Journal of Bangladesh Academy of Sciences, Vol. 33, No. 2, 159-166, 2009

TEMPERATURE AND FREQUENCY DEPENDENT PERMEABILITY OF SPINEL TYPE Li-Cd FERRITE

S. AKHTER*, D. P. PAUL, S. MANJURA HOQUE[1] AND M. A. HAKIM[1]

Department of Physics, University of Chittagong, Chittagong- 4331, Bangladesh

(Received revised copy : July 7, 2009)

ABSTRACT

A series of Li-Cd ferrite samples of composition $Li_{0.5-x/2}Cd_xBi_{0.02}Fe_{2.48-x/2}O_4$ for x = 0.0 to 0.7 were prepared by conventional double sintering ceramic technique. From temperature dependent permeability, μ′ at $T=T_C$ indicates that the samples have high homogeneity according to Globus *et al*. The Curie temperature, T_C is found to decrease with increasing Cd content. The sample with x=0.7 shows anomalous temperature dependent magnetic ordering. Initial permeability, μ′ and magnetic loss factor, tanδ have been investigated up to 13 MHz frequency range. Frequency dependent permeability increase except x = 0.7 with Cd content and also increase with sintering temperature. The magnetic loss factor is minimum at frequency around 1 MHz and rises sharply beyond that frequency.

Key words: Lithium ferrite, Curie temperature, Initial permeability, Loss factor.

INTRODUCTION

The study of spinel ferrite is of great importance from both the fundamental and the applied research points of view. Li-ferrites and mixed Li-ferrites are equally important materials as compared with Mn-Zn, Mg-Zn and Ni-Zn ferrites in the field of microwave technology [(1)]. High resistivity, low dielectric losses, mechanical toughness, chemical stability, squareness of hysteresis loop and moderate saturation magnetization along with superior high-temperature performance due to their high Curie temperature have made them very promising candidates for microwave devices [(2-6)]. The Li-Cd ferrite is considered as one of the important magnetic oxides with spinel structure because of their applications in microwave devices such as isolators, circulators, gyrators and phase-shifters. Due to their high frequency, high resistivity, low eddy current losses, excellent square-loop properties, a low cost replacement for the rare earth-iron granets, improved temperature performance and loss factors, Li-Cd ferrite plays an important role in such microwave applications. In this report, a study of the temperature and frequency dependent behavior of permeability of Cd substituted mixed Li-ferrite is undertaken.

EXPERIMENTAL

Sample preparation

The samples of stoichometric composition $Li_{0.5-x/2}Cd_xBi_{0.02}Fe_{2.48-x/2}O_4$ (for x =0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7) were prepared by conventional ceramic technique.

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* Author for correspondence: E-mail address: shahida212@yahoo.com Tel. No: +880 1716143980

[1] Materials Science Division, Atomic Energy Centre, Dhaka- 1000, Bangladesh

Small amount of Bi_2O_3 (melting point 825°C) was added to increase the densification at lower sintering temperature to minimize Li volatization during sintering as well as to improve magnetic and transport properties. Pure oxide powders of Li_2CO_3, CdO, Bi_2O_3, Fe_2O_3 were weighed precisely according to their molecular weight. Intimate mixing of the materials was carried out using agate mortar for 4 h and then ball milled in a planetary ball mill in ethyl alcohol media for 2 h with stainless steel balls of different diameters. The slurry was dried and the dried powder was pressed into disc shape. The disc shaped sample was pre-sintered at 850°C for 10 hours and then cooled to room temperature. The presintered powders were again grounded thoroughly and then applying a pressure of 2 ton/cm^2, pellets were made of 1.34 cm diameter and 0.69 cm thick, torroids of 1.2 cm outer diameter and 0.6 cm inner diameter. Final sintering of the samples was carried out at 950°C and 1000 °C for 4 hours to avoid the loss of lithium.

Measurement

The spinel phase formation of the ferrite system was confirmed by X-ray diffraction patterns obtained by using PHILIPS X Pert PRO X-ray diffractometer. The initial magnetic permeability, μ′ calculated from the inductance values measured by an Inductance Analyzer, (WAYNE KERR, model 3255B) was measured at room temperature on coil wound toroidal samples with an ac driving field of ~ 10^{-3} Oe up to 500 kHz. The sample was kept in a tubular furnace, which had good thermal insulation. The initial permeability was calculated using the relation $\mu' = L/L_0$, where L is the measured sample inductance and L_0 is the air core inductance using same dimensions of the toroid. The Curie temperature of the samples was determined from the temperature dependence of permeability. T_C of the sample x= 0.7 (paramagnetic at room temperature) was determined from the temperature dependence of low field (5 Oe) magnetization by using a SQUID magnetometer (MPMS XL 5).

