X-ray and magnetic studies of Zn^{2+} substituted Ni–Pb ferrites

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Abstract. Seven samples of the polycrystalline, $Ni_{1.25-x}Zn_xPb_{0.25}Fe_{1.5}O_4$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6) ferrites, were prepared by usual double sintering ceramic method. X-ray diffraction patterns of the samples revealed single-phase cubic spinel structure. The magnetic properties were investigated by means of magnetization and a.c. susceptibility (c) measurements. A.C. susceptibility was measured from room temperature to the Curie temperature (T_C) of the samples. Variation of a.c. susceptibility (c) with temperature showed that the samples with $x = 0.3$ and 0.5 contain single-domain (SD) particles whereas the samples with $x = 0.4$ and 0.6 showed multi-domain (MD) nature. Values of Curie temperature (T_C) as obtained from the study of variation of a.c. susceptibility with temperature were found to decrease with increase in the Zn^{2+} concentration (x). Magnetic measurements showed increase in magnetization as Zn^{2+} content was increased from 0.0 to 0.5. Further increase in Zn^{2+} content (x) reduces the magnetization.

Keywords. Mixed ferrites; a.c. susceptibility; cation distribution; magnetization.

1. Introduction

Zinc substituted ferrites are technologically important materials because of their high magnetic permeability and low core losses. These ferrites have been used in electronic applications such as transformers, choke coils, noise filters, recording heads etc. Nickel ferrites and Zn^{2+} substituted nickel-ferrites are widely used in electronics and electrical industries as they exhibit interesting variations in the electrical and magnetic properties. Electrical and magnetic properties are influenced by the concentration of the Zn^{2+} ions in the Ni–Zn ferrites. Structural formula of the zinc substituted nickel ferrites is $(Zn_xFe_{1-x})[Ni_{1-x}Fe_{1+x}]O_4$, Ni occupies the octahedral (B) site, Zn^{2+} occupies tetrahedral (A) site and Fe^{3+} is distributed between the tetrahedral and octahedral sites (Smit and Wijn 1959). By increasing Zn^{2+} concentration, the Fe^{3+} ions at A-site decrease while the Fe^{3+} ions at B-site increase causing the total magnetic moment to increase. However, for $x > 0.5$ the B–B interaction becomes stronger and a non-collinear Yaffet–Kittel type magnetic ordering sets in the B sublattice.

It has been investigated by various workers that the addition of tetravalent ions like Ti^{4+}, Sn^{4+}, Ge^{4+}, Si^{4+}, Mn^{4+} etc influences the magnetic properties of the basic ferrites (Mazen *et al* 1985, 1996; Bhise *et al* 1991; Shinde and Jadhao 1998; Rao *et al* 1999). The effect of substitution of Zr^{4+}, Sb^{4+} and Hf^{4+} ions on the bulk magnetic and electrical properties of Ni–Zn and Mg–Zn ferrites is re-

ported in the literature (Femenko and Bastrikozov 1982; Das *et al* 1985; Rana and Brijlal 1985a,b). However, no information exists in the literature regarding the structural and magnetic properties of Zn^{2+} substituted Ni–Pb ferrites. Therefore, in this paper, we have reported X-ray and magnetic studies of $Ni_{1.25-x}Zn_xPb_{0.25}Fe_{1.5}O_4$ system.

2. Experimental

The samples having general chemical formula, $Ni_{1.25-x}Zn_xPb_{0.25}Fe_{1.5}O_4$ (where $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6), were prepared by using analytical grade reagents of NiO, ZnO, PbO_2 and Fe_2O_3. The ferrite samples were prepared by usual double sintering ceramic method. The oxides were mixed well in an agate mortar. Compositions were presintered in a furnace at 1173 K in the presence of air for 24 h and were furnace cooled. The presintered compositions were ground finely and then pressed in the form of discs at a pressure of 5 tons/square inch using 1% polyvinyl alcohol as a binder. Final sintering was carried out at 1473 K for 24 h in the presence of air. In order to confirm the completion of solid state reaction, X-ray diffraction patterns of the powdered product samples were recorded on a X-ray diffractometer, Siemens D-500, with Cu–K_a radiation. Saturation magnetization of the pelletized samples was measured at room temperature by using high field B–H loop tracer (Radhakrishnamurthy *et al* 1971). By using a double coil set up (Radhakrishnamurthy *et al* 1978), an a.c. susceptibility of the polycrystalline samples as a function of temperature was measured from room temperature to the Curie temperature.

