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Magnetic and electrical properties of hot-pressed Ni–Zn–Li ferrites

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The magnetic properties of Ni–Zn ferrites have been upgraded by preparing hot-pressed $Ni_{0.4}Zn_{0.6-2x}Li_xFe_{2+x}O_4$ ferrites wherein $2xZn^{2+}$ ions have been substituted by xLi^{1+} and xFe^{3+} ions. This results in an increase of saturation magnetization, Curie temperature and dielectric constant, whereas resistivity and initial permeability are reduced. The values of saturation magnetization, Curie temperature and dielectric constant are improved due to hot pressing in which grain growth and densification are controlled simultaneously. The variations of saturation magnetization and Curie temperature can be explained by the preferential site occupancy of Li^{1+} and Ni^{2+} ions at the tetrahedral site, sublattice magnetization with canted spin structure, and magnetic exchange interactions. The inferences drawn from the bulk magnetic properties of these ferrites conform with the conclusions drawn from variations of internal magnetic field, obtained from Mössbauer studies of these samples. The decrease in d.c. resistivity due to substitution of Li^{1+} ions is attributed to increased hopping due to formation of Fe^{2+} and Ni^{3+} ions.

1. Introduction

Ni–Zn ferrites have been extensively used as core materials for large number of devices and electrical components such as phase shifters, circulators, isolators, inductors, transformers etc. These ferrites, prepared by normal ceramic methods, are not suitable for magnetic recording heads and memory devices as they require superior microstructural and magnetic properties. This has necessitated the development of ferrite materials of higher saturation magnetization and Curie temperature, low coercivity, large hardness and low porosity which can be achieved by hot pressing these ferrites to control grain growth and porosity simultaneously. It is also known [1–3] that substitution of suitable diamagnetic and ferromagnetic ions in these ferrites can modify their microstructural, electrical and magnetic properties. The present work is aimed at possible upgrading of microstructural and magnetic properties by hot pressing Ni–Zn–Li ferrites wherein $2xZn^{2+}$ ions have been replaced by xLi^{1+} and xFe^{3+} ions, and understanding the physical mechanisms responsible for modification of these properties.

2. Experimental details

Amongst Ni–Zn ferrites of different compositions [4, 5], $Ni_{0.4}Zn_{0.6}Fe_2O_4$ ferrite has the maximum values of saturation magnetization and initial permeability, and was therefore chosen as the basic ferrite composition in which $2xZn^{2+}$ ions were substituted by xLi^{1+} and xFe^{3+} ions. The ferrite series, $Ni_{0.4}Zn_{0.6-2x}Li_xFe_{2+x}O_4$, was prepared by conventional ceramic as well as hot pressing methods wherein x varied from 0.0 to 0.3 in steps of 0.05. The analytical reagents NiO, ZnO, Li_2CO_3 and Fe_2O_3 were weighed in proper proportions and thoroughly mixed. The ferrite powder was presintered at 800 °C for 2 h, and 0.005 wt % of Bi_2O_3 was added to the presintered mixture which acted as a fluxing agent, resulting in improved densification and homogenization of the sample as well as avoiding oxygen losses and formation of irreversible lithia [6, 7]. The reacted material was wet-milled and a small quantity of polyvinyl alcohol was added as a binder. The ferrite granules were cold-pressed to form pellets and toroids. A part of the material was finally sintered at 1300 °C for 3 h to prepare ferrite samples by the normal ceramic method. The ferrites of the same composition were also uniaxially hot pressed at 1250 °C for 3 h under a constant pressure of 350 kg cm^{-2}. The measurements for d.c. resistivity were made by a two-terminal method using spring-loaded copper electrodes connected to a Keithley Electrometer model 610C and dielectric constant was determined by using a Hewlett Packard L.C.R. Meter Bridge, model 4275A. The saturation magnetization, initial permeability and coercive field of the normal and hot-pressed samples were determined by using a Vibrating Sample Magnetometer EC&G model 155, LCR Meter Bridge and Hysteresis Loop Tracer, respectively.

