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Magnetic Properties of Zn substituted Copper Ferrites

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Abstract

The magnetic properties were studied for Cu_{1-x} $Zn_xFe_2O_4$ ferrites for x = 0, 0.4, prepared by standard double sintering ceramic technique sintered at different sintering temperatures and characterized by X-Ray diffraction (XRD) technique. The single-phase cubic spinel structure of all the samples has been confirmed from X-ray diffraction analysis. Magnetic properties have been measured as a function of field using Vibrating Sample Magnetometer (VSM). It is well known that the distribution of cations in the tetrahedral A-sites and octahedral B-sites determines to a great extent the magnetic properties of ferrites. Curie temperatures T_C of the studied ferrite system has been determined from the μ'-T curves where Hopkinson type effect at the T_C has been observed with the manifestation of sharp fall of permeability. The sharp decrease of μ´ at $T=T_C$ indicates that the samples have high homogeneity according to Globus. Curie temperature is found to decrease with Zn content and with increasing sintering temperature. The saturation magnetization (M_S) is found to increase with Zn content. The increase of magnetization is due to the dilution of magnetic moment of A sub-lattice by the substitution of non-magnetic Zn ions.

I. Introduction

Spinel ferrites constitute a special branch of ferrimagnetics. Ferrites are certain double oxide of iron and another metal which have two unequal sublattices and are ordered anti-parallel to each other. Each sublattice exhibits spontaneous magnetization at room temperature, like the ferrimagnetics. Spinel ferrites and their properties has been the subject of many recent investigations [1]. They have many applications in high frequency devices and play a useful role in technological and magnetic applications because of their high electrical resistivity and consequently low magnetic losses over a wide range of frequency. The magnetic properties of the spinel ferrites are governed by the type of magnetic ions residing on the A- and B-sites and the relative strengths of the inter-(J_{AB}) and intra-sublattice (J_{AA}, J_{BB}) exchange interactions. When the A-B inter-sublattice interactions are much stronger than the A-A and B-B intra-sublattice interactions, the spins have a collinear structure in which moments on the A-sites are anti-parallel to the moments on the B-sites. The advantage of the mixed spinel is that all interactions are well defined near-neighbour antiferromagnetic, with $|J_{AB}| \gg |J_{BB}| > |J_{AA}|$.

The polycrystalline Cu-Zn ferrite could be considered as the most versatile ferrites, due to their high resistivity and low eddy current losses. Generally Cu-Zn ferrites were commercially used in radio frequency circuits, transformer cores, antennas and read /write heads for high-speed digital tape and in high quality filters [2, 3]. In the present investigation, the magnetic properties of Cu-Zn ferrites have been studied.

Experimental Method

Samples of the Cu-Zn ferrites having the chemical formula $Cu_{1-x}Zn_xFe_2O_4$ (x = 0, 0.4) were prepared by the standard double sintering ceramic technique using high purity oxides of CuO, ZnO and Fe_2O_3. The reagent powders were weighed precisely according to their molecular weight. The oxides were thoroughly mixed in an agate mortar, heat-treated and compacted in the form of pellets and toroids. During this preparation, pre-sintering at 900°C for 5hours and powdering of the formed products was followed by final sintering at 1050°C, 1150°C for 3hours and 1200°C for 2 hours. The surfaces of all the samples were polished in order to remove any oxide layer during the process of sintering.

Phase analysis was done by X-ray diffraction using Phillips (PW3040) X'Pert Pro X-ray diffractometer. X-ray diffraction patterns confirmed the spinel phase for all the samples. The initial permeability as a function of temperature at 100kHz was measured in the temperature range from room temperature to 460°C for x = 0 and to 260°C for x = 0.4. For temperature dependence of initial permeability (μ'), the toroids were wound with windings of 5 turns. The initial permeability was calculated using $\mu' = L / L_O$, where L is the measured sample inductance and L_O is the air core inductance using the dimensions of the toroid. The magnetization measurements of the samples were done by a vibrating sample magnetometer (Model VSM-02, Hirstlab, UK) at room temperature as a function of field. The experiments were done at Materials Science Divisions, Atomic Energy Center, Dhaka.

