EFFECTS OF Cd ON PHYSICAL AND SOME MAGNETIC PROPERTIES OF Co-Cd FERRITES

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ABSTRACT

Polycrystalline samples of Cd substituted cobalt ferrites with composition Co$_{1-x}$Cd$_x$Fe$_2$O$_4$ (x = 0.0-0.6 in steps of 0.1) were prepared by double sintering ceramic method. The samples were sintered at 1050°C for 3 hours. X-ray diffraction pattern of the samples showed single phase cubic spinel structure. It was found that the lattice parameter increases linearly with increasing Cd content following Vegard’s law. The apparent density and X-ray density exhibited similar behavior. The Curie temperature $T_c$ has been determined from the temperature dependence of permeability. It was found that the Curie temperature continuously decreased with increasing Cd content and is attributed to the weakening of $J_{AB}$ exchange interaction. The initial permeability, $\mu'$ increases with increasing Cd content up to $x = 0.6$ and then decreases.

Key words: Co-Cd ferrite, Lattice parameter, Permeability

INTRODUCTION

Ferrites play a useful role in many magnetic applications. They have been extensively investigated and are the subject of great interest from both the fundamental and the applied research point of view. The important structural, electrical and magnetic properties of these spinels are responsible for their applications in various fields specially in electronics and electrical circuits. The soft ferrites belong to an important class of magnetic materials, because of their remarkable magnetic properties, particularly in radio frequency region and show physical flexibility, high electrical resistivity, mechanical hardness and chemical stability (Augustin et al. 1993). The magnetic properties of ferrites depend on chemical composition, cation distribution, porosity, grain size etc. In ferrites the cations occupy the tetrahedral (A) and octahedral (B) sites of the cubic spinel lattice and experience competing nearest neighbour ($J_{AB}$) and the next nearest neighbour ($J_{AA}$ and $J_{BB}$) interactions with $|J_{AB}| > |J_{BB}| > |J_{AA}|$. The magnetic properties of ferrites are strongly dependent on the type of magnetic ions residing on the A and B sites and the relative strengths of the inter ($J_{AB}$) and intrasublattice ($J_{BB}$, $J_{AA}$) interactions. When the $J_{AB}$ is

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much stronger than $J_{BB}$ and $J_{AA}$ interactions, the magnetic spins have a collinear structure in which the magnetic moments on the A sublattice are antiparallel to the moments on the B sublattice. But when $J_{BB}$ or $J_{AA}$ becomes comparable with $J_{AB}$, it may lead to non-collinear spin structure (Yafet and Kittel 1952). Physical properties of ferrites such as density, porosity, grain size etc. are dependent on the type and amount of additives, dopants, substituents as well as sintering temperature and time. CoFe$_2$O$_4$ is generally an almost inverse ferrite in which Co$^{2+}$ ions mainly occupies B-sites and Fe$^{3+}$ ions are distributed almost equally between A and B sites. CdFe$_2$O$_4$ and ZnFe$_2$O$_4$ are generally assumed to be normal spinel with all Fe$^{3+}$ ions on B-sites and all Cd$^{2+}$ and Zn$^{2+}$ ions on A-sites. Zinc substituted spinel ferrites showed good magnetic properties for technical applications and have been studied previously by many authors (Arulmurugan et al. 1952, Bayoumi 2007, Verma and Chatterijee 2006).

As Zn and Cd are both divalent and nonmagnetic, Cd substituted mixed ferrite is similarly interesting from applications point of view and has not been studied much in detail. The magnetic properties of ferrites such as permeability, magnetization, coercive field, Curie temperature are affected by composition as well as by the type of substitution, cation distribution and method of preparation. The partial replacement of nonmagnetic Cd ions in cobalt ferrite is expected to weaken the magnetic coupling resulting in decrease of Curie temperature. A few reports are available on mixed Co-Cd ferrites (Abdeen et al. 2002, Ghani et al. 1991). The aim of the present work is to investigate in detail the effects of substitution of Cd$^{2+}$ ions in place of Co$^{2+}$ ions covering a wide range of concentration on the structural and some magnetic properties of Co-Cd ferrites.