3. Results and discussion

X-ray diffraction (XRD) analyses confirmed a single-phase spinel structure for all the samples. The porosity of hot-pressed samples, calculated from X-ray and experimental density, was found to lie between 0.15

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and 0.20% and the hardness of the samples exceeded 750 Vickers' units. The grain size of hot-pressed samples was found to be between 10 and 16 μm. The lattice constant was reduced from 0.841 to 0.830 nm when the concentration of Li^{1+} ions, x, was increased up to 0.3. It is attributed to replacement of Zn^{2+} ions of larger size, 0.074 nm, by Li^{1+} and Fe^{3+} ions of smaller size, 0.068 and 0.067 nm, respectively.

The variations of saturation magnetization, M_s, as a function of concentration of Li^{1+} ions, x, are shown in Fig. 1. These variations indicated an increase of M_s up to x equal to 0.15 for hot-pressed as well as normally sintered samples. M_s for hot-pressed samples is, however, higher than that of normal ferrites of the same composition. This is attributed to an increase in net magnetic moment per unit volume, due to the negligibly small number of pores (< 0.2 %) present in hot-pressed samples. It has been shown by Satyamurthy *et al.* [8] that spins at the B sublattice in $Ni_{0.4}Zn_{0.6}Fe_2O_4$ ferrites are canted through an angle ranging between 40 and 60 °, for which the following cation distribution was given:

$$(Zn^{2+}_{0.6}Fe^{3+}_{0.4})[Ni^{2+}_{0.4}Fe^{3+}_{1.6}]O^{2-}_4$$

where the cations in parenthesis are present at the tetrahedral site and those enclosed in the square brackets occupy the octahedral site.

It is known that Li^{1+} ions preferentially occupy the A site [9]. Mössbauer studies also show that Li^{1+} ions occupy the tetrahedral site [10]. Since $2xZn^{2+}$ ions are being replaced by non-magnetic xLi^{1+} ions at the A site and xFe^{3+} ions at the B site, the contribution by non-magnetic Zn^{2+} and Li^{1+} ions to M_s is negligible, whereas Ni^{2+} and Fe^{3+} ions contribute significantly. It has been reported by Blasse [11] that Ni^{2+} ions drift from the B site to the A site when concentration of Fe^{3+} ions increases at the B site. As xFe^{3+} ions increase at the B site, xNi^{2+} ions are likely to drift to the A site which may yield the following possible cation distribution

$$(Zn^{2+}_{0.6-2x}Li_xFe^{3+}_{0.4}Ni^{2+}_x)[Ni^{2+}_{0.4-x}Fe^{3+}_{1.6+x}]O^{2-}_4,\quad 0.0 \leqslant x \leqslant 0.15$$

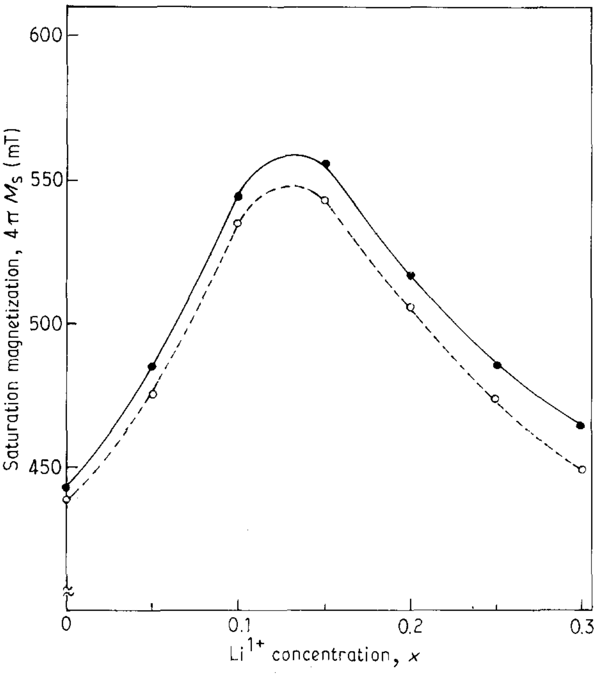

Figure 1 Variations of saturation magnetization with concentrations of Li^{1+} ions for $Ni_{0.4}Zn_{0.6-2x}Li_xFe_{2+x}O_4$ ferrites, ● hot-pressed; ○ normal.

