

## Effect of $\text{Al}^{3+}$ -substitution on the electrical and magnetic properties of $\text{Ni}_{1-0.5}\text{Sn}_{0.05}\text{Fe}_{1.9}\text{O}_4$ ferrites<sup>†</sup>

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**Abstract.** The effect of  $\text{Al}^{3+}$ -substitution on d.c. resistivity, dielectric constant, initial permeability, saturation magnetization and Curie temperature has been studied for  $\text{Ni}_{1-0.5}\text{Sn}_{0.05}\text{Al}_x\text{Fe}_{1.9-x}\text{O}_4$  ferrites, wherein  $x$  varies from 0 to 0.5 in steps of 0.1. The d.c. resistivity increases slowly for  $x \leq 0.3$  followed by a rapid increase for  $x > 0.3$ . The variation is explained on the basis of Verwey hopping as well as polaron hopping mechanisms, and the dilution effect of  $\text{Al}^{3+}$  ions. The behaviour of dielectric constant is attributed to interfacial polarization and follows the Koops model. The saturation magnetization and the Curie temperature decrease continuously with increasing  $\text{Al}^{3+}$  content and are explained using the concepts of sublattice magnetization and exchange interactions. The decrease in initial permeability is attributed primarily to decrease in saturation magnetization. The dispersions in initial permeability and magnetic loss tangent are also discussed.

**Keywords.** Ni–Sn–Al ferrites; electrical properties; magnetic properties.

### 1. Introduction

The substituted Ni-ferrites find a variety of applications at radio and microwave frequencies where the electrical and magnetic losses are required to be minimum (Varshney *et al* 1980; Puri and Varshney 1983; Prakash and Bajjal 1984; Chandel *et al* 1988; Bajjal *et al* 1989). Ni–Sn ferrites of different compositions have been investigated by various workers (Varshney *et al* 1980; Chandel *et al* 1988; Bajjal *et al* 1989). It has been reported that a smaller substitution of  $\text{Sn}^{4+}$  ions in Ni-ferrites increases the resistivity by segregating at grain boundaries and hence acts to decrease the dielectric and eddy current losses (Varshney *et al* 1980). A larger substitution of these ions, however, causes discontinuous grain growth which deteriorates the magnetic properties (Jain *et al* 1980). The decrease in initial permeability and increase in magnetic loss tangent at radio frequencies have been reported for larger substitution of  $\text{Sn}^{4+}$  ions in Ni–Sn ferrites (Bajjal *et al* 1989). The substitution of  $\text{Al}^{3+}$  ions, on the other hand, increases resistivity, thereby lowering the dielectric losses, and decreases the saturation magnetization which are the desired characteristics of ferrites used to prepare microwave devices operating in L, S and C bands (Derry and Wills 1957). Besides these, aluminium additions inhibit grain growth, reduce domain wall losses and improve the mechanical strength of microwave ferrites (Bradley 1971). The present work is an attempt to draw advantages of both  $\text{Sn}^{4+}$  and  $\text{Al}^{3+}$  substitutions in Ni-ferrites and to obtain Ni–Sn–Al ferrites with properties better than Ni–Sn or Ni–Al ferrites. The results on d.c. resistivity, dielectric constant, initial permeability, dielectric and magnetic loss tangents, saturation magnetization and Curie temperature have been described and discussed.

