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Study of bismuth substitution in cobalt ferrite

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Abstract : The bismuth substituted cobalt ferrite, that is, $CoBi_{2x}Fe_{2-2x}O_4$ has been prepared by ceramic method. The single phase has been confirmed by X-ray diffractograms The electrical behaviour of the system is studied by the measurements of electrical resistivity and dielectric constant The magnetic behaviour is studied through low field ac susceptibility. The electrical and magnetic behaviours are explained on the basis of single domain (SD) to superparamagnetic (SP) transition

Keywords : Bismuth substituted cobalt, resistivity, susceptibility

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1. Introduction

The pure cobalt ferrite has been well studied by many researchers [1–3]. The substituted $CoFe_2O_4$ has also been studied by various researchers [4–6]. Some people have also studied the mixed cobalt ferrite [7,8]. As far our knowledge goes, there have been no studies on the bismuth substituted cobalt ferrite. In this paper, we represent the effect of bismuth substitution in place of Fe in cobalt ferrite. The system $CoBi_{2x}Fe_{2-2x}O_4$ has been characterized by X-ray diffraction and found single phase. The resistivity and dielectric constants have been measured as a function of temperature. The resistivity against temperature curves exhibit prominent rise after the critical temperatures of the samples. This is attributed to superparamagnetic (SP) to paramagnetic transition. The susceptibility measurements indicate the presence of single domain particles.

2. Experimental techniques

All the samples of the system $CoBi_{2x}Fe_{2-2x}O_4$ with $x = 0.0$ to $x = 0.1$ in steps of 0.025 were prepared using the standard ceramic method. The stoichiometric proportion of CoO, Bi_2O_3 and Fe_2O_3 of high purity were thoroughly mixed, pelletized and sintered at 950°C for 12 hours. These samples were reground and refired at 950°C for 12 hours. The X-ray diffractograms were obtained with the help of Philips (PM 9220) diffractometer using FeK_{α} radiation.

The resistivity and dielectric constant measurements were performed on all the samples of thickness 4 mm and diameter 10 mm. The Aplab made microprocessor based LCR bridge was used for above measurements. Before measurements, the faces of the pellets were carefully polished and rubbed with graphite. The low field ac susceptibility of powdered samples for all the samples were measured using double coil apparatus [9], from room temperature to 800 K.

3. Results and discussion

The X-ray diffractograms exhibited a well-defined pattern of lines. When these lines were indexed they indicated a single phase. This is shown in Figure 1. The extra lines for the

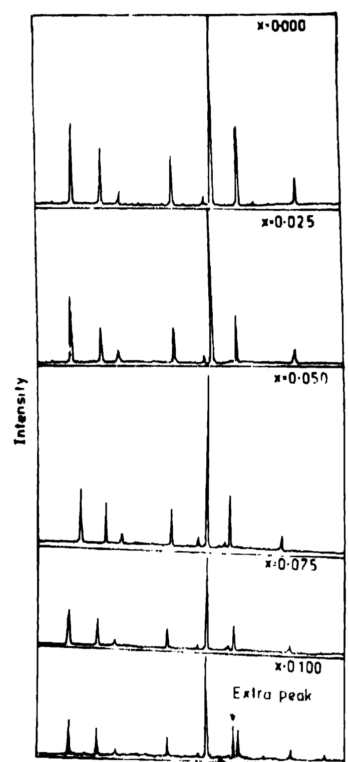

Figure 1. X-ray diffractograms of the system $CoBi_{2x}Fe_{2-2x}O_4$.

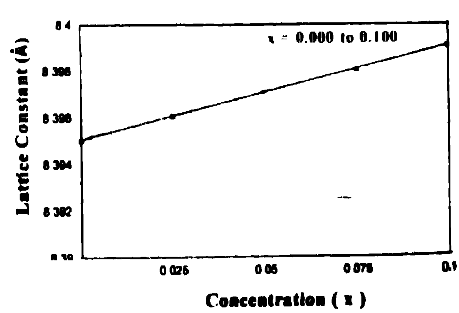

Figure 2. Lattice parameter a *versus* concentration x.

sample $x = 0.100$ which is shown with arrow in Figure 1 indicates that for $x > 0.100$ the cobalt ferrite does not accommodate bismuth in its cubic phase. The variation of lattice constants against concentration is shown in Figure 2. From Figure 2, it is clear that substitution of bismuth ions slightly but steadily increases the lattice constant. Of course, this rise is not noteworthy because of the very small concentration of bismuth. The steady rise can be attributed to the replacement of Fe ions of smaller radius by bismuth ions of larger radius.

The low field ac susceptibility for all the samples as a function of temperature is shown in Figure 3. The sample $x = 0.000$, that is, cobalt ferrite exhibits a constant rise upto

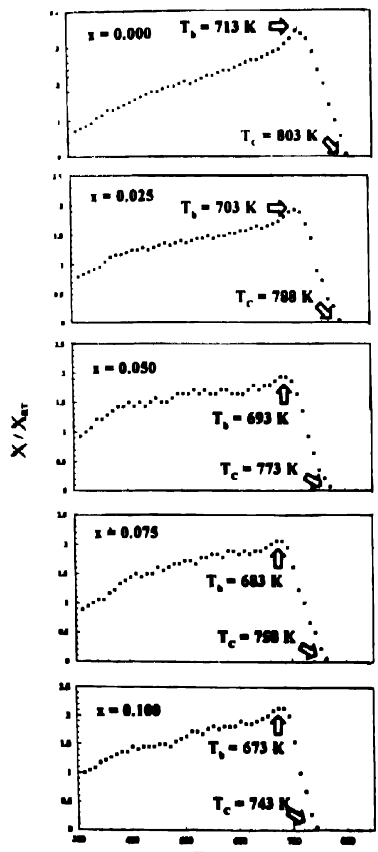

Figure 3. Low field ac susceptibility *versus* temperature for $x = 0.000$, 0.025, 0.050, 0.075 and 0.100.