As Ni^{2+} ions possess a magnetic moment of $2\mu_B$, whereas Fe^{3+} ions possess a higher magnetic moment of $5\mu_B$, this results in an overall increase of magnetization of the B sublattice, M_B, and thus increases M_s.

As further addition of Li^{1+} ions results in decreasing M_s, this implies that further drifting of Ni^{2+} ions to the A site does not take place and additional Fe^{3+} ions also go to the A site. It would thus increase tetrahedral sublattice magnetization, whereas B sublattice magnetization remains constant as the amount of Fe^{3+} and Ni^{2+} ions remains constant at the B site. The net saturation magnetization therefore decreases which conforms with the above suggestions.

The Mössbauer spectra of $Ni_{0.4}Zn_{0.6}Fe_4O_4$ ferrite is a relaxed one, whereas the spectra of Li^{1+} substituted Ni–Zn ferrites could be resolved into two well-defined sextets. The Mössbauer spectra of samples with $x = 0.0$ and 0.3 is shown in Fig. 2. This shows that the magnetic ordering increases successively with large substitution of Zn^{2+} ions by Li^{1+} and Fe^{3+} ions. The variations of internal magnetic field at the A and B sites as a function of concentration of Li^{1+} ions are shown in Fig. 3. The figure indicates that the hyperfine field increases rapidly for a smaller concentration of Li^{1+} ions, followed by a gradual increase of internal magnetic field at A as well as B sites. These variations can be quantitatively explained on the basis of preferential site occupancy of Li^{1+} ions at the A site, and stronger intersublattice magnetic exchange interactions than intrasublattice exchange interactions. The variations of internal magnetic field conform with the cation distribution obtained from saturation magnetization, which suggests that Ni^{2+} and Fe^{3+} ions increase initially at A and B sites, respectively, whereas tetrahedral sublattice magnetization increases for the larger substitution of Li^{1+} ions when the additional Fe^{3+} ions drift to the A site. This results

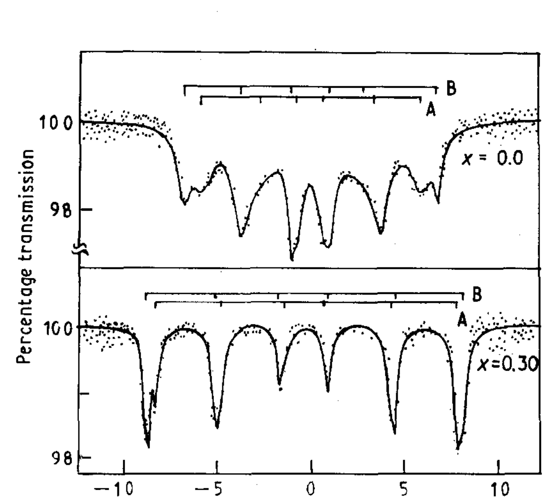

Figure 2 Mössbauer spectra of $Ni_{0.4}Zn_{0.6-2x}Li_xFe_{2+x}O_4$ ferrites ($x = 0.0$ and 0.3).

