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EFFECT OF SUBSTITUTION OF Al FOR Fe ON THE MAGNETIC PHASE TRANSI-TION AND INITIAL PERMEABILITY OF Zn-Co FERRITES

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ABSTRACT

The spinel oxides $Zn_{0.4}Co_{0.6}Al_xFe_{2-x}O_4$ (x=0.0, 0.25, 0.50, 0.75 & 1.0) have been synthesized in the solid state sintering process in air. X-ray diffraction measurements have been carried out in order to check the phase which showed single phase spinel structure for all the samples. Initial permeability, frequency dependence of the complex permeability sintered at different temperatures has been measured on toroidal samples in the frequency range 1-500 KHz at room temperature. Temperature dependence of the complex permeability has been measured from room temperature to 435°C. Transition temperatures (T_C) have been estimated from the temperature dependence of the permeability spectra for all the samples. It is found that the values of transition temperatures (T_C) and initial permeability (μ_i) decrease with increasing substitution of Al content in the system. The values of T_C obtained from permeability spectra are compared with those obtained from neutron diffraction data and magnetization measurements.

1. INTRODUCTION

Ferrites are considered to be the most suitable material for electronic devices used at high frequency and is quite unique as a high frequency material [1,2]. One special advantage of ferrites is that its composition can conveniently be altered in order to tailor its magnetic properties which suits a particular application. Sintering temperature is another variable which can be controlled to alter the density, grain size and voids affecting the magnetization process. Initial permeability of polycrystalline ferrite is an important factor in the application of electronic devices. In particular, the frequency dispersion of the complex permeability $\mu^* = \mu' - i\mu''$ determines high frequency characteristics of these materials. Many experimental and theoretical investigations on the frequency dispersion in polycrystalline ferrite have been performed [3-8]. The results of these investigations show much variations because of the subtle dependence of initial permeability on sintering temperature which affects the grain size, density and presence of voids in the polycrystalline specimens [9-11]. The permeability of polycrystalline ferrites is guided by two basic mechanisms such as domain rotation and domain wall movement and in the case of frequency response spin resonance it plays an important role [1,7]. Usually for grain size smaller than 6 microns domain rotations is the dominating factor but for bigger grain sizes domain wall movements is also important. The domain wall movement is mostly hindered by the presence of pores which introduces demagnetizing affect at the boundaries. The temperature dependence of permeability is important because it gives information about the dynamics of domain wall movement and determines the optimum temperature range for the technical applications of the materials. As the temperature increases it becomes easier for the domain walls to overcome the local potential barriers. This process continues upto the Curie temperature beyond which the cooperative magnetism ceases to exist. Temperature variation of permeability, as an important finding, has been carried out by others. M. Guyot et al. studied temperature variation of the permeability in polycrystalline Ni-Zn ferrite in wide frequency and temperature ranges [12].

The temperature dependence of permeability gives a consistent picture for all the compositions and has been used for estimating Curie temperatures at which a sharp change of permeability is observed. These results have been compared with those obtained by neutron diffraction (ND) technique and magnetization measurement using VSM. Although the three methods we have used for estimating Curie temperature are related to different processes where permeability gives a measure of the domain wall movements, magnetization measurement by VSM gives the average magnetization of the system and ND technique gives the behavior of the magnetic moments of the individual lattice sites, the results are quite in agreement. This shows that our assumptions involved in all the processes are consistent.

In the present paper, we report the frequency dependence of permeability and effect of Al substitution on the transition temperature of the spinel samples $Zn_{0.4}Co_{0.6}Al_xFe_{2-x}O_4$ (x=0.0, 0.25, 0.50, 0.75 & 1.0) prepared in the solid state sintering method. The estimated Curie temperatures have been compared with those obtained by neutron diffraction (ND) technique and magnetization measurement using VSM.