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## 2. Experimental

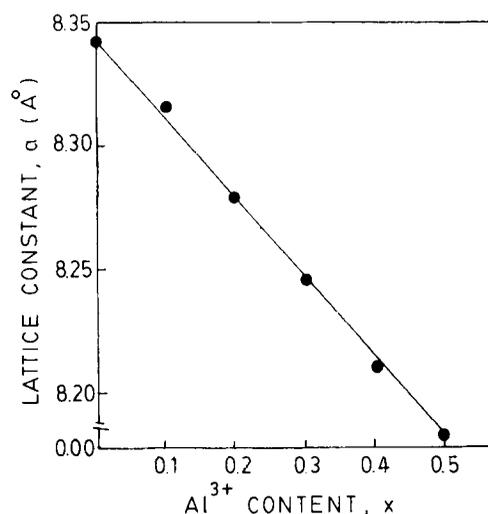
A ferrite series of the composition  $\text{Ni}_{1.05}\text{Sn}_{0.05}\text{Al}_x\text{Fe}_{1.9-x}\text{O}_4$ , wherein  $x$  varies from 0 to 0.5 in steps of 0.1, has been prepared by the conventional ceramic method. The AR-graded  $\text{NiCO}_3$ ,  $\text{SnO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  were wet-blended with acetone in an agate mortar and pestle. The material was dried and calcined at  $900^\circ\text{C}$  for 3 h. It was wet-milled again and then granulated using a small quantity of polyvinyl alcohol as a binder. The granules were compressed under a pressure of about 8 MPa to form pellets and toroids which were sintered at  $1350^\circ\text{C}$  for 3 h followed by controlled cooling at the rate of  $100^\circ\text{C}$  per h.

X-ray diffraction patterns of all the samples were obtained using a Rigaku Denki X-ray diffractometer. Scanning electron micrographs of freshly fractured samples were taken using a Cambridge stereoscan electron microscope (Model S4-10). The d.c. resistivity was determined by a two-terminal method with constant pressure copper electrodes connected to an electrometer (Keithley Model 610C). The values of dielectric constant, initial permeability, and dielectric and magnetic loss tangents at different frequencies were obtained by using an LCR Meter Bridge (HP Model 4275A). The saturation magnetization was measured with a vibrating sample magnetometer (EG & G PARC Model 155). All the measurements were taken at room temperature. A simple set-up described by Soohoo (1960) was employed to determine the Curie temperature.

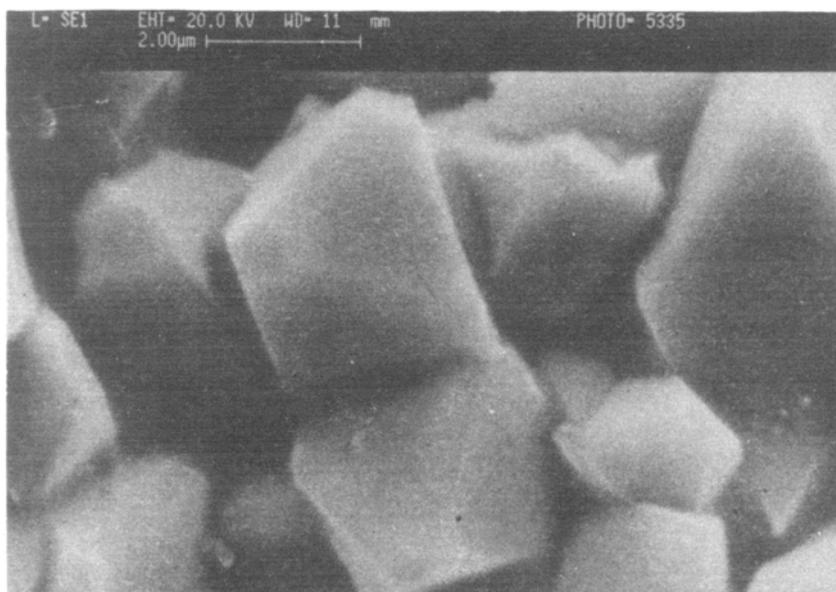
## 3. Results and discussion

### 3.1 Microstructural studies

X-ray diffraction analyses reveal a single phase spinel structure for all the samples. The lattice parameter decreases linearly with  $\text{Al}^{3+}$  content as shown in figure 1 which is due



**Figure 1.** Variation of lattice constant with  $\text{Al}^{3+}$  content in  $\text{Ni}_{1.05}\text{Sn}_{0.05}\text{Al}_x\text{Fe}_{1.9-x}\text{O}_4$  ferrites.

