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Electrical and magnetic properties of $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite prepared by sol-gel method

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Ultrafine $Ni_{0.8}Zn_{0.2}Fe_2O_4$ particles dispersed in silica (SiO_2) matrix are produced by sol-gel method. The powders were subjected to X-ray diffraction to confirm the formation of crystalline phases. The physical properties such as bulk density, true density, % of porosity and % of linear shrinkage were studied. The magnetic permeability as the function of frequency from 1 kHz to 13 MHz and temperatures from room temperature to 300°C were studied for samples sintered at temperature 1250°C. The AC electrical resistivity as the function of frequency and DC electrical resistivity as the function of temperature were studied. The AC-resistivity of the order of $\geq 10^5$ Ωcmand DC-resistivity $\geq 10^8$ Ωcm were obtained at room temperature. Microstructural features of sintered samples show the presence of ferrite grains of 1–2 μm size.

1. Introduction

In recent years, there has been much interest on the preparation of ultrafine ferrite particles, dispersed in the insulating matrix. One composite model is that when fine ferrite particles are embedded in a matrix, they possess completely different electric and magnetic properties from those of the bulk particles [1, 2]. Many systems such as Fe [3, 4], Fe_2O_3 [5], Ni [6], Iron and Iron chromium alloys [7], Ni-Zn ferrite [1, 8] of nanoparticles dispersed in the insulating silica matrix have been reported by different methods. Preparation of ultrafine $CoFe_2O_4$ [9] and Mn-Zn ferrite [10] by chemical precipitation has also been reported. Chemical processes, like sol-gel, are widely used to produce very pure and homogeneous nanostructures with relatively large quantities of final product [11, 12]. There is no report on the electrical resistivity, dielectric constant and magnetic initial permeability studies of $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite prepared by sol-gel technique. In the present work, the Ni-Zn ferrite of composition $Ni_{0.8}Zn_{0.2}Fe_2O_4$ embedded in the insulating SiO_2 matrix was prepared by sol-gel processing. The physical, electrical and magnetic properties were studied for the sintered samples of Ni-Zn ferrite/silica composites. The microstructural features were also studied.

2. Experimental

The starting materials used for the preparation of $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite were nickel nitrate (98%), zinc nitrate (98%), ferric nitrate (98%) and tetra ethyl ortho silicate (TEOS). The metal nitrates were weighed for the composition of $Ni_{0.8}Zn_{0.2}Fe_2O_4$ and were dissolved in the distilled water. These solutions were mixed together to obtain a clear solution. TEOS was added slowly to this solution under vigorous stirring. After homogenization few drops of concentrated nitric acid were added under stirring and then it was allowed to form gel in a plastic petridish during drying at 60°C. Two different molar ratios of TEOS were used in the preparation of $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite. The theoretical volume fractions of the Ni-Zn ferrite in the silica matrix were 34% (S1) and 52% (S2). Then the gels were calcined at 900°C for 2 h under atmospheric condition. The calcined powders were milled for 5 h. Then the milled powders were fabricated into pellets and toroids. PVA was used as a binder. The fabricated samples were sintered at 1250°C for 3 h under normal sintering conditions. The calcined samples were subjected to XRD analysis using Shimadzu Corporation Japan, Model XD-DI with Cu K_α radiation to confirm the phases. The physical properties were studied for the sintered samples by using ASTM C-373 test

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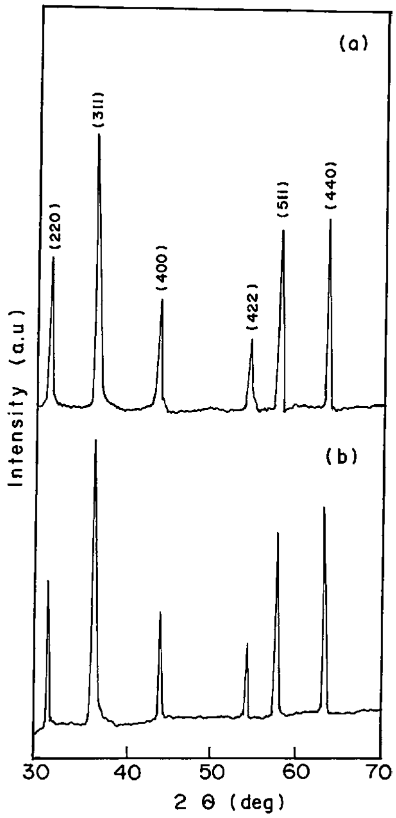