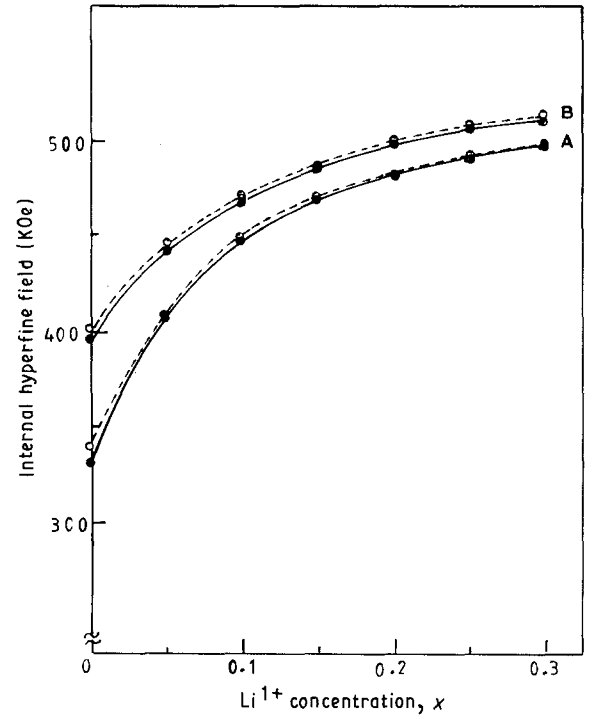

Figure 3 Variations of hyperfine fields at tetrahedral (A) and octahedral (B) sites with concentrations of Li^{1+} ions for $Ni_{0.4}Zn_{0.6-2x}Li_xFe_{2+x}O_4$ ferrites. ●, hot pressed; ○, normal.

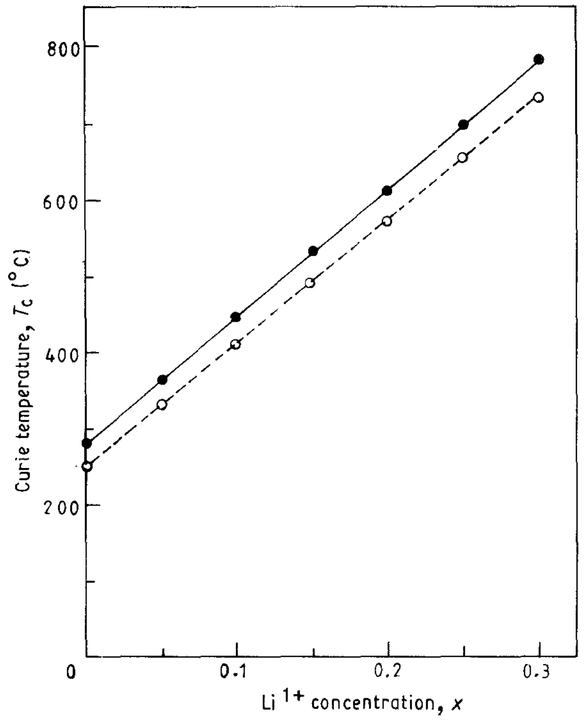

Figure 4 Variations of Curie temperature with concentrations of Li^{1+} ions for $Ni_{0.4}Zn_{0.6-2x}Li_xFe_{2+x}O_4$ ferrites. ●, hot-pressed; ○, normal.

in a gradual increase of internal magnetic field at both sites, due to larger substitution by Li^{1+} and Fe^{3+} ions. The inferences drawn from variations of internal magnetic field support the conclusions drawn from the bulk magnetic properties.

Fig. 4 shows that Curie temperature increases when the concentration of Li^{1+} and Fe^{3+} ions increases in place of Zn^{2+} ions. As the number of Fe^{3+} ions increases at the B site, it results in an increase of strength of AB exchange interactions of the type Fe_A^{3+}–O^{2-}–Fe_B^{3+}, apart from the increasing number of bonds or linkages between magnetic ions [12]. Thus the thermal energy required to offset the spin alignment increases, which results in an increase of Curie temperature. As the number of magnetic ions per unit volume is larger in high density hot-pressed ferrites, their Curie temperature is higher than those of normally sintered ferrites.

The initial permeability decreases as a function of concentration of Li^{1+} ions as shown in Fig. 5. Though it has been observed that the substitution of Li^{1+} ions does not affect the grain size and porosity appreciably, yet the decrease in initial permeability primarily results from an increase of magnetocrystalline anisotropy and variations of saturation magnetization. As Fe^{2+} ions are formed due to the reaction $Ni^{2+} + Fe^{3+} \rightleftharpoons Fe^{2+} + Ni^{3+}$, a large number of Fe^{2+} ions are therefore formed due to increasing substitution of Fe^{3+} and Li^{1+} ions. As Fe^{2+} ions possess a large positive value of anisotropy constant, an additional formation of Fe^{2+} ions will increase the overall anisotropy constant, K, which results in a net decrease of initial permeability. Hot-pressed Ni–Zn–Li ferrites possess appreciably larger values of initial permeability than those of normal ferrites having the same composition, because of their low porosity and large grain size [13, 14]. Hot-pressed ferrites possess a coercive field, H_c, lying between 0.570 and 2.840e, and a remanence ratio, B_r/B_s, lying in the range from 58 to 94%.