The frequency characteristics of the Li-Cd ferrite samples i.e. initial permeability spectra were investigated using Impedance Analyzer (Hewlett Packed model no. 4192A). The complex permeability measurements on toroid-shaped specimen were carried out at room temperature on all samples in the frequency range 1 kHz-13 MHz.

RESULTS AND DISCUSSION

Fig.1 shows the XRD pattern of the synthesized Cd substituted mixed ferrite $Li_{0.5-x/2}Cd_xBi_{0.02}Fe_{2.48-x/2}O_4$ (for x =0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7). The X-ray lines show considerable broadening, indicating the fine particle nature of the ferrite. The observed peaks at (220), (311), (400), (422), (511), (440) and (533) confirmed the spinel structure of the samples. This indicates that the synthesized ferrite compositions are of single-phase cubic spinel since no ambiguous reflections other than the spinel structured are evidenced. This also demonstrates the homogeneity of the prepared samples.

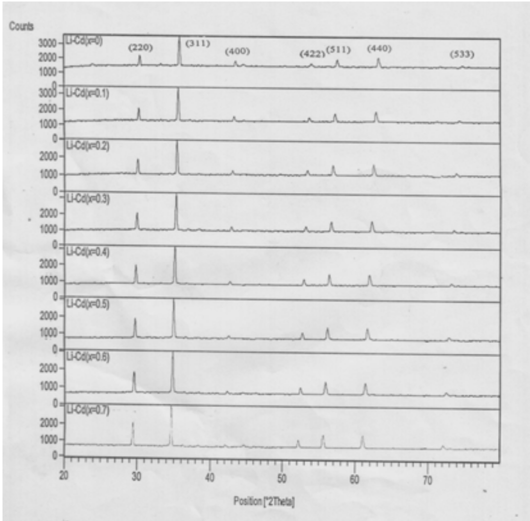


Fig.1. X-Ray Diffraction (XRD) pattern of $Li_{0.5-x/2}Cd_xBi_{0.02}Fe_{2.48-x/2}O_4$ ferrite amples.

Fig.2 shows the variation of x-ray or theoretical density and bulk density with Cd content of all the samples. It is observed that the X-ray density increased linearly with the increase of Cd concentration. The bulk density also increased almost linearly with the increase of Cd content. The result signifies that Cd as well as small addition of Bi_2O_3 has a pronounced effect on the densification of the Li-ferrite. The addition of Bi_2O_3 having lower melting point of 825°C which act as liquid phase sintering enhances the mass transfer and sintering kinetics enabling grain growth along with the densification. 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 the sintering process. The highest density 5.72 g/cc is obtained for the composition of x= 0.7.

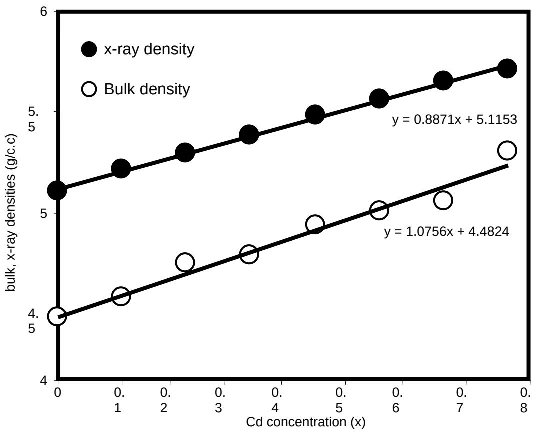


Fig. 2. Variation of Bulk densities and x-ray densities on Cd content.

