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MAGNETISATION, CURIE TEMPERATURE AND Y–K ANGLE STUDIES OF Cu SUBSTITUTED AND NON SUBSTITUTED Ni–Zn MIXED FERRITES

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The compositional variation of saturization magnetization and Curie temperature for $Ni_{1-y-x}Zn_xCu_yFe_2O_4$ where $x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$ for $y = 0$ and $x = 0.0, 0.2, 0.4, 0.6, 0.8$ for $y = 0.2$ have been reported. It is observed that Néel type of spins are favoured in $NiFe_2O_4$, $Zn_{0.2}Ni_{0.8}Fe_2O_4$, $Ni_{0.8}Cu_{0.2}Fe_2O_4$ and $Zn_{0.2}Ni_{0.6}Cu_{0.2}Fe_2O_4$. However, in the remaining samples non-collinear spin arrangement is favoured. This is concluded from the computation of Y–K angles for both the ferrite systems. The Curie temperatures have been evaluated by the technique described by Loria *et al.* The non-collinear arrangement is also evidenced by the compositional variation of Curie temperatures for both the systems. On addition of copper, the Curie temperatures and magnetization of the Ni–Zn ferrite system are lowered which is attributed to lower magnetic moment for Cu^{+2}.

INTRODUCTION

FERRITE SYSTEM $Ni_xZn_{1-x}Fe_2O_4$ has been studied for its magnetization behaviour by many workers [1–5]. The magnetization behaviour has been explained on the basis of various theories. Magnetic ordering studies in Cu–Zn ferrite have been reported [6]. However, no data is available on the magnetization studies of copper substituted Ni–Zn ferrites. The present paper reports the magnetization studies of copper substituted and on substituted Ni–Zn mixed ferrite systems. These studies are carried out to gain information regarding the role of copper ions in influencing the structural, electrical and magnetic properties of mixed Ni–Zn ferrite system. Also, Curie temperatures have been evaluated for both the systems and compared.

EXPERIMENTAL

The ferrite samples were prepared by standard ceramic method using A.R. grade CuO, ZnO, NiO and Fe_2O_3. The powders of these oxides were mixed in proportion and sintered for 48 h at 1100°C in a globar furnace. The product was cooled at the rate of $80°C\,h^{-1}$ in the furnace. The completion of the solid state reaction was checked from the X-ray diffractometer studies carried out using Siemens computerized diffractometer.

A high field loop tracer HS 869 supplied by Electronics Corporation of India was used for the measurements on hysteresis and the method by Loria [7] *et al.* was used to determine Curie temperatures of the samples.

RESULTS AND DISCUSSION

In Table 1 values of saturation magnetization (Ms), Curie temperature (T_c) and Y–K angles for both the systems are reported.

In Fig. 1 compositional variation of saturation magnetization has been shown for the ferrites $Zn_xNi_{1-x}Fe_2O_4$ and $Zn_xNi_{0.8-x}Cu_{0.2}Fe_2O_4$. It is seen that as the content of Zinc is increased the value of *Ms* also shows increasing trend up to 40% content of zinc beyond which a decreasing trend is exhibited by the compositional variation of *Ms*. The values of *Ms* are maximum for $Zn_{0.4}Ni_{0.6}Fe_2O_4$ and $Zn_{0.4}Ni_{0.4}Cu_{0.2}Fe_2O_4$. For Ni–Zn ferrite the values of *Ms* are found upto 80% content of zinc but with the addition of 0.2 copper the values of *Ms* are found up to 60% content of zinc. Also, the values of *Ms*, in general, are lowered with the addition of copper.

Srivastava *et al.* [8] have calculated the Y–K angles for $Zn_xFe_{3-x}O_4$. R.G. Kulkarni *et al.* [6] have carried out studies on magnetic ordering in Cu–Zn ferrites. They have calculated theoretical values of Y–K angles using the formula

$$\cos\alpha_{YK} = \frac{5(1-x)^2 + 25(1-x^2)}{(1-x^2) + 25(1+x^2) + 10(1-x^2)}.$$

They have used the values of exchange constants as follows:

Table 1.