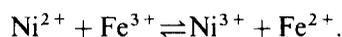


**Figure 2.** SEM photograph of  $Ni_{1.05}Sn_{0.05}Al_{0.3}Fe_{1.6}O_4$  ferrite.

to the difference in the ionic radii of  $Al^{3+}$  and  $Fe^{3+}$  ions. Since  $Al^{3+}$  and  $Fe^{3+}$  ions have ionic radii of about  $0.51 \text{ \AA}$  and  $0.67 \text{ \AA}$  respectively, a partial replacement of the latter by the former causes the shrinkage of the unit cell dimensions. The microstructural investigation indicates almost uniform grain size and grain size distribution for all the samples with an average grain size of  $2 \mu\text{m}$  and negligible intragranular porosity. The scanning electron micrograph of a typical Ni–Sn–Al ferrite is shown in figure 2.

### 3.2 Electrical properties

**3.2a D.C. resistivity:** The d.c. resistivity increases first slowly for  $x \leq 0.3$  and then rapidly for  $x > 0.3$  as shown in figure 3. The mechanisms which appear to be mainly responsible for conduction in the present system are the Verwey hopping mechanism (Verwey and DeBoer 1936) and the polaron hopping mechanism (Manjula 1990). The conduction in  $Ni_{1.05}Sn_{0.05}Fe_{1.9}O_4$  ferrites results mainly from the hopping of electrons between  $Fe^{2+}$  and  $Fe^{3+}$  ions present at octahedral or B-sites (Baijal *et al* 1989). In addition to this, the presence of  $Ni^{3+}$  ions, if any, at B-sites may also initiate hopping between  $Ni^{2+}$  and  $Ni^{3+}$  ions and thus may have a small contribution to conductivity. The occurrence of a small percentage of  $Fe^{2+}$  and  $Ni^{3+}$  ions in these ferrites might be due partly to reduction of  $Fe_2O_3$  and partly to slight dissociation of ferrite during the sintering process (Van Uitert 1956a). The following electronic exchange reaction may accompany the sintering process:



Since both  $Fe^{2+}$  and  $Ni^{3+}$  ions have a strong preference for B-sites (Van Uitert 1956b), they can produce *n*-type and *p*-type conduction respectively (Manjula 1990). The  $Sn^{4+}$

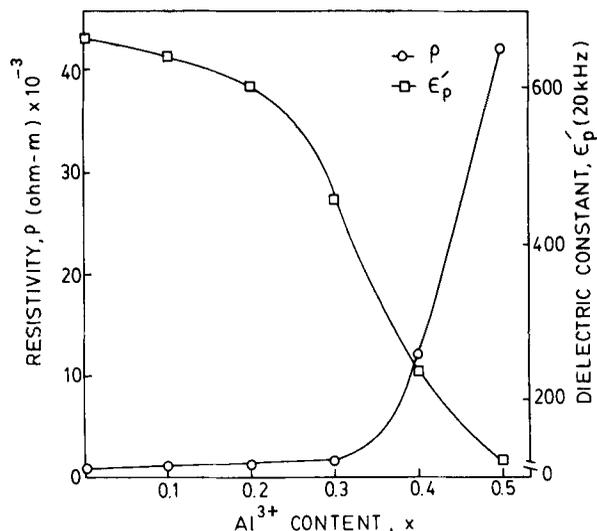
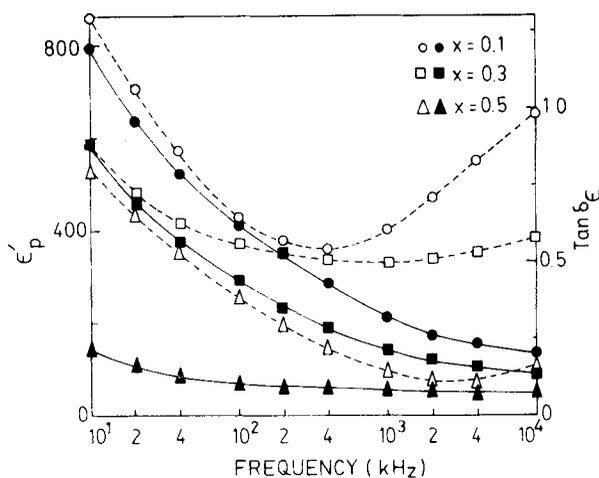


Figure 3. Variations of d.c. resistivity and dielectric constant with  $\text{Al}^{3+}$  content in  $\text{Ni}_{1.05}\text{Sn}_{0.05}\text{Al}_x\text{Fe}_{1.9-x}\text{O}_4$  ferrites.