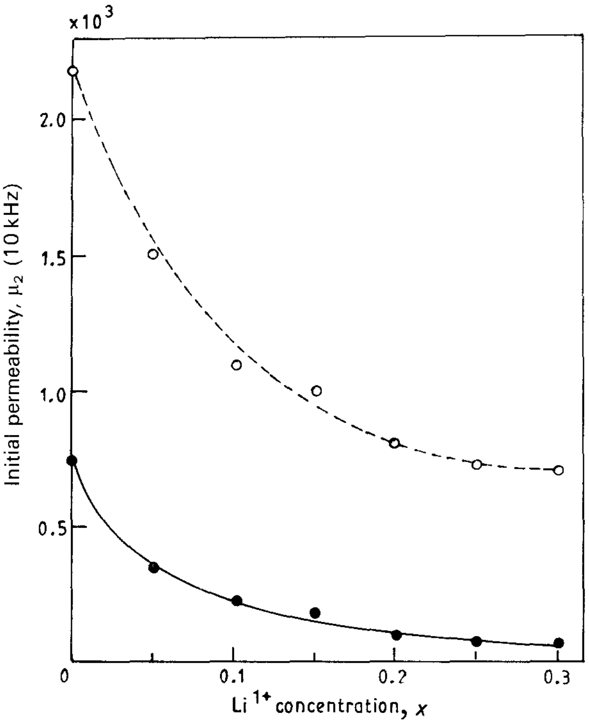

Figure 5 Dependence of initial permeability on concentrations of Li^{1+} ions for $Ni_{0.4}Zn_{0.6-2x}Li_xFe_{2+x}O_4$ ferrites. ●, hot-pressed; ○, normal.

D.c. resistivity of these ferrites was reduced due to substitution of Li^{1+} ions, as shown in Fig. 6. This is attributed to the following conduction processes.

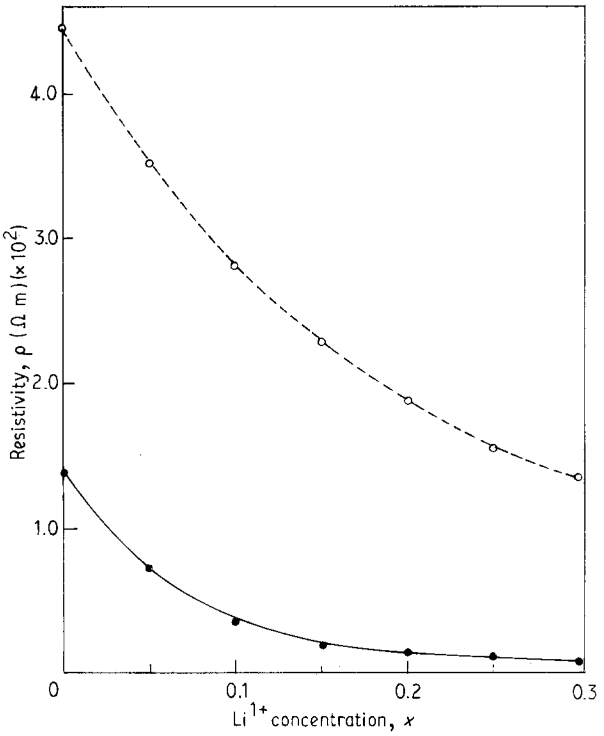

Figure 6 Variations of d.c. resistivity with concentrations of Li^{1+} ions for $Ni_{0.4}Zn_{0.6-2x}Li_xFe_{2+x}O_4$ ferrites. ●, hot-pressed; ○, normal.