Sr. No.	Composition	Ms emu gm^{-1} $\pm 5\%$	T_c °K $\pm 5\%$	Y–K angle
1.	$NiFe_2O_4$	52.5	907	0°
2.	$Ni_{0.8}Zn_{0.2}Fe_2O_4$	68.0	805	0°
3.	$Ni_{0.6}Zn_{0.4}Fe_2O_4$	75.0	698	14°14′ ± 1°
4.	$Ni_{0.4}Zn_{0.6}Fe_2O_4$	57.5	553	46°58′ ± 3°15′
5.	$Ni_{0.2}Zn_{0.8}Fe_2O_4$	2.6	473	80°36′ ± 5°30′
6.	$ZnFe_2O_4$	–	–	90°
7.	$Ni_{0.8}Cu_{0.2}Fe_2O_4$	49.0	868	0°
8.	$Ni_{0.6}Zn_{0.2}Cu_{0.2}Fe_2O_4$	66.5	766	0°
9.	$Ni_{0.4}Zn_{0.4}Cu_{0.2}Fe_2O_4$	72.5	644	21° ± 1°30′
10.	$Ni_{0.2}Zn_{0.6}Cu_{0.2}Fe_2O_4$	47.5	482	52°10′ ± 3°36′
11.	$Zn_{0.8}Cu_{0.2}Fe_2O_4$	–	–	–

Measurements on Ms and T_c are accurate to within 5%.

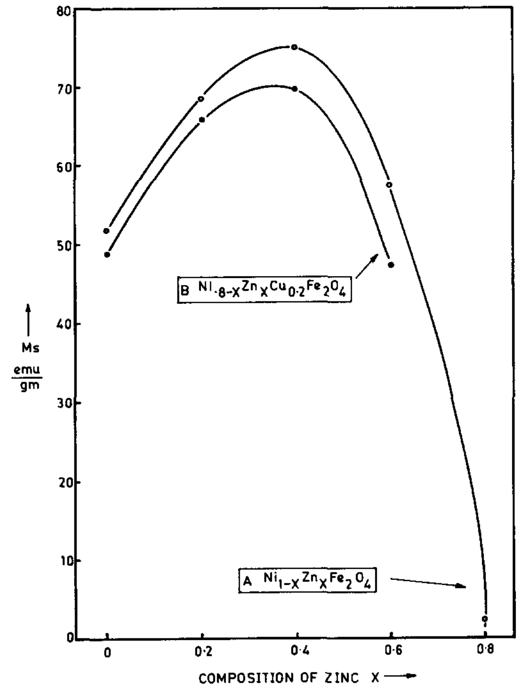

Fig. 1. Saturation magnetisation (Ms) vs composition of zinc (x).

$$J_\alpha = -5.25,\ J_\beta = -14.8,\ J_\delta = -10,\ J_\gamma = 389,$$
$$\times\ J_\varepsilon = -4.53,$$

which are calculated by Srivastava *et al.*

Comparing the theoretical values of Y–K angles with those of experimental values, they have come to the conclusion that canted type of spins are favoured on B sub-lattice in the case of Cu–Zn ferrite. We have used the following formula for the calculation fo Y–K angles.

$$n_B = (6 + x)\cos\alpha_{Y\text{-}K} - 5(1 - x),$$

where n_B is expressed in the units of Bohr-magneton and x represents the content of zinc. The experimental values of magnetic moment were obtained using the formula [9]

$$n_B = \frac{\text{Mol. Wt.} \times Ms}{5585 \times ds},$$

where ds is density of the sample, and Ms was calculated by using the formula

$$Ms = (1 - p)\sigma s\ ds,$$

where p is the porosity, and σs = saturation magnetization in e.m.u. per gm.

From Table 1 it is seen that the Y–K angles for $NiFe_2O_4$, $Zn_{0.2}Ni_{0.8}Fe_2O_4$, $Ni_{0.8}Cu_{0.2}Fe_2O_4$, and $Zn_{0.2}Ni_{0.6}Cu_{0.2}Fe_2O_4$ are zero.

This suggests that the magnetization variation in these ferrites can be explained on Néel two sub-lattice model. For $Zn_xNi_{1-x}Fe_2O_4$ (x = 0, 0.2) the cation distribution can be given as

$$(Zn_x^{2+}Fe_{1-x}^{3+})^A(Fe_{1+x}^{3+}Ni_{1-x}^{2+})^BO_4.$$

This cation distribution is presented from the fact that Zn^{2+} is a non magnetic ion and has strong preference for A site [10]. On going to A site it forces equal number of Fe^{3+} ions to B site. Ni^{2+} has strong preference for B site. The net magnetic moment per formula unit is given by

$$n_B = 5(1 + x) + m(1 - x) - 5(1 - x),$$

Bohr magneton, where m is the magnetic moment of Ni^{2+} ions in Bohr magnetons.