Fig.3 shows the thermal variation of initial permeability, μ′ for x= 0.0 to 0.6. It is seen that μ′ gradually increased with temperature reaching a maximum value and then dropped sharply toward zero near the Curie temperature. The sharp decrease near Curie temperature suggests single-phase formation of the ferrites. This observation is supported by XRD studies, which do not show any impurity peaks. The compositional variation μ′ can be explained on the basis of Globus model[7]. According to this model μ′ is given by

$$\mu' = (M^2_s \, dm) / K_1 \quad (1)$$

where M_s is equal to saturation magnetization, dm to average grain diameter and K_1 to magneto-crystalline anisotropy constant. Addition of Cd^{2+} to Li-ferrite initially increases M_s, dm and reduces K_1. The anisotropy constant and saturation magnetization usually decreases with increase in temperature, due to thermal agitation, which disturbs the alignment of magnetic moment. However, decrease of anisotropy constant with temperature is much faster than the decrease of M_s. When the anisotropy constant reaches zero, μ′ attains its maximum value and then drops off to very low value. Thus, the effect of K_1 appears to be more significant in controlling the μ′ of the ferrite materials. Similar results have been reported by Bellad *et al.*[8, 9] in the case of Li-Cd ferrites and also Shaikh *et al.* [10] in Li-Mg ferrites.

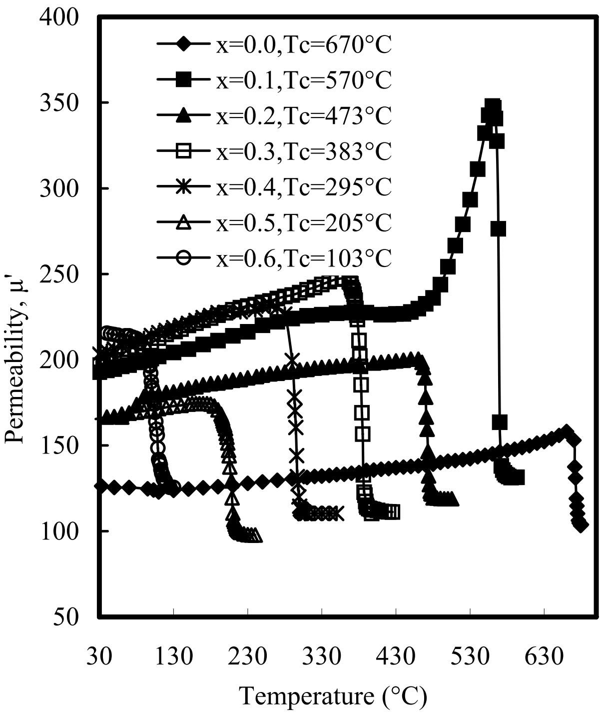


Fig. 3. Variation of Permeability with temperature

Fig. 4 shows the temperature dependence of magnetization with an applied field of 5 Oe from 20K-350K using a SQUID magnetometer for the samples with x=0.7. An increase of M starts at a temperature of 50 K and then falls on further lowering of temperature. The low temperature fall of magnetization may be ascribed to antiferromagnetic ordering of magnetic moments. Thus T_c = 271 K is a ferromagnetic ordering temperature, while T_N=30 K may be considered as antiferromagnetic ordering temperature. This experimental evidence shows that higher dilution of a ferrite with nonmagnetic ion like Cd displays complex magnetic ordering as the temperature decreases toward very low value.