MATERIALS AND METHODS

A series of polycrystalline samples of mixed ferrites Co$_{1-x}$Cd$_x$Fe$_2$O$_4$ (with $x = 0.0$-0.5 in steps of 0.1) were prepared by the standard double sintering ceramic method at the Materials Science Division, Atomic Energy Center, Dhaka. In this method high purity oxides (99.99%) were weighted precisely according to their molecular weight. The prepared samples were sintered at 1050ºC for 3 hours with a microprocessor controlled muffle furnace. Phase analysis was done by X-ray diffraction using Phillips (PW 3040) X’pert PRO X-ray diffractometer. Temperature dependence of initial permeability of the toroid samples were measured with the Hewlett Packart impedance analyzer (HP4192A).

RESULTS AND DISCUSSION

A phase analysis using X-ray diffraction technique was performed to confirm the formation of single-phase cubic spinel structure as shown in Fig. 1 with no extra lines corresponding to any other crystallographic phase. The results obtained from XRD pattern for all the samples of Co$_{1-x}$Cd$_x$Fe$_2$O$_4$ with the (hkl) values corresponding to the diffraction peaks of different planes (111), (220), (311), (222), (400), (422), (511), and
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(440) which represent either odd or even indicating the samples are spinel cubic phase. The peaks are found to shift slightly towards the lower d-spacing values.

The accurate lattice parameter has been determined from the calculated lattice parameter, a corresponding to each plane of XRD pattern using Nelson-Riley function (Nelson and Riley 1945) 

\[ F(\theta) = \frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right) \]

where \( \theta \) is the Bragg’s angle, by extrapolating the lattice parameter values to \( F(\theta) = 0 \) or \( \theta = 90^\circ \).

Variation of lattice parameter ‘a’ as a function of Cd content (x) is shown in Fig. 2 and also in Table 1. From Fig. 2 it is observed that the lattice parameter increases linearly with the increase of Cd content obeying Vegard’s law (Vegard 1921).
This enhancement of lattice parameter is attributed to Cd$^{2+}$ with larger ionic radius (1.03 Å) which replaces Co$^{2+}$ (0.72 Å) having smaller ionic radii. It is well-known that the distribution of cations on the octahedral B-sites and tetrahedral A-sites determines to a great extent the physical, electrical and magnetic properties of ferrites.

There exists a correlation between the ionic radius and the lattice constant, the increase of the lattice constant is proportional to the increase of the ionic radius (Globus et al. 1977). It is observed that the bulk density is lower than the X-ray density. This may be due to the existence of pores, which were formed and developed during the sample preparation or sintering process. The X-ray density and bulk density increase significantly with increase in Cd content.

Fig. 3 shows the temperature dependence of initial permeability, $\mu'$ for the toroid shaped samples, which is measured at a constant frequency (100 kHz) of an AC signal by using Impedance Analyzer. It is observed that the initial permeability increases with the increase in Cd content while it falls abruptly close to the Curie point. This is because Cd in these compositions not only increases the magnetic moment and, but also lowers anisotropy, $K_1$ (Goldman 1999). On the other hand, permeability increases with the decrease of $K_1$ as the temperature increases according to the relation $\mu' \propto \frac{M^2 D}{\sqrt{K_1}}$ (Jain et al. 1976, Chikazumi 1966). When the anisotropy constant reaches to zero just below the Curie temperature, $\mu'$ attains its maximum value and then drops off sharply to minimum value at the Curie point. The sharpness of the permeability drops at the Curie point can be used as a measure of the degree of compositional homogeneity (Srivastava et al. 1976) which has also been confirmed by X-ray diffraction that no impurity phases could be detected. Fig. 4 a, b represents the variation of complex permeability and temperature derivatives of permeability as a function of temperature of the sample $x = 0.5$.

It is observed that the imaginary part of permeability $\mu''$ and temperature derivatives of permeability, $d\mu'/dT$ show peaks at temperature, $T$ which excellently matches with the temperature of sharp fall of permeability at $T = T_c$. The $T_c$ values are shown in Table 1. It is observed that Curie temperature linearly decreases with the increase of Cd content. The non-magnetic Cd$^{2+}$ ions that replaced the magnetic Fe$^{3+}$ ions on A-sites and thus the number of Fe$^{3+}$ decreases on A-sites. The decrease of $T_c$ is due to the weakening of the A-B exchange interaction as well as due to increase of lattice parameter with Cd$^{2+}$ content which increases the distance between the magnetic cations.