ions present in  $\text{Ni}_{1.05}\text{Sn}_{0.05}\text{Fe}_{1.9}\text{O}_4$  ferrites, although have a strong preference for B-sites (Baijal *et al* 1989), do not participate in hopping. These ions displace an equal number of  $\text{Fe}^{3+}$  ions from B-sites, thus increasing the resistivity. The substitution of  $\text{Al}^{3+}$  ions for  $\text{Fe}^{3+}$  ions in  $\text{Ni}_{1.05}\text{Sn}_{0.05}\text{Fe}_{1.9}\text{O}_4$  ferrites has a similar effect on resistivity except that  $\text{Al}^{3+}$  ions, besides occupying B-sites, have also a tendency to occupy tetrahedral or A-sites (Von Aulock 1965), thus displacing an equal number of  $\text{Fe}^{3+}$  ions to B-sites which results in the slow increase in resistivity for  $x \leq 0.3$ . The rapid increase in resistivity for  $x$  exceeding 0.3 can be explained by taking into account the dilution effect (Van Uitert 1956b) of  $\text{Al}^{3+}$  ions, wherein the increased concentration of  $\text{Al}^{3+}$  ions inhibit  $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e^-$  conduction process.

The measured values of activation energy and carrier mobility (Purushotham *et al* 1995), however, indicate the applicability of the polaron hopping mechanism as the principal conduction mechanism. The partial substitution of  $\text{Al}^{3+}$  ions for  $\text{Fe}^{3+}$  ions increases the number of distorted sites due to the size effect and hence favour the formation of small polarons. However, since the concentration of  $\text{Fe}^{2+}$  ions, which contribute the  $n$ -type carriers to form polarons, decreases with  $\text{Al}^{3+}$ -substitution, the polaron concentration and hence conductivity is likely to decrease as  $x$  increases from 0 to 0.3. The decrease in conductivity for  $x$  exceeding 0.3 might again be due to the dilution effect of  $\text{Al}^{3+}$  ions as described above. Thus the observed variation of resistivity can be explained by both the Verwey hopping and polaron hopping mechanisms and it is difficult to determine the most effective mechanism with certainty.

**3.2b Dielectric constant and loss tangent:** The real part of parallel dielectric constant,  $\epsilon'_p$ , decreases with increasing  $\text{Al}^{3+}$  content as shown in figure 3. The dielectric behaviour of ferrites is attributed primarily to interfacial polarization resulting from their heterogeneous structure comprising low resistivity grains separated by high resistivity grain boundaries as proposed by Koops (1951). The  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions



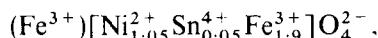
**Figure 4.** Dispersions in dielectric constant (solid curves) and dielectric loss tangent (broken curves) for some typical compositions of  $Ni_{1.05}Sn_{0.05}Al_xFe_{1.9-x}O_4$  ferrites.

present in ferrites contribute effectively to produce interfacial polarization. This is supported by the inverse proportionality between dielectric constant and resistivity as observed by various researchers (Polder 1950; Koops 1951; Baijal *et al* 1989). Thus the partial replacement of  $Fe^{3+}$  ions by  $Al^{3+}$  ions decreases the interfacial polarization, thereby decreasing the dielectric constant.

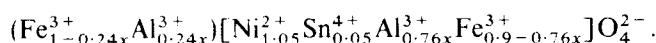
The dispersions in dielectric constant and dielectric loss tangent for some typical compositions are shown in figure 4 and appear to be consistent with the Koops model. The samples with  $x \geq 0.3$  exhibit low values of  $\tan \delta_\epsilon$ , particularly, above 100 kHz. The peaks in  $\tan \delta_\epsilon$  do not lie within the frequency range employed in the present study and are expected to appear beyond 10 MHz.