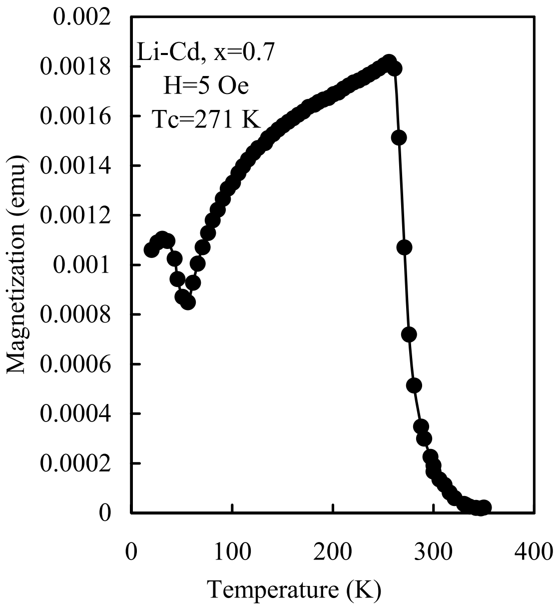


Fig. 4. Temperature dependence of low field magnetization for x=0.7

The Curie temperature of ferrite is a temperature at which the ferromagnetic material becomes paramagnetic. Curie temperature, T_C of the studied ferrite system have been determined from the μ′-T curve where the Hopkinson type of effect at the T_C has been observed with the manifestation of a sharp fall of permeability. The Curie temperature mainly depends upon the strength of A-B exchange interaction. Fig. 5 shows the variation of T_C with Cd content. T_C shows the decreasing trend with increasing Cd content. The Curie temperature for the sample with Cd=0 is 670^0C while for the sample Cd=0.6 it is 103^0C. However for the sample with Cd=0.7, Curie temperature has been found below the room temperature (-2^0C) [Fig.4] as it is paramagnetic. Similar trend in T_C is observed in case of Li-Zn ferrites [(11)] and Li-Cd ferrites [(8)]. The change in Curie temperature has been ascribed to a decrease of the A-B exchange interaction strength due to the change of the iron distribution between A and B sites when non-magnetic Cd is substituted. The reason for the decrease is that when non-magnetic Cd is substituted then the magnetization of A-sublattice is so much diluted that the A-B lattice interaction remains no longer stronger and thereby B-B sublattice interaction becomes strong, which in turn disturbs the parallel arrangement of spin magnetic moments on the B-site.

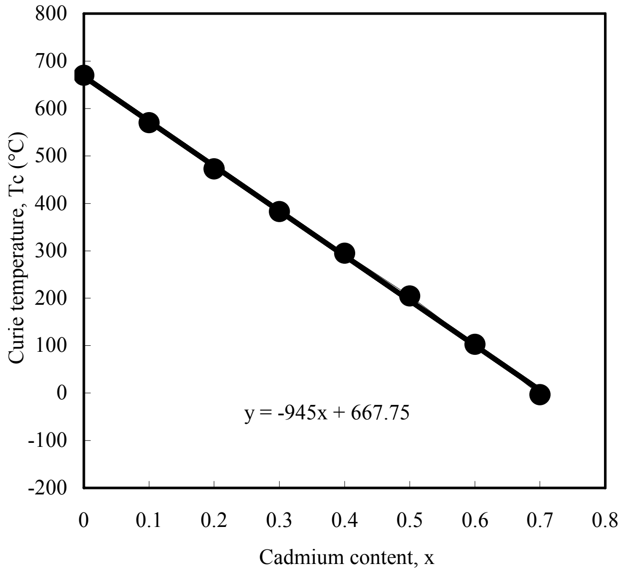


Fig. 5. Variation of Curie temperature with Cd contents.

Fig 6(a, b) and 7 (a, b) show the frequency dependence real and imaginary permeability spectra of $Li_{0.5-x/2}Cd_xBi_{0.02}Fe_{2.48-x/2}O_4$ samples sintered at 950^0C and 1000^0C, respectively. It is clearly evident from Fig. 6 (a) and 7 (a) that with the increasing of Cd content, x the permeability μ′ increases monotonically except for x=0.7. The sample with x=0.7 is paramagnetic at room temperature.

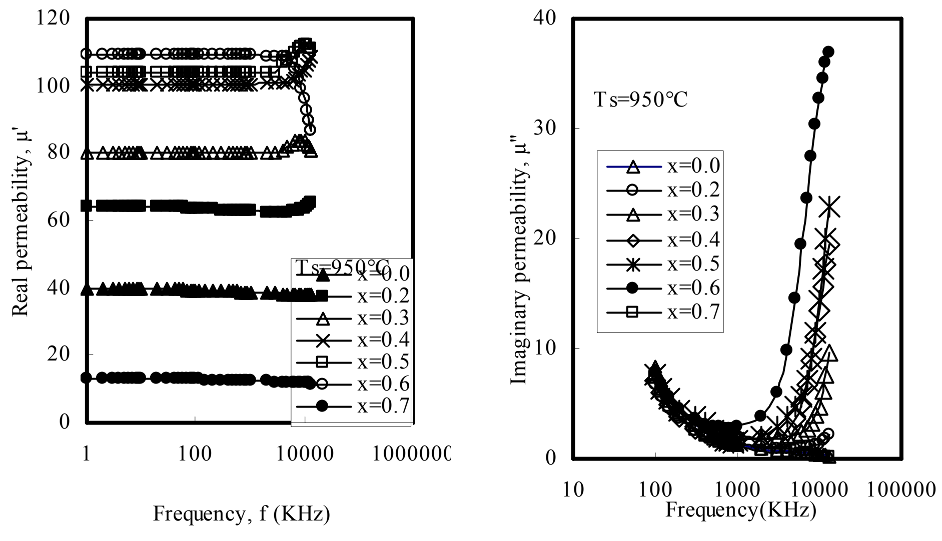
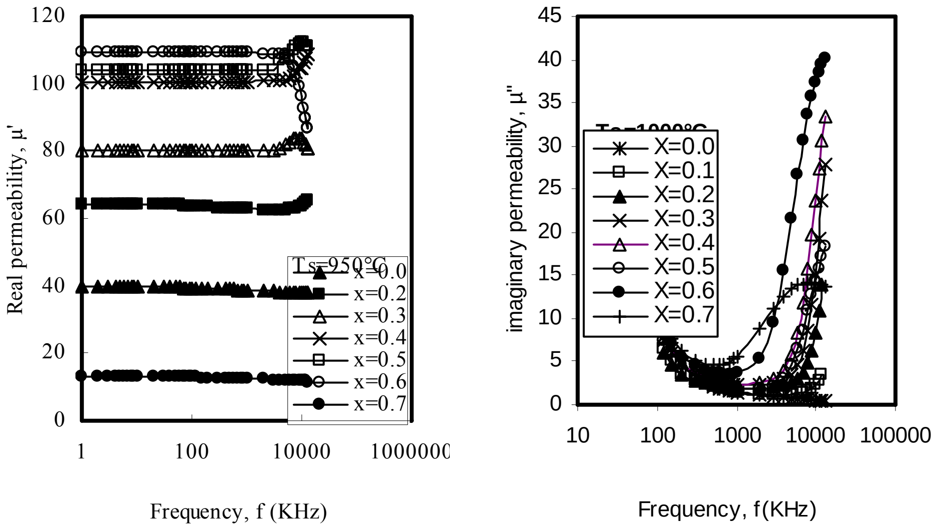


