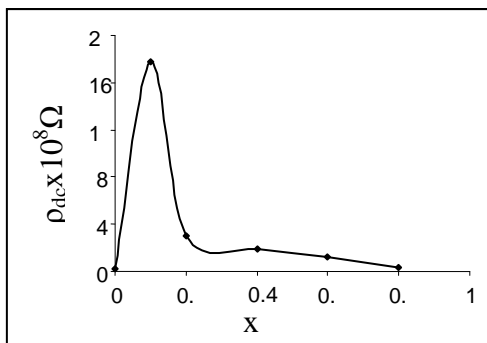

Fig.4 Variation of Room temperature dc resistivity

with Cd in $Ba_3Co_{2-x}Cd_xFe_{24}O_{41}$ **Hexaferrite**

Table1

Values average grain size (dm) and dc resistivity with

Cd concentration in $Ba_3Co_{2-x}Cd_xFe_{24}O_{41}$ Hexaferrite

x	$d_m\mu m$	$\rho_{dc} \times 10^8 \Omega$ m
0.0	16	0.191
0.1	2	17.8
0.2	8	3.03
0.4	10	1.91
0.6	11	1.2
0.8	12	0.303

On increasing the concentration of Cd to x=0.2, the grain size is found to increase. From the density measurement, it is observed that the sample with x = 0.2 has the maximum density, that is less porosity. Owing to the larger density the grains come closer to each other. As a consequence of this, the effective area of grain to grain contact increases and hence the resistivity of this sample reduces to the observed value.

It is also observed that on increasing the Cd concentration from x =0.2, the density is found to decrease. This decrease in density indicates the increased rate of inter granular porosity and voids resulting from Cd volatisation. These pores may isolate grains to some extent and decrease the grain to grain area of contact and cause an increase in the resistivity (7). But in the present case, for higher concentration of Cd i.e. x > 0.2, even though percentage of porosity and voids are larger, a decrease in resistivity is observed. This may be due to the dominant effect of increased grain size on the resistivity. The presence of pores and voids tends to increase the resistivity whereas the grain growth decreases the resistivity.

4.2 Variation of dielectric constant with frequency

Variation of real part (ε') dielectric constant and loss 'tan δ' with log frequency at room temperature for the investigated samples in the frequency range 100Hz to 1MHz are shown in fig. 5 and fig.6 respectively. It can be seen from these figures that the value of the dielectric constant decreases continuously with increase of frequency, which is a normal dielectric behaviour of most of the ferrites. The maximum value of dielectric constant lies in the range 333-121 for all samples. This value is found to be low when compared with the spinel ferrites prepared in the conventional ceramic technique. The high value of dielectric constant is due to the inhomogeneous nature of dielectric structure which is supposed to be composed of two layers (8). The grain boundaries are found to be more effective at lower frequencies while the ferrite grains are more effective at higher frequencies (9,10). It is also observed that the value of dielectric constant depends on the percentage of Fe^{2+} ions present in the A and B sublattices (11-13).A large number of Fe^{2+} ions cause high dielectric constant since Fe^{2+} ions are easily polarisable
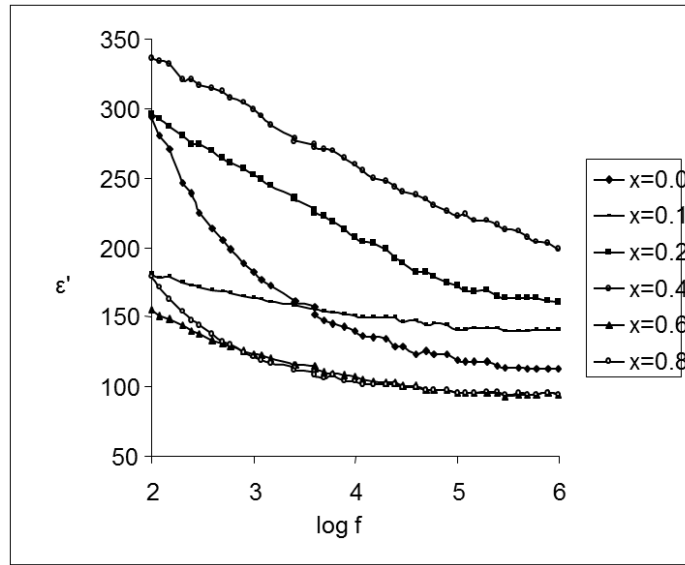
Fig. 5 Variation of real part of dielectric constant (ε') with log(f) at RTfor $Ba_3Co_{2-x} Cd_xFe_{24}O_{41}$Ferrite
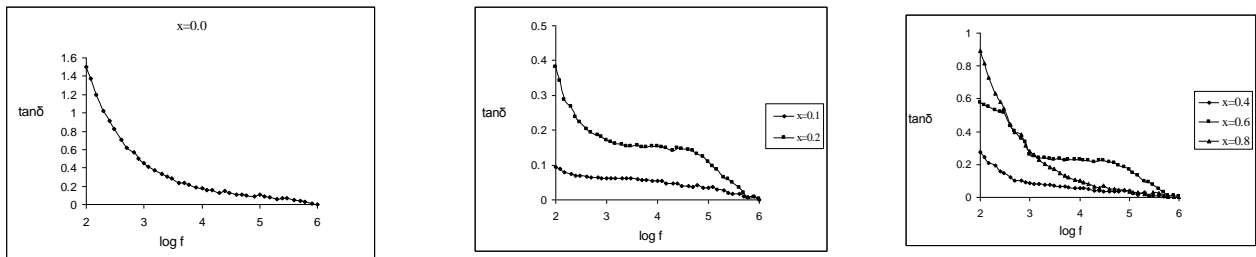