2. EXPERIMENTAL DETAILS

2.1 Sample preparation and characterization:

Five samples of the ferrite series $Zn_{0.4}Co_{0.6}Al_xFe_{2-x}O_4$ with x=0.0, 0.25, 0.50, 0.75 and 1.0 were prepared by the solid state double sintering method at the Institute of Nuclear Science and Technology (INST), Bangladesh Atomic Energy Commission, Dhaka, Bangladesh. For each of the samples, high purity oxides (99.99%) of ZnO, Co_3O_4, Al_2O_3 and Fe_2O_3 were taken in exact stoichiometric proportions and then mixed intimately by ball milling for about 6 hours in a stainless steel ball mill. For fine mixing of the ingredients, a small amount of distilled water was used as a milling fluid. The mixtures were then dried in air in an oven. After drying, the mixtures were heated in alumina crucible at 800ºC for 6 hours following the furnace cooling in air. A small amount of polyvinyl alcohol (PVA) was added as a binder to this dried mixture and was intimately mixed in agate mortar. The samples were then pressed into small pellets in a hydraulic press. The pellets were then heated at a temperature of 1000ºC in a furnace for 8 hours followed by slow cooling (~ 4ºC/min.). After this pre-sintering operation, the pellets were further powdered. The milling, drying, pressing and pre-sintering operations were repeated once. The final sintering of the materials was done in air at 1300ºC for 6 hours and subsequently cooled to room temperature in a furnace at a slow rate (~ 4ºC/min.). The heating schedule for the final sintering is shown in Figure 1. X-ray powder diffraction patterns for all the samples were recorded in order to check their quality and phase purity using a X-ray diffractometer (Shimadzu XRD-6000) with CuK_{α} radiation (λ =1.540598 Å). The diffraction patterns showed sharp peaks corresponding to the single phased spinel structure for all the samples. One such X-ray diffraction pattern for the sample with x=0.50 is shown in Figure 2.

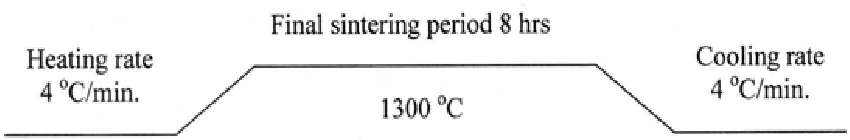

Figure 1. The heating schedule employed for the final sintering.

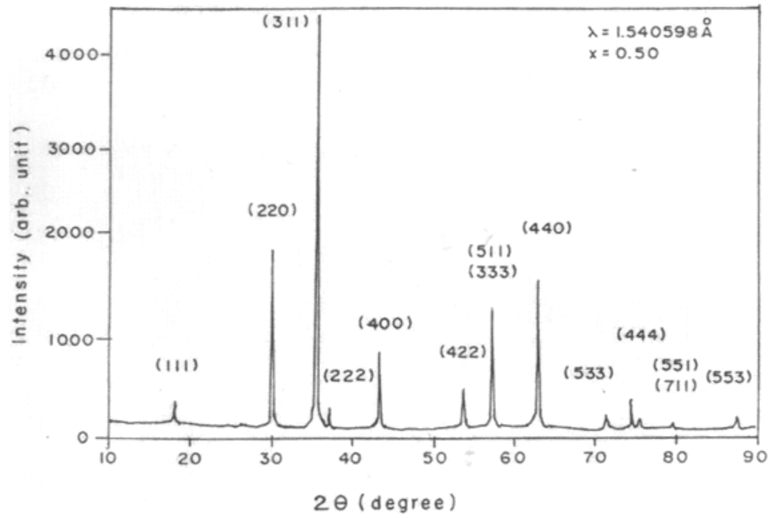

Figure 2. X-ray diffraction pattern for the spinel oxide $Zn_{0.4}Co_{0.6}Al_xFe_{2-x}O_4$ with x=0.5 at room temperature showing a single phase cubic spinel structure.

2.2 Complex permeability measurements:

The pre-sintered powders were pressed into ring shape sample using metal dies for the measurement of complex permeability. The prepared rings had an outer diameter 10.0 mm, an inner diameter 5.0 mm and height 4.0 mm. The rings were then sintered at various temperatures in the range 1200 to 1300°C at an interval of 50°C in air for 6 hours. The complex permeability as a function of frequency for the ferrite system $Zn_{0.4}Co_{0.6}Al_xFe_{2-x}O_4$ (x=0.0, 0.25, 0.50, 0.75 and 1.0) were measured for the samples sintered at temperatures 1200°C, 1250°C and 1300°C by changing the frequency from 1 KHz to 500 KHz at room temperature with an impedance analyzer at Atomic Energy Centre, Dhaka (AECD). The temperature dependence of the complex permeability was measured in order to determine the transition temperatures (T_C) for all the samples.