Figure 1 X-ray diffraction pattern of $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite calcined at 900°C: (a) S1-34 vol% Ni-Zn ferrite and (b) S2-52 vol% Ni-Zn ferrite.

procedure. The initial permeability (μ_i) as the function of frequency and temperature was studied. The disc shaped samples were polished well to be parallel and smooth, and then silver paint was coated for electrical contact to measure the AC-resistivity (ρ_{AC}), dielectric constant (ε') and dielectric loss (tan δ). The μ_i, ρ_{AC}, and ε' values were calculated from the inductance, resistance and capacitance measurements respectively, made using Hewlett Packard 4192-A Impendence Analyzer in the frequency range 1 kHz to 13 MHz. The DC-resistivity as the function of temperature was also studied using MECO digital multimeter. The microstructure of the sintered samples was recorded using Leica Stereo Scan 440 Scanning Electron Microscope (SEM).

3. Results and discussion

Fig. 1 shows the XRD patterns of the powder samples calcined at a temperature of 900°C. The dominance of spinel phases is observed which confirms the formation of Ni-Zn ferrites. All the peaks in the pattern match well with the characteristic reflections reported earlier [1, 8]. The crystallite size (D) of the ferrite nanoparticles is calculated from the X-ray line broadening technique as per the Scherrer equation [13],

$$D = 0.9\lambda/\beta\cos\theta$$

where λ is the wavelength of the radiation, β is the full width at half maxima and θ is the diffraction angle. The average diameter of the crystallite size is about 14 and 20 nm for samples containing 34 and 52 vol% of Ni-Zn ferrite respectively. Table I shows the physical properties of Ni-Zn ferrite/silica composites of two different vol% of Ni-Zn ferrite content. About 85% of theoretical density is obtained for the samples sintered at 1250°C for 3 h. The magnetic properties of ferrites are known to be influenced by chemical composition, crystal structure, grain size and porosity. Initial permeability is an important magnetic property to study the quality of soft ferrites. Initial permeability would be resolved into two types of mechanisms such as contribution from spin rotation and contribution from domain-wall motion. But the contribution from spin rotation was found to be smaller than domain-wall motion and it is mainly due to reversible motion of domain walls in the presence of a weak magnetic field [14, 15]. Fig. 2 shows initial permeability as the function of frequency in the range 1 kHz to 13 MHz and it was observed that the initial permeability is gradually decreasing with an increase of the frequency. A maximum initial permeability of 13 is obtained at 10 kHz at room temperature. Fig. 3 shows the initial permeability of Ni-Zn ferrite/silica composite from room temperature to 300°C. At first, the initial permeability increases from room temperature to 50°C and then it slowly decreases with an increase in the temperature from 50 to 300°C. This may be due to the non-magnetic (silica) phase present in the composite. The silica phase may act as a barrier to the domain wall motion and it is more effective when increasing the temperature. The maximum initial permeability of about 25 is obtained for both samples at 50°C. The same order of value has been reported for Ni-Zn ferrite with lower zinc concentration [16]. Ni-Zn ferrites with lower zinc concentration ($Ni_{0.8}Zn_{0.2}Fe_2O_4$) are likely to have relatively less amount of Fe^{2+} as the probability of zinc evaporation would be less in those ferrites. Because of the lower zinc concentration present in the composite the Curie point may occur at above 300°C.

The AC-resistivity decreases as the frequency increases from 1 kHz to 13 MHz and is shown in Fig. 4. Highest AC-resistivity of 5.84×10^5 Ωcm at 1 kHz and 4.37×10^5 Ωcm at 10 kHz is obtained at 20°C for samples containing 34 and 52 vol% Ni-Zn ferrite respectively. The resistivity of the ferrites is expected to decrease with an increase in the frequency; this may be due to the low dielectric constant and also depends on the porosity and composition [17].