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3. Results and discussion

X-ray diffraction patterns revealed the formation of single-phase cubic spinels. Variation of lattice constant with zinc content (x) is given in table 1. Lattice parameters were found to increase with the increase in Zn^{2+} concentration. This is attributed to the replacement of smaller Ni^{2+} (0·78 Å) ions by the greater Zn^{2+} (0·83 Å) ions. The values of magneton number (n_B) were calculated by using the relation (Smit 1971)

$$n_B = (\boldsymbol{s}_s M)/(\mu_B N), \tag{1}$$

where M is the molecular weight of ferrite sample, $\boldsymbol{s}_s$ the saturation magnetization, N the Avogadro's number and μ_B the Bohr magneton.

The values of magneton numbers (n_B) for each of the samples measured at room temperature (300°K) are given in table 1. Variation of magneton number with Zn^{2+} content is shown in figure 1. It can be seen from figure 1 that the value of n_B gradually increases with increase in Zn^{2+} concentration, becomes maximum for Zn^{2+} content, $x = 0.5$, and then decreases with further increase in Zn^{2+} ($x = 0.6$). The decrease in the magnetization for higher values of Zn^{2+} content (x) is due to the canting effect (Yafet and Kittle 1952; Geller 1966, 1969; Patton and Liu 1983).

According to Hastings and Corliss (1953), nickel ferrite is 80% inverse. The cation distribution in the present system as derived from site preference energies, X-ray diffraction intensity ratio calculations and magnetization studies is represented as

$$(Zn_x Fe_{0·723-0·74x} Ni_{0·277-0·34x} Pb_{0·08x})$$
$$[Fe_{0·777+0·74x} Ni_{0·973-0·66x} Pb_{0·25-0·08x} O_4,$$
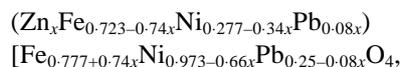
where $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6.

From the theoretical values of n_B obtained from this cation distribution and figure 1, it can be seen that Neel type of spin arrangement occurs for zinc content, $x \leq 0.3$. According to Neel's (1948) theory of ferrimagnetism, the magnetic moment per formula unit in μ_B is represented as

$$n_B^N = |M_B(x) - M_A(x)|, \tag{2}$$

where $M_B(x)$ and $M_A(x)$ are B and A sub-lattice magnetic moments in μ_B.

The fall of magnetization on addition of zinc content, $x > 0.5$, can be explained on the basis of nonlinear or canted spin ordering. According to random canting model, substitution of diamagnetic cations in one sublattice of
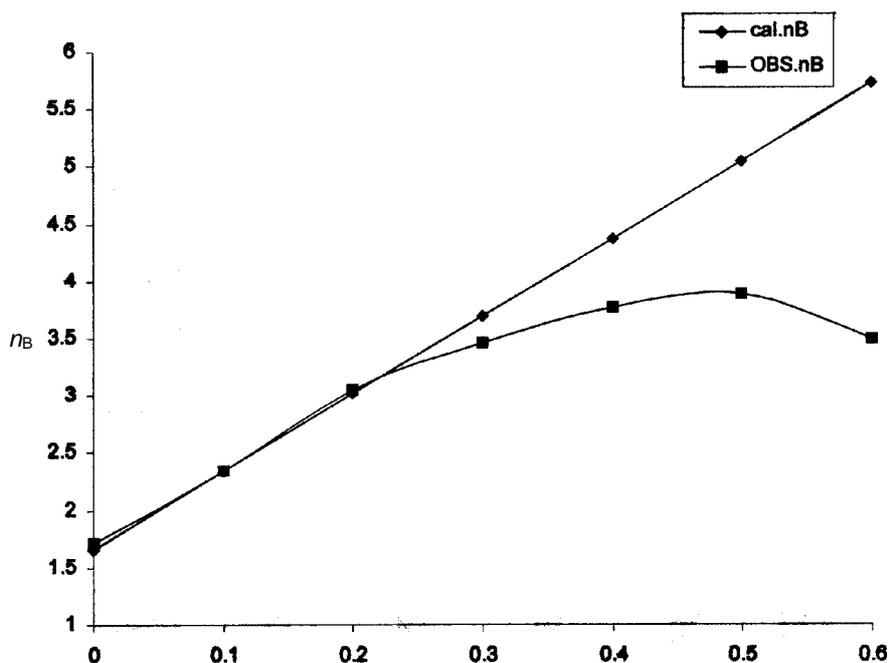
Table 1. Lattice parameter (a), magnetic moment (n_B) and Curie temperature (T_C) for the system, $Ni_{1·25-x} Zn_x Pb_{0·25} Fe_{1·5} O_4$.