Fig .6 Variation of loss tangent tanδ with log (f) at RT for Ba3Co2-x CdxFe24O41Ferrite

Table 2

Dielectric data obtained from Cavity resonator technique at 3.29GHz

for $Ba_3Co_{2-x} Cd_xFe_{24}O_{41}$Ferrite

x	ε'	ε''	tanδ
0.0	5.132	.065	.013
0.1	3.478	.013	.004
0.2	5.959	.012	.002
0.4	5.859	.029	.005

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0.6	5.088	.036	.007
0.8	3.555	.013	.004

The sample with Cd content x=0.1 shows the minimum dielectric dispersion which indicates greater structural homogeneity. The microstructure of this sample also shows well packed small sized grains with greater structural homogeneity. In smaller size grains the probability of Fe^{2+} formation is low thus resulting in lower dielectric constant (13). From the dielectric data it is observed that the values of dielectric loss are significantly low especially at high frequency region when compared to other ferrites. The dielectric data obtained by cavity resonator technique in GHz region is given in table 2.The higher resistivity and comparatively lower dielectric constant makes this sample suitable for high frequency applications.

4.3 Variation of dielectric constant with temperature

 The dielectric constantε increases with increase of temperature and reaches to a maximum value around Curie temperature and drops to zero followed by a sharp rise which is a typical ferroelectric behaviour (Fig.7).
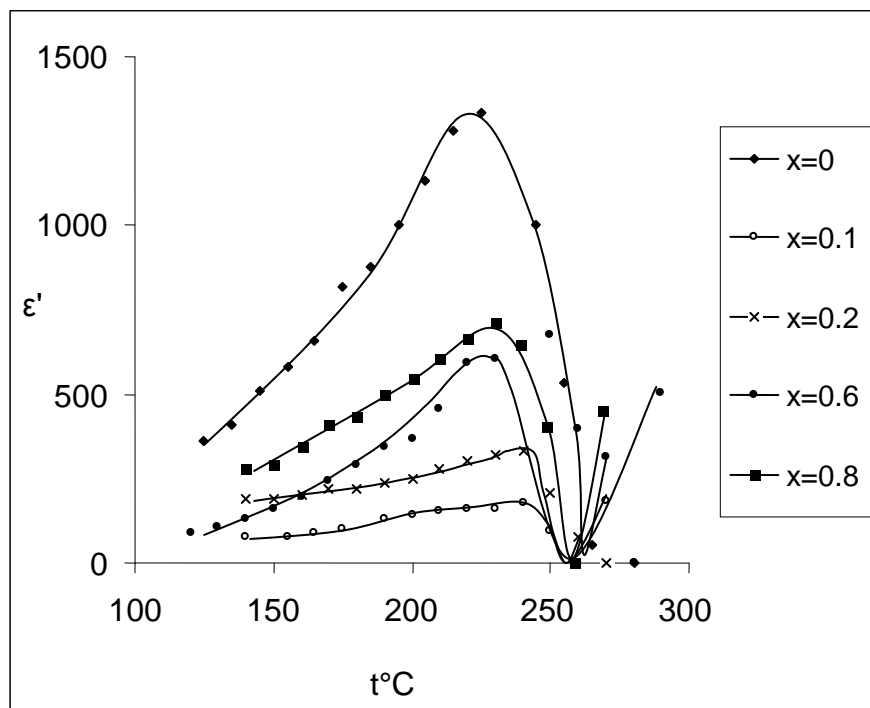