Thus, it is seen that n_B has minimum value equal to m for $x = 0$ for $NiFe_2O_4$ and which tends to 10 as the content of zinc is increased. However, this value of n_B is never realized in practice. In Fig. 1 it is seen that the value of Ms and hence n_B goes on decreasing beyond 40% content of zinc.

For the ferrites $Zn_xNi_{1-x}Fe_2O_4$ and $Zn_xNi_{0.8-x}$-$Cu_{0.2}Fe_2O_4$ ($x > 0.2$) the Néel two sub-lattice model can not be used to explain the compositional variation of Ms which is evidence by the non-zero Y–K angles for these samples (Table 1). In both the ferrite series as the content of zinc is increased the Y–K angles go on increasing. Thus, the change in magnetization on zinc substitution occurs due to the presence of Y–K angles in the spin system on B sites. The condition for Y–K angles to occur in Ni–Zn system has been investigated in the molecular field approximation by Satyamurthy *et al.* [8] using a noncolinear three sub-lattice model. The increase in the Y–K angles indicate the increasing favouring of triangular spin arrangements on B sites leading to reduction in A–B interaction. B–B interactions are antiferromagnetic even in a mixed magnetic zinc ferrite. The effect of B–B interaction is usually masked by strong A–B interaction which causes the spin on B sites to be aligned parallel to each other. However, the substitution of zinc in excess of 20% leads to canted type of arrangements on B sites weakening the A–B interaction as suggested by Yafet and Kittel [11].

When nickel in Ni–Zn ferrites is completely replaced by zinc, cos α_{YK} becomes zero as $\alpha_{YK} = 90°$ suggesting that B–B interaction collapses leading to a zero Ms for $ZnFe_2O_4$. Similar explanation can be applied for copper containing Ni–Zn ferrites which show zero value of Ms.

In Fig. 1 it is seen that with the addition of copper the values of Ms are lowered. Nickel ferrite has magnetic moment 2.3 while copper ferrite has magnetic moment 1.3 [12]. Thus, the substitution of copper of lower magnetic moment in the ferrite is expected to lower the value of Ms, for $Zn_xNi_{0.8-x}Cu_{0.2}Fe_2O_4$.

In Fig. 2 the variation of Curie temperature with the content of zinc in the ferrite samples Zn_xNi_{1-x}-Fe_2O_4 and $Zn_xNi_{1-x}Cu_{0.2}Fe_2O_4$ is shown. It is seen that as the content zinc in both the ferrite systems increases the value of T_c goes on decreasing. T_c is maximum for $NiFe_2O_4$ and $Ni_{0.8}Cu_{0.2}Fe_2O_4$ while it is minimum for $Zn_{0.8}Ni_{0.2}Fe_2O_4$ and $Zn_{0.6}Ni_{0.2}Cu_{0.2}$-Fe_2O_4 for the rest of the samples the values of T_c were not observed at room temperature.

The lowering of T_c can be well correlated with the observed values of Y–K angles in the ferrite. As explained previously the increase in $\alpha_{Y\text{-}K}$ angles is characterised by a decrease in A–B interaction leading to lowering of T_c in the ferrites. It is also seen from

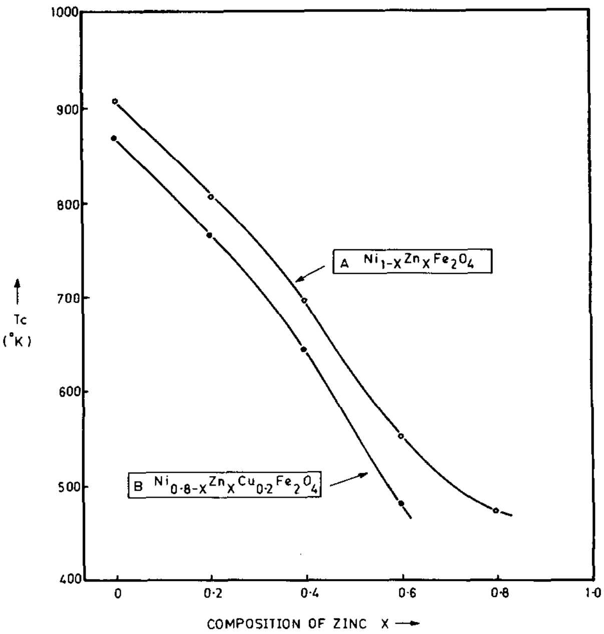

Fig. 2. Curie temperature (T_c) vs composition of zinc (x).

Fig. 2 that the addition of copper lowers the T_c values. This lowering can again be related with the higher magnetic moment of 2.3 for $NiFe_2O_4$ than 1.3 for $CuFe_2O_4$.

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