The initial permeability was found to vary with Cd content of the ferrites. Fig. 5 shows the real ($\mu'$) part of the complex permeability $\mu' = \mu' - i\mu''$ of different compositions sintered at $T_s = 1050°C$ for 3hours as a function of frequency $f$ measured at room temperature. The increase in $\mu'$ with Cd content is clearly evident.
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Fig. 3. Temperature dependence of permeability, $\mu'$ of $\text{Co}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ ferrites.

Fig. 4a, b. Determination of Curie temperature from the temperature dependence of $\mu'$, $\mu''$ and $d\mu'/dT$ as a function of temperature.

The permeability $\mu'$ increases monotonically upto $x = 0.6$ and thereafter decreases. It is quite obvious science the sample above $x > 0.6$ is paramagnetic at room temperature.

Table 1. Data of the lattice parameter ($a_0$), X-ray density ($d_x$), bulk density ($d_B$), porosity ($P\%$), Curie temperature ($T_c$), permeability ($\mu'$) at frequency 100 KHz, of $\text{Co}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ samples sintered at 1050°C/3hrs.

<table>
<thead>
<tr>
<th>Cd content (x)</th>
<th>$a_0$ (Å)</th>
<th>$d_x$ (g/cm$^3$)</th>
<th>$d_B$ (g/cm$^3$)</th>
<th>P%</th>
<th>$T_c$ (K)</th>
<th>$\mu'$ (100 KHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.379</td>
<td>5.28</td>
<td>4.59</td>
<td>14</td>
<td>728</td>
<td>51</td>
</tr>
<tr>
<td>0.1</td>
<td>8.409</td>
<td>5.35</td>
<td>4.87</td>
<td>8.8</td>
<td>683</td>
<td>65</td>
</tr>
<tr>
<td>0.2</td>
<td>8.438</td>
<td>5.41</td>
<td>5.02</td>
<td>7.2</td>
<td>613</td>
<td>86</td>
</tr>
<tr>
<td>0.3</td>
<td>8.468</td>
<td>5.47</td>
<td>5.08</td>
<td>7.3</td>
<td>563</td>
<td>111</td>
</tr>
<tr>
<td>0.4</td>
<td>8.498</td>
<td>5.53</td>
<td>5.09</td>
<td>8.0</td>
<td>491</td>
<td>149</td>
</tr>
<tr>
<td>0.5</td>
<td>8.529</td>
<td>5.59</td>
<td>5.16</td>
<td>7.6</td>
<td>413</td>
<td>226</td>
</tr>
<tr>
<td>0.6</td>
<td>8.557</td>
<td>5.65</td>
<td>5.17</td>
<td>8.6</td>
<td>353</td>
<td>334</td>
</tr>
</tbody>
</table>
From Fig. 5 it is noticed that the real component of permeability $\mu'$ is fairly constant with frequency up to certain frequency range and then falls rather rapidly to very low value at high frequency. The higher the permeability the lower the frequency at which $\mu'$ falls rather fast indicating ferromagnetic resonance where the imaginary part of the complex permeability, $\mu''$ is expected to rise sharply. This really confirms the Snoek’s limit (Snoek 1948).

![Graph showing frequency dependence of real part of permeability of Co$_{1-x}$Cd$_x$Fe$_2$O$_4$ ferrites sintered at 1050°C/3hours.]

**CONCLUSIONS**

Co$_{1-x}$Cd$_x$Fe$_2$O$_4$ samples were characterized by X-ray diffraction which confirms the single phase cubic spinel structure. Lattice parameter increases linearly with increasing Cd concentration. Bulk density increases monotonically with increasing Cd content signifying that Cd has a pronounced effect on the densification of the ferrites. The Curie temperatures decrease almost linearly with cadmium substitution due to weakening of A-B exchange interaction. From the observation of $\mu'$-f curves for all the samples $\mu'$ increases with increasing Cd$^{2+}$ content up to $x = 0.6$ and obeys the Snoek’s limit and thereafter decreases. It is quite obvious science the sample above $x > 0.6$ is paramagnetic at room temperature.

**ACKNOWLEDGMENTS**

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