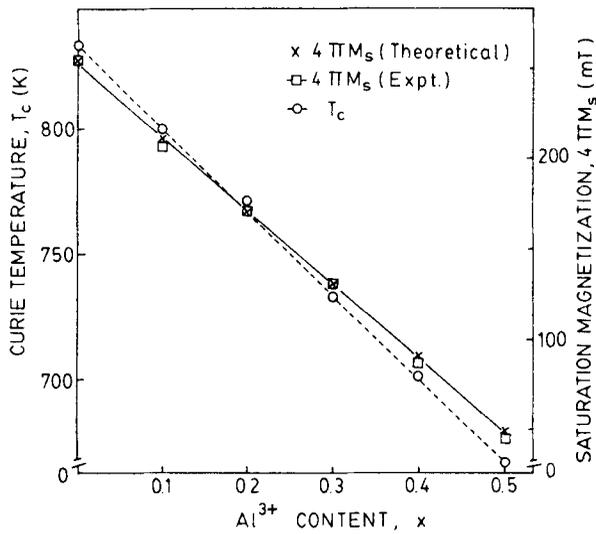
### 3.3 Magnetic properties

**3.3a Saturation magnetization:** The decrease in saturation magnetization,  $4\pi M_s$ , with increasing  $Al^{3+}$  content (figure 5) can be explained on the basis of changes in the magnetizations  $M_A$  and  $M_B$  of tetrahedral (A) and octahedral (B) sublattices respectively. The cation distribution of  $Ni_{1.05}Sn_{0.05}Fe_{1.9}O_4$  ferrites is given as (Chandel *et al* 1988; Baijal *et al* 1989):



where the cations enclosed by parentheses and square brackets occupy A and B sites respectively. As  $Al^{3+}$  ions, besides preferring B-sites, have also a tendency to occupy A sites, the partial replacement of  $Fe^{3+}$  ions, each having a magnetic moment of  $5\mu_B$ , by diamagnetic  $Al^{3+}$  ions results in lowering the value of both  $M_A$  and  $M_B$ . The decrease in  $M_B$ , however, predominates over the decrease in  $M_A$ , thereby decreasing the net magnetization. The cation distribution of  $Ni_{1.05}Sn_{0.05}Al_xFe_{1.9-x}O_4$  ferrites as estimated from the observed variation of  $M_s$  is





**Figure 5.** Variations of saturation magnetization (solid line) and Curie temperature (broken line) with  $\text{Al}^{3+}$  content in  $\text{Ni}_{1-0.5}\text{Sn}_{0.05}\text{Al}_x\text{Fe}_{1.9-x}\text{O}_4$  ferrites.

The values of  $4\pi M_s$  determined from the above cation distribution using the magnetic moments of 0, 2 and  $5\mu_B$  for  $\text{Al}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Fe}^{3+}$  ions respectively are plotted in figure 5 and are in good agreement with the experimental results. This cation distribution is also supported by the Mössbauer studies which will be reported in a subsequent paper.

**3.3b Curie temperature:** The Curie temperature decreases linearly with increased substitution of  $\text{Al}^{3+}$  ions as shown in figure 5. The variation can be explained on the basis of the strength of exchange interactions among the various magnetic ions which, in turn, depends on the density of magnetic ions in the two sublattices and their magnetic moments. As  $\text{Fe}^{3+}$  ions are gradually replaced by  $\text{Al}^{3+}$  ions, the number of magnetic ions begin to decrease at both the sites which also weakens the strength of A–B exchange interactions of the type  $\text{Fe}_A^{3+}-\text{O}^{2-}-\text{Fe}_B^{3+}$ . Thus the thermal energy required to offset the spin alignment decreases which lowers the Curie temperature.

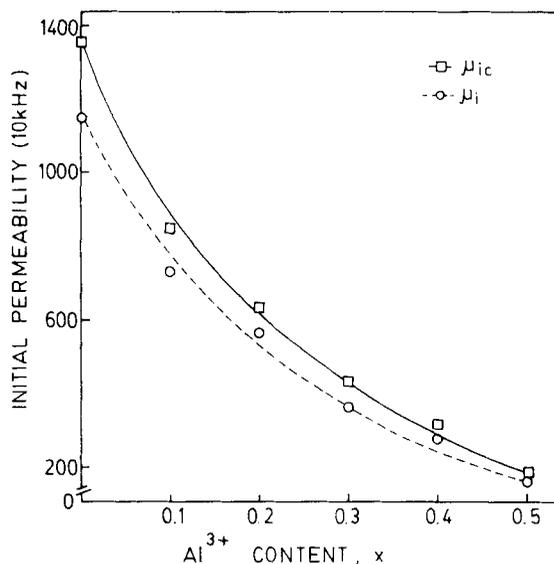
**3.3c Initial permeability and loss tangent:** The initial permeability,  $\mu_i$ , decreases with increasing  $\text{Al}^{3+}$  content as shown in figure 6. The contributions to initial permeability arise due to domain wall displacement and domain rotation and are given by the expressions (Globus and Guyot 1971; Baca *et al* 1983):