Fig 7 Variation of real part of dielectric constant (ε') with temperature

forBa_3Co_{2-x} $Cd_xFe_{24}O_{41}$Ferrite

At relatively low temperature, the charge carriers, in most cases, cannot orient themselves with respect to the direction of the applied field and thus they possess a weak contribution to the polarisation and hence the dielectric constant. As the temperature increases, the bound charge carriers get enough excitation thermal energy to align themselves in the direction of the applied field more easily leading to an increase of the dielectric constant ε to a maximum value.

5. Measurement of initial permeability and Curie temperature

5.1 Variation of initial permeability with composition

The variation of initial permeability with cadmium shows (fig.8) that the value of initial permeability decreases from 10.45 at x=0.0 to its minimum value 7.91 at x=0.1, there after its value slowly increases with cadmium up to 9.63 at x=0.6 followed by a slight decrease in its value with further addition of Cd .

The contribution to initial permeability depends on many factors like spin rotations and domain wall motion as well as the microstructural parameters of the sample.

The sample with x=0.1 has the minimum grain size and minimum value of initial permeability. The increase of initial permeability from x=0.1 to x=0.6 suggests that the grain growth of the micro-structures has a dominant effect on the observed increase in the initial permeability by enhancing the domain wall motion. It is also seen that the linear relation between grain size and initial permeability values holds good for the concentration of Cd region from x=0.0 to x=0.6. The relationship between the grain size and permeability will be linear only if the grain growth is normal, that is, if all the grains grow at the same time and at the same rate (14). This type of linear relationship (fig.9) between permeability and grain size is also observed in the studies of spinel ferrite (15), in Mn-Zn system by Perduijn et al. (16) and Roess et al. (17) and in Ni-Zn ferrites by Globus et al.(18).
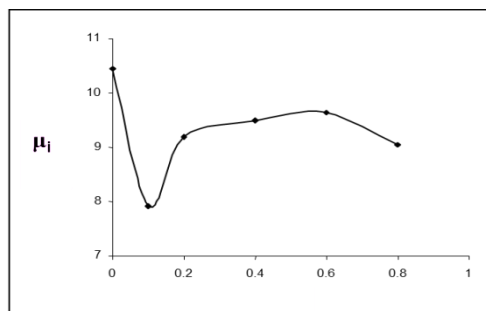

Fig. 8compositional variation of initial permeability (μ_i)
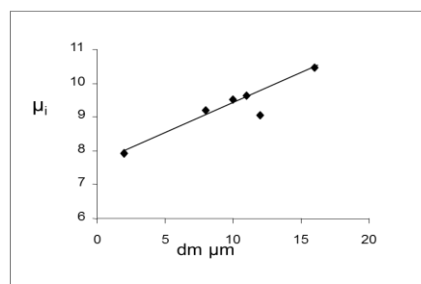

Fig. 9 Variation of initial permeability as a function of grain size.

However for x=0.8, the value of initial permeability is found to be less than the expected value. Density measurement shows that the sample with x=0.8 possesses minimum density and maximum porosity. The observed decrease in the initial permeability at x=0.8 can be explained as follows. Due to the effect of high sintering temperature and long sintering time, cadmium evaporation may takes place from the outer surfaces of the ferrite pieces, which introduces chemical inhomogeneity. Presence of pores within the grain may act as pinning points for domain walls (19) and effectively reduce the grain size to the pore spacing and tend to decrease initial permeability and this may cause reduction in permeability value.