3. RESULTS AND DISCUSSION

The complex permeability of the ferrite system $Zn_{0.4}Co_{0.6}Al_xFe_{2-x}O_4$ with composition x=0.0, 0.25, 0.50, 0.75 & 1.0 have been measured at room temperature in the frequency range 1KHz to 500KHz. The samples were annealed at temperatures 1200°C, 1250°C and 1300°C. The frequency dependence of the real part of complex permeability of the samples is shown in Figures 3-5. The samples sintered at 1200°C and 1250°C showed fluctuating behavior in the permeability spectra below 5KHz for all the compositions and the fluctuation decreases with increasing the sintering temperature as it is evident in Figures 3 and 4. However, the samples sintered at 1300°C showed very stable permeability values as a function of frequency down to 1KHz given in Figure 5. The apparent anomaly observed at the low frequency region in the specimens sintered at relatively low temperatures can be attributed to the non uniformity of the grain sizes and the distributions of voids in the specimens. As a representative result the initial permeability of the sample measured at 100 KHz for three different sintering temperatures are shown in Table 1. The values of initial permeability decrease with increasing sintering temperature as evident from Table 1, which is in contrast with the prediction by Globus [8]. This decrease may be associated with some small amount of second phase, not identified by XRD, which might have constrained the domain wall motion by pinning. The initial permeability is found to be almost independent of Al content in the system. However, permeability is affected by local anisotropy, magnetization and grain size in a complex way. Since these parameters have not been determined, a detailed explanation of the variation of permeability for its temperature, frequency and composition is not possible. However, the empirical results are useful in choosing the most suitable specimens.

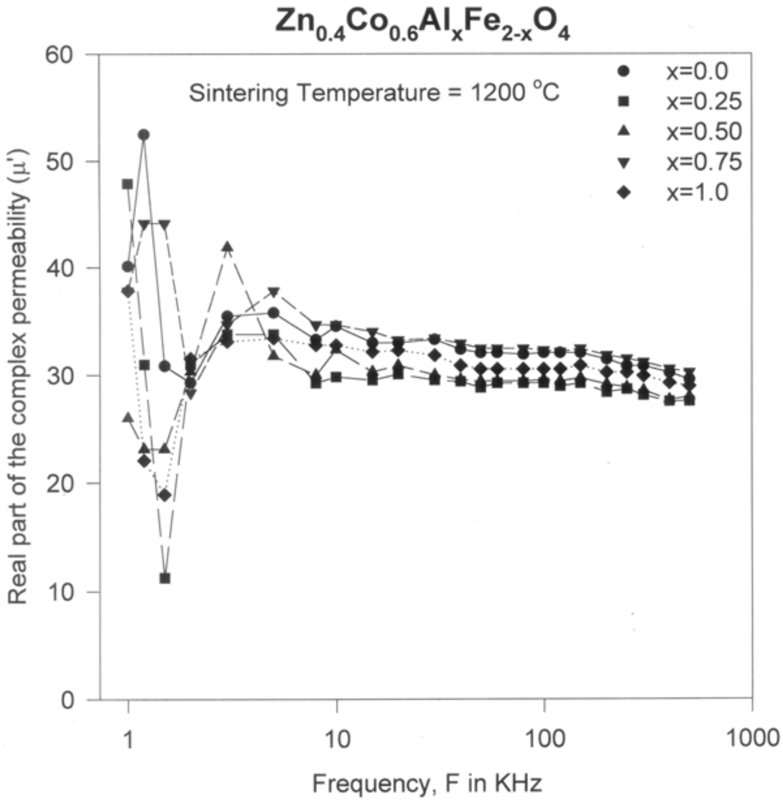

Figure 3. Frequency dependence of the real part of complex permeability for different x values sintered at temperature 1200°C.