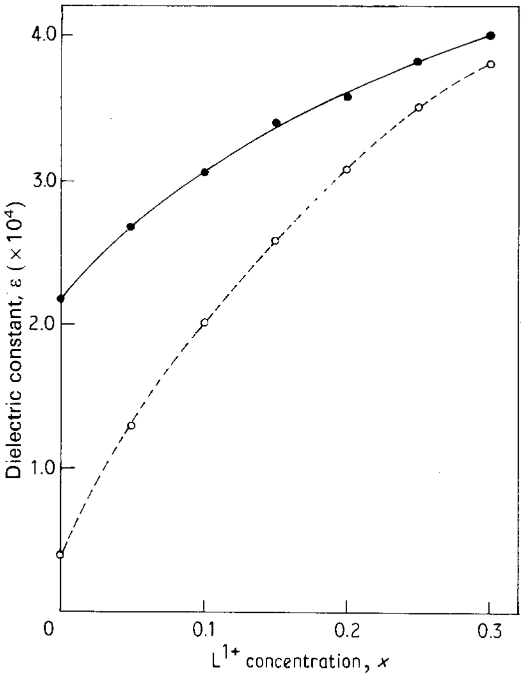

Figure 7 Variations of dielectric constant with concentrations of Li^{1+} ions for $Ni_{0.4}Zn_{0.6-2x}Li_xFe_{2+x}O_4$ ferrites. ●, hot-pressed; ○, normal.

1. A small number of Fe^{2+} ions are generally formed during the sintering process, which increases conductivity due to increased hopping between Fe^{2+} and Fe^{3+} ions when the number of Fe^{3+} ions, x is successively increased.
2. Van Uitert [15] has reported the formation of Ni^{3+} and Fe^{2+} ions due to slight dissociation of Ni–Zn ferrites because of the exchange reaction

   $$Ni^{2+} + Fe^{3+} \rightleftharpoons Ni^{3+} + Fe^{2+}$$

   As Li^{1+} ions, x, are successively increased, the process is accompanied by an increase of xFe^{3+} ions with the result that a large number of Fe^{3+} ions are available to react with the Ni^{2+} ions already present in the crystal lattice, to produce a larger number of Fe^{2+} ions. This enhances electron hopping between Fe^{2+} and Fe^{3+} ions present at equivalent crystallographic sites [16], which results in a decrease of resistivity.
3. It has been shown [17] that part of lithium is lost in the gaseous phase in ferrites, in the form of volatile compounds, when the sintering temperature exceeds 900 °C. This results in conversion of Fe^{3+} ions to Fe^{2+} ions due to charge compensation. A larger volatilization of Li^{1+} ions takes place when Li^{1+} ions are increased, resulting in the formation of a larger number of Fe^{2+}–Fe^{3+} ion pairs, which enhances electron hopping.

A small amount of zinc evaporates from the surface of grains of zinc containing ferrites [18, 19] which increases the probability of formation of Fe^{2+} ions. A larger substitution of $2xZn^{2+}$ ions by xLi^{1+} and xFe^{3+} ions is expected to reduce Zn^{2+} ions, as well as hopping of electrons between Fe^{2+} and Fe^{3+} ions, and to increase resistivity. Such an increase in resistivity is, however, negligibly small.

As the intragranular porosity is drastically reduced in hot-pressed ferrites of high density, this indicates that individual grains are densely packed which increases the effective area of grain to grain contact. The hopping of electrons between the densely packed grains further increases, which reduces the resistivity of hot-pressed ferrites.

Fig. 7 shows that the dielectric constant increases as a function of Li^{1+} ion concentration in normal and hot-pressed Ni–Zn–Li ferrites. As evaporation of zinc takes place from the surface of grains and the conduction processes described earlier lead to the formation of Fe^{2+} ions, it enhances the number of electron transitions taking place between Fe^{2+} and Fe^{3+} ions. The result is an increase of polarization and a consequent increase in dielectric constant [20]. Hot-pressed ferrites, however, possess a larger value of dielectric constant ranging from 2.1×10^4 to 4.0×10^4. This is attributed to the very low intergranular porosity of hot-pressed ferrites, which results in easy electron transfer between Fe^{2+} and Fe^{3+} ions.

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