Results and Discussion

The X-ray diffraction patterns of the samples sintered at different sintering temperatures show that all the diffraction lines correspond to the spinel cubic structure. Nine fundamental reflections from the planes of (220), (311), (222), (400), (422), (511), (440), (531) and (620) characterizing the spinel ferrites are strongly observed. Two peaks between (311) & (222) and (222) & (400) could not be indexed as spinel which are probably due to some microscopic impurity unknown phase. The sharp peak reveals that the samples are in good crystalline form. Typical diffraction patterns indicating (hkl) values of each peak corresponding to the samples x = 0, 0.4 sintered at 1150°C are shown in Fig-1.

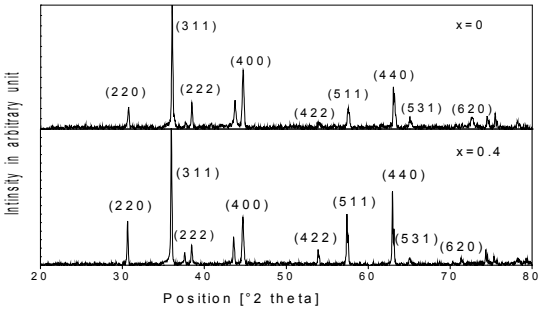

Fig. 1. X-ray diffraction (XRD) pattern of $Cu_{1-x}Zn_xFe_2O_4$ ferrite samples sintered at 1150°C temperature for 3 hours.

For technical applications, temperature dependence of initial permeability is important. Curie temperature (T_C) of all the Cu-Zn ferrite samples has been determined from the initial permeability (μ') versus temperature (T) graph. The μ' – T curves of the $Cu_{1-x}Zn_xFe_2O_4$ samples are shown in fig-2 at different sintering temperatures.

It can be seen that μ' increases with increasing sintering temperature attaining a maximum value just below T_C. The maximum value of μ' just below the Curie temperature (T_C), is a manifestation of Hopkinson peak attributed to the minimization of magnetocrystalline anisotropy energy with temperature. Beyond this peak value of μ', permeability sharply falls to very low value indicating the ferro-paramagnetic phase transition (T_C). T_C has been taken as the temperature at which a sharp fall of permeability is observed i.e. where dμ' / dT attains its maximum value. It is observed that the permeability falls sharply when the magnetic state of the ferrite samples changes and after that the permeability becomes smaller i.e. the paramagnetic character. We can precisely say that the transition takes place from ferrimagnetic to paramagnetic at the Neel temperature T_N. The sharpness of fall of permeability indicates the homogeneity and the single phase of the studied samples, which have also been confirmed by X-ray diffraction by our previous XRD experiment [4, 5]. Measurement of the initial permeability as a function of temperature can therefore be used as a material characterization of ferrite materials.