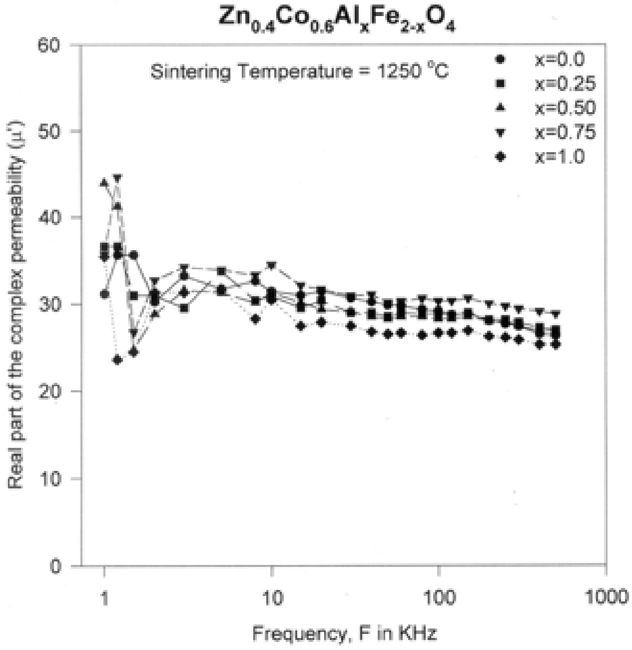

Figure 4. Frequency dependence of the real part of complex permeability for different x values sintered at temperature 1250°C.

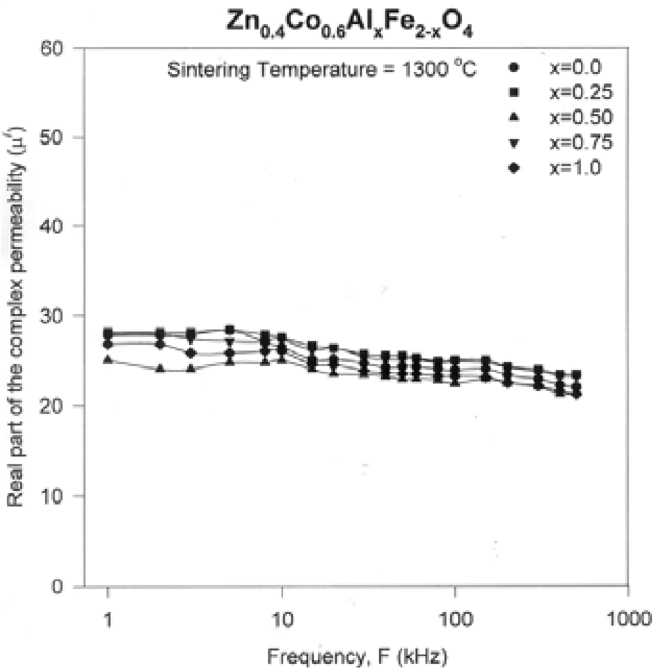

Figure 5. Frequency dependence of the real part of complex permeability for different x values sintered at temperature 1300°C.

Table 1
Initial permeability at 100 KHz for different sintering temperature

Al content (x)	Sintering Temperature		
	1200°C	1250°C	1300°C

0.0	32.099	29.228	24.031
0.25	29.296	28.873	25.133
0.50	29.624	28.297	22.537
0.75	32.334	30.357	25.000
1.0	30.599	26.703	23.349

Figure 6 shows the temperature dependence of the complex permeability of the spinel system $Zn_{0.4}Co_{0.6}Al_xFe_{2-x}O_4$ at a frequency level 50KHz for the samples sintered at 1300°C. Transition temperatures (T_C) estimated from permeability versus temperature curves are found to decrease almost linearly with increasing Al content and may be attributed to the decrease of A-B exchange interaction since Al is found to occupy octahedral or B sublattice which is confirmed by our previous neutron data [10]. The values of T_C obtained from the permeability spectra are compared with those obtained from the neutron diffraction data and magnetization measurements [13,14] in Table 2. The variation of the transition temperature (T_C) with composition (x) in the spinel system $Zn_{0.4}Co_{0.6}Al_xFe_{2-x}O_4$ at different measuring methods is presented in Figure 7. In spite of the differences of the measuring methods there is good consistency between the results for the whole series. The slight variations of T_C values may be due to different measuring methods and are within the acceptable limits.