$$(\mu_{ic} - 1)_w = \frac{3\pi M_s^2 D_m}{4\gamma},$$

and

$$(\mu_{ic} - 1)_{\text{rot}} = \frac{2\pi M_s^2}{|K_1|},$$

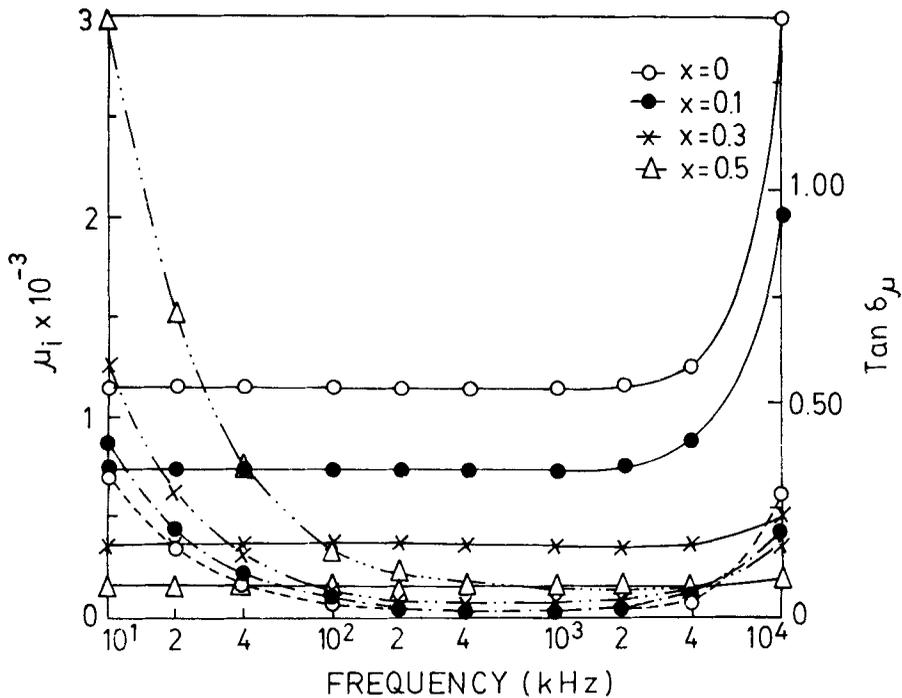
where  $\mu_{ic}$  represents the initial permeability corrected for density,  $D_m$  the mean grain diameter,  $K_1$  the magnetocrystalline anisotropy constant and  $\gamma$  the wall energy per unit area. The contributions of magnetoelastic anisotropy and dipolar energy have not been



**Figure 6.** Variations of observed ( $\mu_i$ ) and corrected ( $\mu_{ic}$ ) initial permeability with  $Al^{3+}$  content in  $Ni_{1.05}Sn_{0.05}Al_xFe_{1.9-x}O_4$  ferrites.