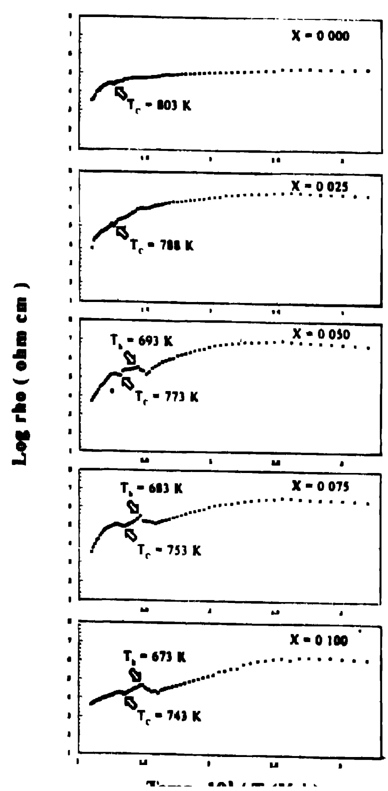

Figure 4. Log ρ *versus* temperature for the system $CoBi_{2x}Fe_{2-2x}O_4$.

a peak and then decreases. Such behaviour is also observed by Baldha *et al* [7]. The constant rise in susceptibility for $x = 0.000$ is indicative of single domain (SD) particles. As the temperature increases, single domain particles become superparamagnetic particles having increased susceptibility. Thus, with rise in temperature, more and more SD particles become SP particles. Before T_c, at blocking temperature T_b, all the SD particles become SP particles. This is known as SD to SP transition. These transition temperatures T_b for all samples are shown in Table 1. The absence of anisotropy peak for $x = 0.000$ suggests the absence of multidomain (MD) particles. As the concentration increases, the steady rise in susceptibility decreases. This shows that addition of bismuth in cobalt ferrite forms a mixture of SD and MD particles. The critical temperature T_c also decreases as the concentration increases. This can be attributed to decrease in Fe ions with the bismuth addition. The transition temperatures T_c are also shown in Table 1.

Table 1. Temperatures at dip and peak of resistivity, blocking temperatures and critical temperatures for the system of $CoBi_{2x}Fe_{2-2x}O_4$.

Concentration x	Second dip in resistivity T_c (K)	Blocking temperature T_b (K)	Critical temperature T_c (K)
0.000	–	713	803
0.025	–	703	788
0.050	773	693	773
0.075	758	683	758
0.100	743	673	743

The resistivity for all the samples as function of temperature is shown in Figure 4. The samples $x = 0.000$ and $x = 0.025$ exhibit normal behaviour but the samples $x = 0.050$, $x = 0.075$ and $x = 0.100$ show two discontinutes at higher temperatures. This suggests that substitution of bismuth upto certain amount into cobalt ferrite makes the resistivity sensitive to some kind of transition.

The comparison of these discontinuity temperatures (see Table 1) with the blocking temperature T_b and the transition temperature T_c of susceptibility suggests that first discontinuity occurring at lower temperature may be due to SD-SP transition while the second discontinuity may be due to superparamagnetic (SP) to paramagnetic transition. The general nature of resistivity is a decrease in resistivity as temperature increases.

Figure 5 shows the dielectric constant as a function of temperature for all the samples. The dielectric constant for all the samples initially increases quite negligibly; but after certain higher temperature, it shows prominent rise. It also reveals that dielectric constant does not get affected due to the SD-SP transition. The critical temperatures T_c of respective samples are indicated in Figure 5. This suggests that superparamegnetic (SP) to paramagnetic transition causes a remarkable rise in dielectric constant. It is also interesting to note that dielectric constant *versus* temperature has almost inverse behaviour compared to resistivity *versus* temperature behaviour. From this relation, rise in

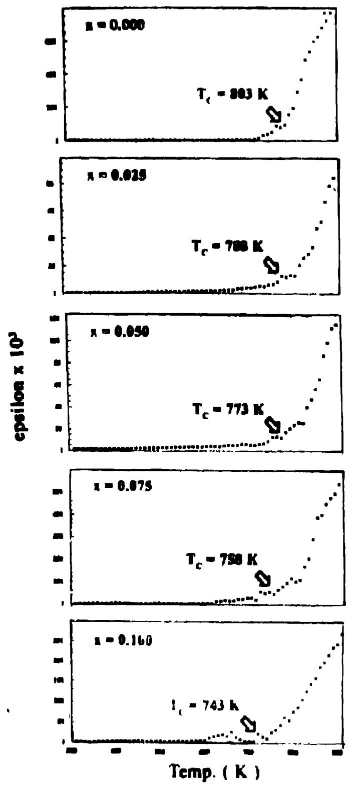

Figure 5. Dielectric constant ε *versus* temperature for the system $CoBi_{2x}Fe_{2-2x}O_4$

dielectric constant can also be attributed to rapid decrease in resistivity after critical temperature.

4. Conclusion

The present study of the system $CoBi_{2x}Fe_{2-2x}O_4$ shows that bismuth can be added only upto 10% in $CoFe_2O_4$. The resistivity becomes sensitive to magnetic transition due to addition of certain amount of bismuth as the temperature is varied. Dielectric constant is affected by rapid decrease in resistivity and superparamagnetic (SP) to paramagnetic transition.

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