5.2. Variation of Initial Permeability with Temperature.

The initial permeability of all samples increase very slowly with temperature up to a certain value, designated as T_i, that lies between 523-573K, characteristic of each sample, followed by a sudden decrease in its value(fig.9). But only a slight decrease in μ_i is observed for the sample with x=0.6 within this temperature range. The curie temperature of all investigated samples is found to be much higher than this observed temperature T_i.

It has been reported that Co_2-Z hexaferrite represents three kinds of crystal anisotropy. At a temperature approximately above 480K, the c-axis is the preferred direction. Now the magnitude of initial permeability is determined by that of K_1 and is therefore small. Between 220K and 480K the basal plane (perpendicular to c-axis) is a preferred plane of magnetisation and below 220K the sample exhibits preferred cone of magnetisation (20).When basal plane is a preferred plane, the sample possesses higher values of initial permeability as a result of the rotations of the magnetisation in the basal plane.

This suggests that at this temperature T_i, the first order crystal anisotropy changes sign and the transition takes place from the preferred plane to preferred direction. Below the temperature T_i, these compounds have a preferred plane of magnetisation and above, T_i, they exhibit a preferred direction of magnetisation.

The present study reveals that all samples show variation of initial permeability with temperature similar to that of Co_2Z ferrite. At room temperature these samples exhibit preferred plane for magnetisation and hence find application in microwave ferrite devices (21).

5.3 Measurement of Curie temperature.

The Curie temperatures of the samples were measured using experimental setup developed in this lab. The ferrite material is made to attach itself to a bar magnet due to the magnetic attraction, and the combination is enclosed inside a glass tube which can be heated up to a temperature800^{0}C. The temperature measured by a chromel aluminal thermocouple inserted in the glass tube. The sample is heated till it is dropped down losing its spontaneous magnetisation and becomes paramagnetic.This temperature is taken as the approximate Curie point. Curie temperature of the undoped sample is about 618K. A small addition of cadmium results an increase in the Curie temperature. On further addition of cd a decrease in the curie temperature is observed.The values of initial Permeability μ_i, Curie temperature (Tc K)and the temperature at which the first order crystal anisotropy changes Curie temperature of the samples(TiK) with different concentration of Cd are given in the table 3
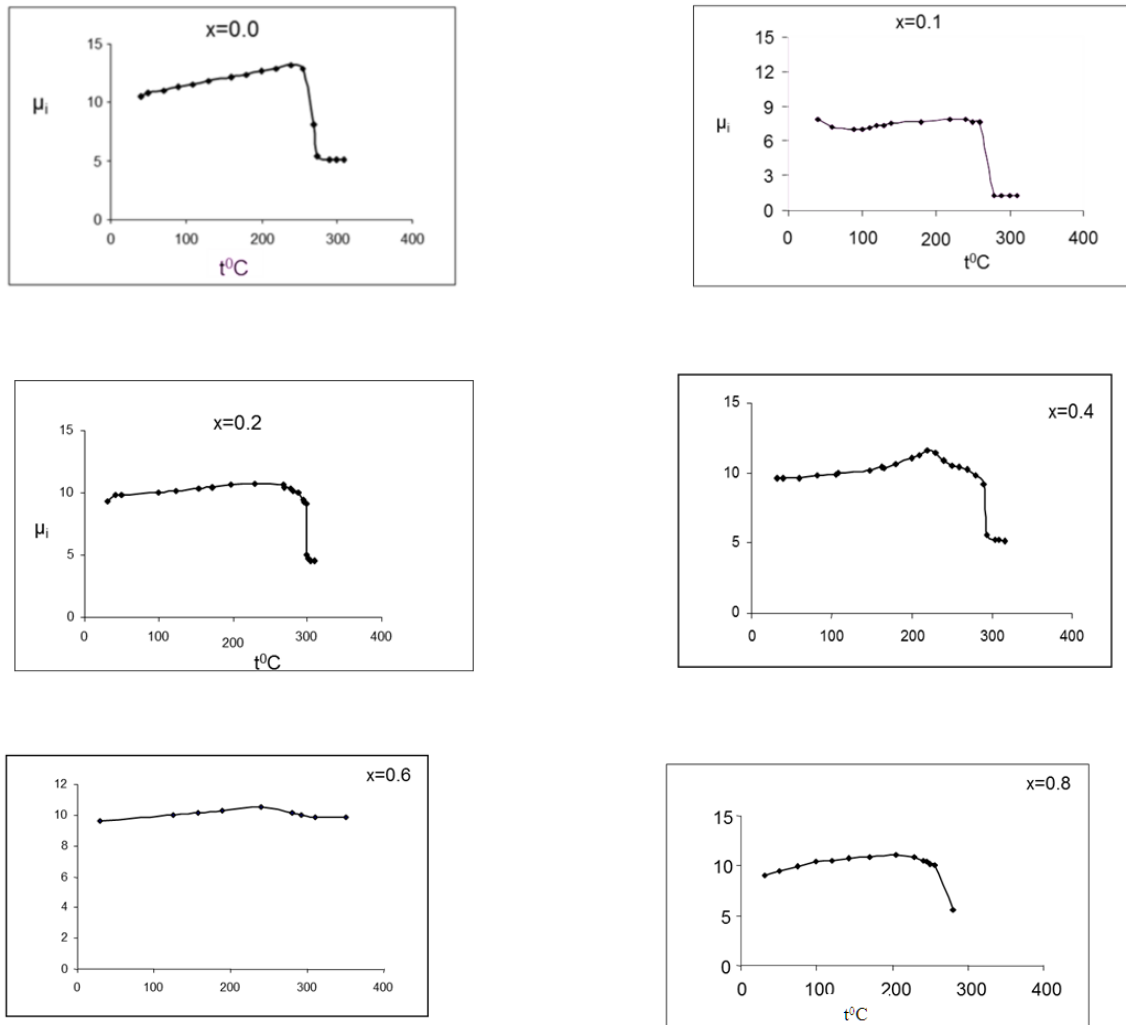
Fig.9 Variation of Initial permeability as a function of temperature for