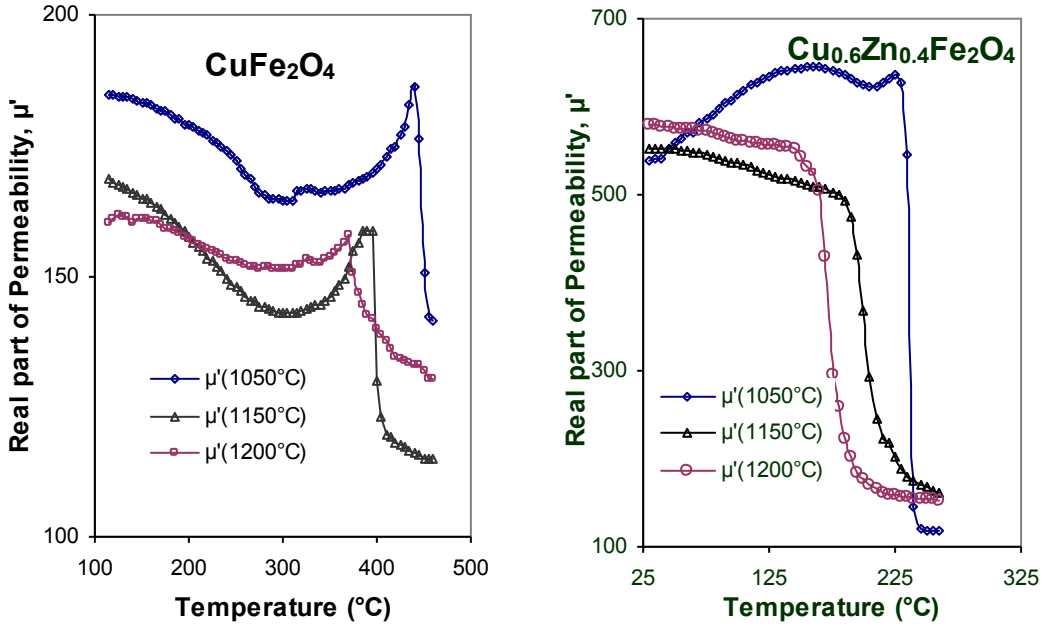

Fig. 2. Permeability vs temperature of $Cu_{1-x}Zn_xFe_2O_4$ samples sintered at different sintering temperatures

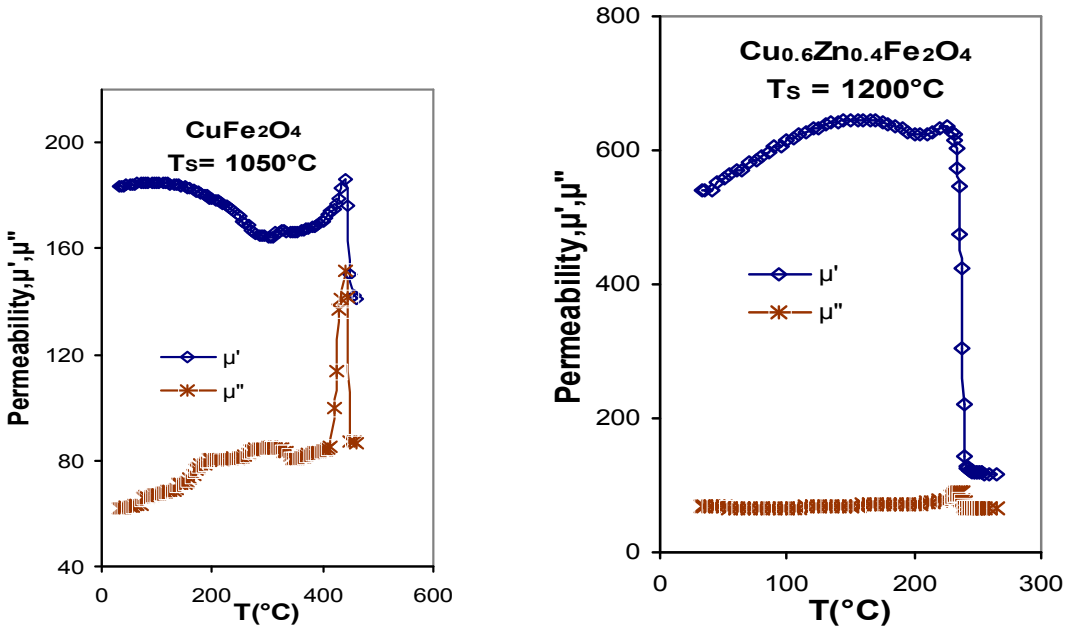

Fig. 3. Temperature dependence of the real and imaginary part of initial permeability of $Cu_{1-x}Zn_xFe_2O_4$ for x = 0 sintered at 1050°C and for x = 0.4 sintered at 1200°C.