Fig. 6. (a) Real and (b) Imaginary permeability spectra for $Li_{0.5-x/2}Cd_xBi_{0.02}Fe_{2.48-x/2}O_4$ samples sintered at 950^0C.

The initial permeability μ' remained almost constant for x=0.0 upto 13 MHz while for x = 0.1 to 0.6 it is almost stable upto 5-7 MHz and then began to decrease at higher frequency. Similar pattern was observed in case Li-Zn ferrites by T. Nakamura (12). Monotonic increase in permeability with increasing Cd content may be attributed to the increase in grain size according to Globus (7) as well as increase in sintered density. The increase of μ' with the increase of Cd content results in a shift of the resonance frequency to lower frequency range according to Snoek's [13] relation, μf_r = constant, where f_r is the resonance frequency. Dispersion or resonance could not be observed in our studied samples with lesser content of Cd as well as sintered at lower temperature since our measurement facility could not be extended beyond 13 MHz. Again this increasing permeability with increasing Cd content is connected with increased density, larger grain size and possibly reduction of anisotropy energy with the addition of nonmagnetic Cd. Moreover, as the sintering temperature increases dispersion of μ' also shifts to the lower frequency range as a result of increasing density and grain size, as proposed by Nakamura (14).

Fig. 6 (b) and Fig. 7 (b) represent the imaginary part of initial permeability, μ'' (loss component) of the samples sintered at 950°C and 1000°C respectively. It is observed from the figures that μ'' increases with increasing frequency and takes a broad maximum at a certain frequency. This feature is well known as the natural resonance. At the natural resonance, the imaginary permeability had a maximum value, shifted toward high frequency. The magnetic loss factor increased as the square of the frequency. Highest value of loss component of the complex permeability was observed for x=0.6 in both sintering temperature in the range of frequency under investigation. Similar trends were reported in the case of Ni-Zn ferrite by Mahmud *et al.*(15).



(a) (b)

Fig. 7. (a) Real and (b) Imaginary permeability spectra for $Li_{0.5-x/2}Cd_xBi_{0.02}Fe_{2.48-x/2}O_4$ samples sintered at 1000°C.

CONCLUSION

The sharp fall of permeability at Curie temperature indicates that the samples have high homogeneity according to Globus. Samples of x=0.7 is paramagnetic at room temperature which undergoes ferromagnetic ordering at -2^0C. A linear decrease of Curie temperature with Cd content has been obtained and this is attributed to the weakening of J_{AB} exchange interaction. Initial permeability increases continuously with increase of Cd content as well as sintering temperature. Again this increasing permeability with increasing Cd content is connected with increased density, grain size and reduction of anisotropy energy with the addition of nonmagnetic Cd. Loss factor is minimum at around 1 MHz frequency and rises sharply after 1 MHz can be associated with resonance phenomenon occurring in the domains passing through a maximum at a frequency known as resonance frequency.

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