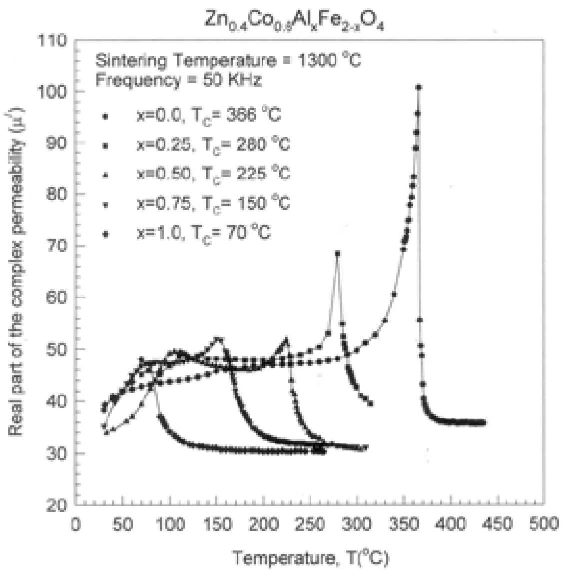

Figure 6. Temperature dependence of the complex permeability for different x values in the spinel oxide $Zn_{0.4}Co_{0.6}Al_xFe_{2-x}O_4$.

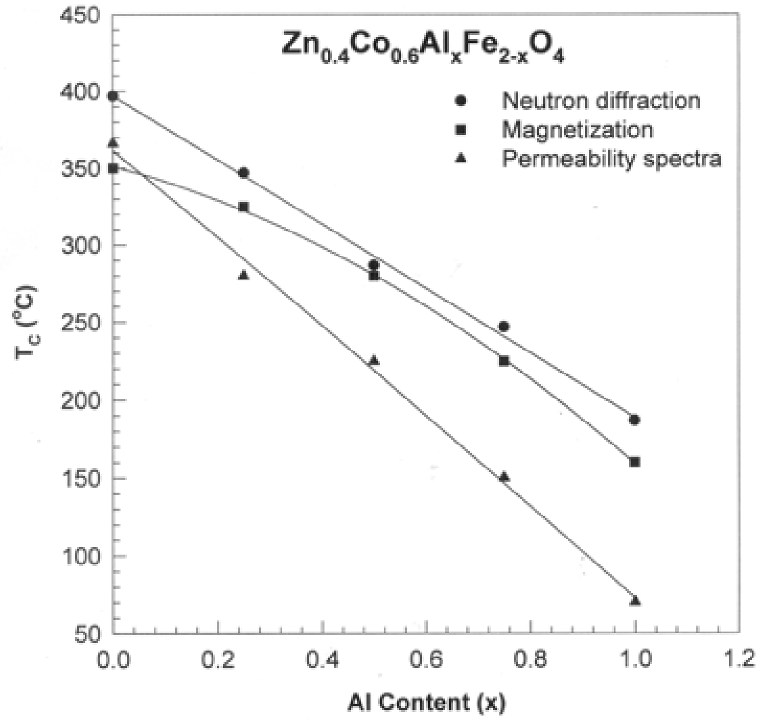

Figure 7. Variation of transition temperature (T_C) with composition (x) in the spinel system $Zn_{0.4}Co_{0.6}Al_xFe_{2-x}O_4$ at different measuring methods.

Table 2
Comparison of transition temperatures measured by different methods for different x values in the spinel system $Zn_{0.4}Co_{0.6}Al_xFe_{2-x}O_4$

Al content (x)	T_C (°C) Permeability spectra	T_C (°C) Magnetization	T_C (°C) Neutron diffraction
0.0	366	350	397
0.25	280	325	347
0.50	225	280	287
0.75	150	225	247
1.0	70	160	187

4. CONCLUSIONS

The addition of different amount of Al in Zn-Co ferrite showed that the effect of adding Al on permeability is not very significant specially when the sintering temperature is quite high (1300°C). For this sintering temperature the permeability is found to be quite stable and almost constant for different frequencies and also for different compositions. Although the permeability is not very high for these samples, when annealed at 1300°C, the steady value of the permeability in respect of frequency is a desired characteristic for soft magnetic materials. The Curie temperature (T_C) as determined by permeability spectra, neutron diffraction and magnetization methods showed very good consistency for all the different compositions where there is a systematic decrease of T_C with increasing Al content in the system. This reinforces the reliability of the methods used for Curie temperature determination. The detailed explanation of the results requires further investigation of secondary effects like magnetostriction and anisotropy & the structural parameters like grain size distribution and voids.

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