Fig-3 shows the real and imaginary part (magnetic loss component) of the complex permeability as dependent on temperature. At the Curie temperature, where complete spin disorder takes place, corresponds to maximum of imaginary part of the permeability and sharp fall of the real part of permeability towards zero. Therefore, for accurate determination of Curie temperature, the maxima of imaginary part and the corresponding sharp fall of the real part of the permeability towards zero is very essential, simultaneously to determine T_C accurately. For all the samples at different sintering temperatures, Curie temperatures have been determined, following the above mentioned principle as shown in Fig-2, where the imaginary component of the permeability μ″ has not been shown for the clarity of the graph.

Curie temperature of a ferrite is a temperature at which the materials become paramagnetic. It is observed that the decrease of T_C with Zn content may be explained by a modification of the A-B exchange interaction strength due to the change of the Fe^{3+} distribution between A and B sites when non-magnetic Zn is substituted for Cu. The basic magnetic properties of $CuFe_2O_4$ system originate from Cu^{2+} ions only in the octahedral B-sites since Fe^{3+} ions are distributed equally in both the A and B-site. The substituted Zn^{2+} preferentially occupies the tetrahedral A-site replacing an equal amount of Fe^{3+} to octahedral B-sites. In such a situation J_{AA} becomes weaker resulting in the weakening of the strength of J_{AB} exchange interactions which reduces the Curie temperature, T_C.

Fig-2 also shows that T_C decrease with increasing sintering temperature for both the samples. This may be explained as due to the fact that the volatile nature of CuO at 1026°C [6] which may have some effect on the compositional gradients of the ferrite samples and these compositional gradients may have influence on the reduction of T_C. Another factor which may affects the T_C is the existence of the Cu^{1+} ions in the samples [7] i.e. Cu^{1+} ions are non-magnetic due to completely filled 3d shells which might be migrated to tetrahedral (A) site reducing the AB exchange interaction strength and accounts for lowering of T_C. It is observed that when sintering temperature is 1050°C then the T_C of pure $CuFe_2O_4$ is 440°C which is very close to reported value of 455°C [8].

Magnetization measurements for the system $Cu_{1-x}Zn_xFe_2O_4$ where carried out using the vibrating sample magnetometer (VSM) at room temperature as a function of field to reach saturation values and results are plotted in fig-4. The magnetization of all the samples is saturated. It is observed that the saturation magnetization increases with Zn content. The saturation magnetization, M_S value of a sample has been taken the magnetization at high field where magnetization is independent of magnetic field. Since the resultant magnetization is the difference between the B and A sub-lattice magnetization according to equation $M = M_B - M_A$. It is obvious that increase of net magnetization is expected on dilution of the A sub-lattice magnetization due to occupation of A-site by non-magnetic Zn content as well as enhancement of B sub-lattice magnetization due to the introduction of Fe^{3+} ions having $5\mu_B$ migrated from A-site to B-site due to the occupation of Zn ion on the A-site [9]. This rise of magnetization can be explained on the basis of Neel's two sub-lattice model. The saturation magnetization of $CuFe_2O_4$ is found to be 28.59emu/gm at room temperature compared with the reported value of 25emu/gm at 20°C [8].