considered as they remain practically constant and do not change with composition unless the substituted ions produce lattice distortions. Also, since  $D_m$  does not change significantly, the variation of  $\mu_i$  can be attributed primarily to the variations of  $M_s$  and  $|K_1|$ . The change in  $|K_1|$  with increased  $Al^{3+}$ -substitution can be estimated qualitatively by applying the single ion anisotropy model (Pearson and Annis 1968). An  $Fe^{3+}$  ion occupying A-site has a positive value of anisotropy constant while the one occupying B-site has a negative value of it which is twice as large as the positive value at A-site (Kanamori *et al* 1964). Since  $Ni^{2+}$  and  $Sn^{4+}$  ions contribute insignificantly to the anisotropy constant, the ferrite of the composition  $Ni_{1.05}Sn_{0.05}Fe_{1.9}O_4$  is expected to have a negative value of  $K_1$ . Also, since  $Al^{3+}$  ions being diamagnetic, have negligible anisotropy constant, a partial replacement of  $Fe^{3+}$  ions by  $Al^{3+}$  ions reduces  $K_1$  at both the sites. However, according to the proposed cation distribution of Ni-Sn-Al ferrites, the decrease in  $K_1$  at B-site should be faster than that at A-site. This would reduce the net value of  $K_1$  which tends to increase the permeability. From the observed variation of permeability, it is thus apparent that the effect of decrease in  $M_s$  predominates over that of decrease in  $|K_1|$  to produce an overall decrease in permeability.

The dispersions in initial permeability and magnetic loss tangent for some typical compositions are shown in figure 7. The initial permeability remains almost constant up to a frequency of 4 MHz and increases sharply thereafter. The complete resonance peaks could not be observed in the frequency range presently employed and are expected to appear beyond 10 MHz. These expected peaks might be attributed to the phenomenon of domain wall resonance as resonance due to domain rotation occurs in the microwave region (Globus *et al* 1971). A comparison of the permeability spectra of the samples with  $x$  equal to 0.1, 0.3 and 0.5 indicates that the expected resonance peaks are likely to appear at higher frequencies with increase in  $Al^{3+}$  content or decrease in permeability. This is in accordance with the Globus model (Globus 1977) which relates



**Figure 7.** Dispersions in initial permeability (solid curves) and magnetic loss tangent (broken curves) for some typical compositions of  $\text{Ni}_{1.05}\text{Sn}_{0.05}\text{Al}_x\text{Fe}_{1.9-x}\text{O}_4$  ferrites.

the resonance frequency,  $f_r$ , with permeability as:

$$(\mu_i - 1)^{1/2} \cdot f_r = \text{constant.}$$

It has been proposed that for materials of lower permeability, the demagnetizing fields appearing during wall movement result in enhancement of the restoring force and hence increase the resonance frequency.

The magnetic loss tangent,  $\tan \delta_\mu$ , exhibits high values at frequencies of about 10 kHz and 10 MHz but almost stabilizes at very low values between 100 kHz and 4 MHz. The increase in loss factor at 10 MHz may be attributed to the phenomenon of domain wall relaxation which involves the hinderance of domain wall motions of small grains by those of large grains where the latter type of grains occur in small number (Kramer and Panova 1983). The critical relaxation frequency,  $f_c$ , is not apparent in the present spectra and, presumably, lies beyond 10 MHz. Hence it is difficult to determine the effect of  $\text{Al}^{3+}$ -substitution on the relaxation frequency. The occurrence of high values of  $\tan \delta_\mu$  near 10 kHz is due to a different type of wall relaxation process (Smit 1977). It is supposed that the magnetic energy levels of a magnetic ion depend on the orientation of the magnetization. For each orientation, there exists an equilibrium Boltzmann distribution. In a moving wall the magnetization changes its direction, and hence the energy levels, resulting in a change in the equilibrium distribution. A thermally activated redistribution occurs in a finite relaxation time,  $\tau$ , causing the magnetization to lag behind the applied field. The maximum loss occurs at a frequency  $\tau = 1/\omega$  which is proportional to conductivity. The observed variations appear to follow this behaviour.

#### 4. Conclusions

A partial substitution of  $Al^{3+}$  ions for  $Fe^{3+}$  ions in  $Ni_{1.05}Sn_{0.05}Fe_{1.9}O_4$  ferrites has resulted in increase in resistivity, change in dielectric properties, and decrease in saturation magnetization, Curie temperature and initial permeability. The frequency range in which the initial permeability remains practically constant increases with increase in  $Al^{3+}$  content in Ni–Sn–Al ferrites. The dielectric and magnetic loss tangents decrease for larger substitution of  $Al^{3+}$  ions in the mega-hertz range. Hence these materials might find applications, particularly in the mega-hertz range, where electrical and magnetic losses are of prime concern.

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