		n_B		
x	a(Å)	Experimental	Theoretical	T_C (°K)
0·0	8·3471	1·72	1·66	...
0·1	8·3824	2·65	2·34	...
0·2	8·3947	2·83	3·02	...
0·3	8·3997	3·45	3·69	700·5
0·4	8·4084	3·77	4·37	695·0
0·5	8·4085	3·88	5·04	623·0
0·6	8·4196	3·49	5·72	558·0

Figure 1. Variation of magnetic moment, n_B, with Zn^{2+} content (x).

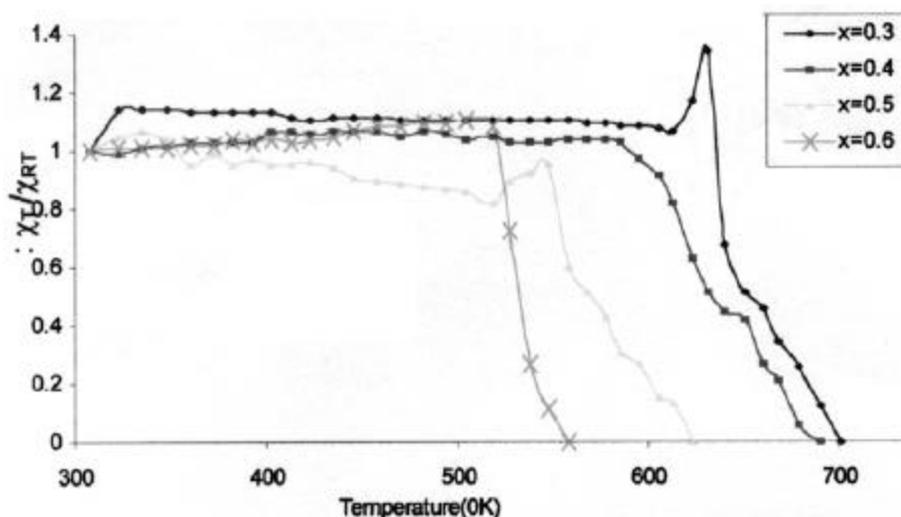**Figure 2.** Temperature dependence of a.c. susceptibility for $Ni_{1.25-x}Zn_xPb_{0.25}Fe_{1.5}O_4$ with $x = 0.3, 0.4, 0.5$ and 0.6.

ferrimagnet leads to spin canting in the other sublattice resulting in decrease in total magnetization per formula unit which is given by

$$n_B^C = M_B(x) \cos <\mathbf{a}_c> - M_A(x), \qquad (3)$$

where $M_A(x)$ and $M_B(x)$ are magnetic moments of A and B sites to be determined from cation distribution, $<\mathbf{a}_c>$ canting angle.

Variation of normalized a.c. susceptibility with temperature for samples with $x = 0.3-0.6$ is shown in figure 2. From figure 2 it can be seen that the samples with $x = 0.3$ and 0.5 show a peak near Curie temperature (T_C) indicating that these samples possess single domain (SD) states. The samples with Zn contents, $x = 0.4$ and 0.6, do not show any peak near the Curie temperature. This means that the samples with $x = 0.4$ and 0.6 possess multi-domain (MD) state. Blocking temperature (T_b) at which ferromagnetic substance changes into superparamagnetic substance is observed to decrease with increase in Zn^{2+} content (x). Values of Curie temperature determined from a.c. susceptibility data are listed in table 1. In case of the samples with $x = 0.0-0.2$, it was observed that the normalized a.c. susceptibility does not decrease to zero within the available temperature range between 300 K and 750 K in the laboratory indicating that the Curie temperature for these samples are well beyond 750 K. The decrease in the Curie temperature with increase in the Zn^{2+} content is attributed to the fact that with the addition of zinc content (x) the magnetic coupling becomes weak.

4. Conclusions

(I) Magnetization measurements exhibit Neel's collinear ferrimagnetic structure for samples with $x \leq 0.3$.

(II) Curie temperature (T_C) decreases with increase in Zn^{2+} content (x).

(III) Samples with $x = 0.3$ and 0.5 possess SD states whereas the samples with $x = 0.4$ and 0.6 possess MD states.

(IV) Cation distribution shows that the Pb^{4+} occupies both A and B sites.

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