$Ba_3 Co_{2-x}Cd_x Fe_{24} O_{41}$hexaferrite

Table 3

Compositional variation of Initial Permeability $\mu_{i, Curie}$ temperature (T_c) and the temperature at which the first order crystal anisotropy changes its sign in $Ba_3 Co_{2-x}Cd_x Fe_{24} O_{41}$hexaferrite.

t^0C

x	Initial Permeability μ_i	T_c K (Lauria technique)	T_i K
0.0	10.45	618	543
0.1	7.91	771	553
0.2	9.2	774	573
0.4	9.5	630	563
0.6	9.63	609	553
0.8	9.03	599	529

6. Conclusion

The grain size of the Co_2Z hexaferrite is modified with the substitution of Cd. A small addition of Cd results in a decrease in grain size. But on increasing the concentration of Cd, grain size increases. Substitution of Cd also affects the densification and porosity. The maximum density is obtained for sample with the concentration x=0.2 of Cd. The density is found to decrease with the further addition of Cd content. This decrease in density is due to the increased rate of inter granular porosity and voids resulting from Cd volatisation. Conductivity of the sample is found to be very much dependent on grain size and hence in Cd concentration.

All the investigated samples show normal dielectric spectrum .Low dielectric constant of the samples indicates greater structural homogeneity and the presence of lesser number of Fe^{2+} ions. The sample with Cd content x=0.1 possesses highest resistivity and lowest dielectric dispersion. The variation of dielectric constant with temperature shows ferroelectric behaviour.

The effect of grain size on initial permeability is more significant than that of the anticipated effect of porosity till x=0.6 and for further increase of cadmium content i.e. for x=0.8 the influence of porosity is quite high enough to reduce the initial permeability value. All the samples show variation of initial permeability with temperature similar to that of Co_2Z hexaferrite. However the sample with x=0.6 exhibits only a slight decrease in initial permeability at $T_i k$.

Since electric and magnetic properties are very much depending on the microstructure, by controlling the grain size, these properties can be modified to a great extent. Hence at the usual temperature of operation, these samples find application in microwave devices. Moreover, the substituted samples offer high resistivity and low dielectric loss and high thermal stability. The high resistivity and low dielectric loss together with good dielectric behaviour especially in the hyper frequency region make these samples useful in the hyper frequency region. The properties of the investigated ferrites can be further modified by controlling the grain growth, optimising sintering temperature, and adding suitable quantity of cadmium.

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