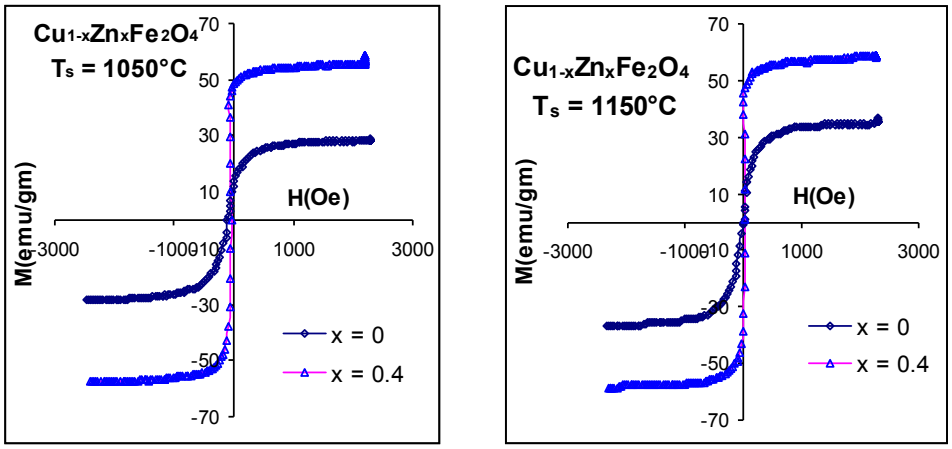

Fig. 4. Magnetization curve measured at room temperature as a function of field of $Cu_{1-x}Zn_xFe_2O_4$ ferrites sintered at 1050°C and 1150°C for 3 hours.

It is observed that the sintering temperature has great influence on pure $CuFe_2O_4$ and saturation magnetization increases with increasing sintering temperature. This may be explained as follows: CuO reduces to Cu_2O at 1026°C [6]. Cu^{1+} ions are non-magnetic and may be migrated to the tetrahedral (A) site replacing an equal amount of Fe^{3+} ions to the octahedral (B) sites [7]. This increases the magnetization of the B-site. As a result overall magnetization of the sample with x = 0 increases according to the equation $M = M_A - M_B$. It is observed that the saturation magnetization for the sample x = 0.4 is almost independent of sintering temperature.

The experimental magnetic moment in Bohr magneton has been calculated from the measured saturation magnetization value per unit mass using the formula.

$$n_B = \frac{M'M_S}{N\mu_B} \quad (1)$$

where M_S is the saturation magnetization, M is the molecular weight. n_B the magnetic moment in Bohr magneton, μ_B, N the Avogadro's number. A theoretical calculation of magnetic moment in Bohr magneton of $[Cu_{1-x}Zn_xFe_2O_4]$ system is demonstrated in Table-1. The experimental values of magnetic moment for samples are also given in table-1 for different sintering temperatures. The theoretical values of magnetic moment for x = 0.4 samples depart from the experimental values. This ferrite system exhibits the Yafet-Kittel (Y-K) type of magnetic structure [10]. When the Zn content on A-site is higher, the Fe^{3+} ions on the A-sites are no longer able to align all the moments of the B-site ions anti-parallel to themselves since this is opposed by the negative B-B exchange interaction. The B sub-lattice will then divide itself into sub-lattices, the magnetization of the B sub-lattices make an angle (called Y-K angle) with each other differing from 0° or 180° [11]. For this region the calculated magnetic moment is smaller than theoretical value. It can be also explained that the theoretical magnetic moment is calculated on basis of 0K temperatures, while experimental magnetic moment calculated at 300K. Therefore, a difference between these two values is expected.

Table. 1. The values of Curie temperature (T_C), Saturation magnetization (M_S), Magnetic moment (μ_B) at room temperature and theoretical magnetic moment per molecule at 0K in μ_B of the system $Cu_{1-x}Zn_xFe_2O_4$ sintered at different sintering temperatures.

Zn content x	Sintering temperature T_S (°C)	Curie temperature T_C (°C)	Saturation magnetization M_S (emu/gm)	Theoretical magnetic moment per molecule at 0K in μ_B	Magnetic moment μ_B at room temperature
0	1050	440	28.6	1 μ_B	1.2
	1150	395	36.5		1.6
	1200	370	34.6		1.5
0.4	1050	230	58.4	4.6 μ_B	2.3
	1150	190	58.6		2.5
	1200	160	57.4		2.5

Conclusions

On the basis of the above results and discussion, the following conclusions can be drawn:

(1) The analysis of XRD patterns indicated that the studied Cu-Zn ferrite samples have spinel cubic structures with a single phase.
(2) The sharp decrease of μ_i at $T = T_C$ indicates that the samples have high homogeneity according to Globus.
(3) Curie temperature decreases with sintering temperature and with Zn content.
(4) The saturation magnetization increases with Zn content. For pure $CuFe_2O_4$, M_S increases with sintering temperature.

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