TABLE I Physical properties of $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composites sintered at 1250°C

Ni-Zn ferrite:Silica (vol%)	Theoretical density (gm/cc)	Bulk density (gm/cc)	True density (gm/cc)	Porosity (%)	Linear shrinkage (%)
34:66	3.54	2.97	3.12	5.6	19.9
52:48	4.06	3.38	3.51	5.2	19.8

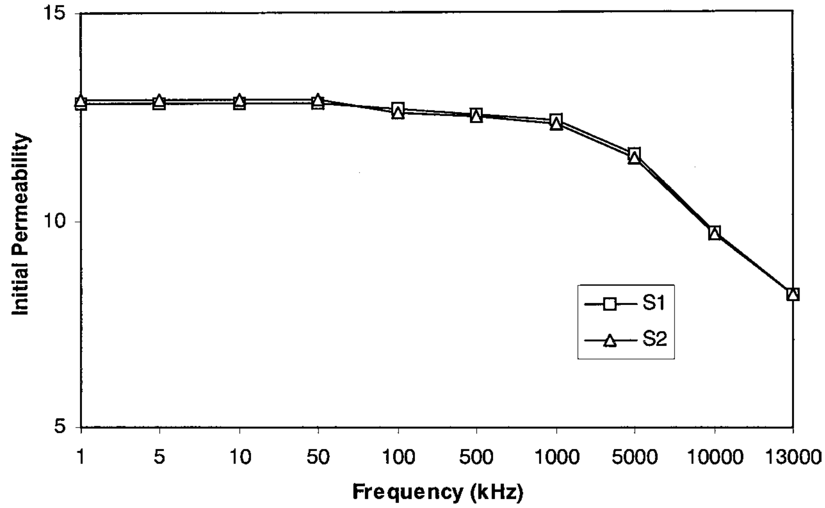

Figure 2 Variation of initial permeability as a function of frequency for $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite sintered at 1250°C.

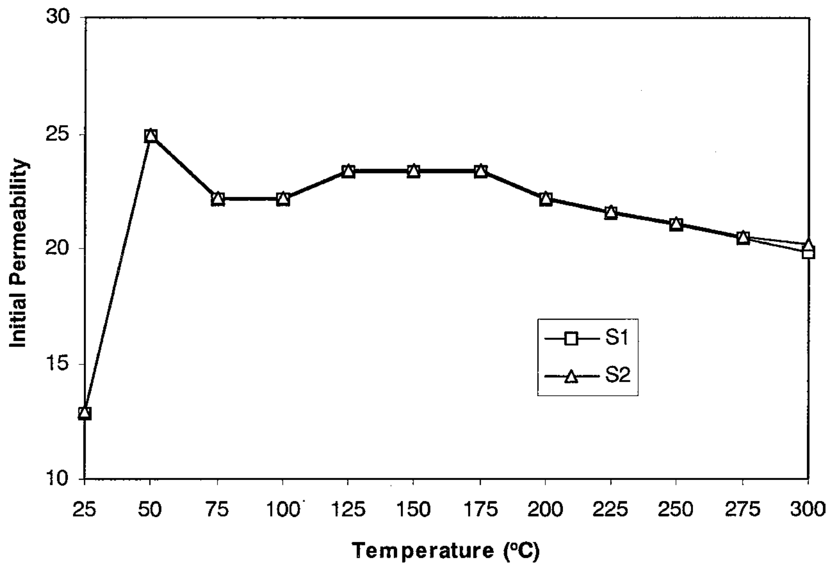

Figure 3 Variation of initial permeability as a function of temperature for $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite sintered at 1250°C.

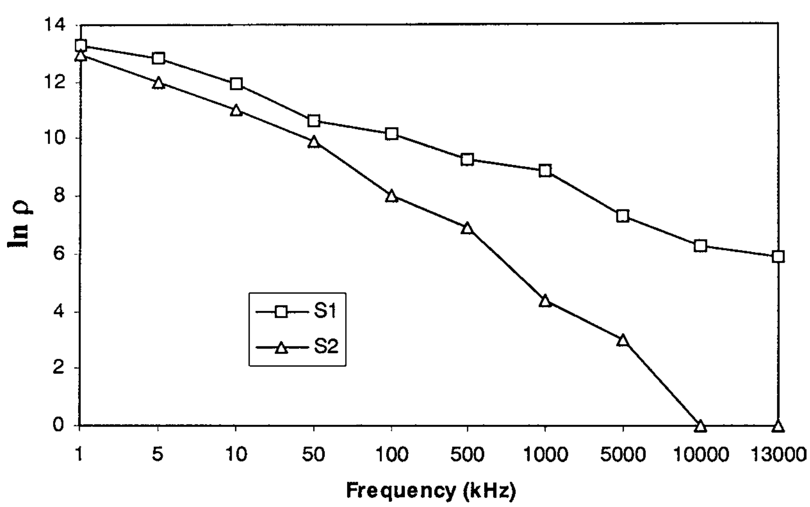

Figure 4 Variation of AC-resistivity as a function of frequency for $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite sintered at 1250°C.

Fig. 5 shows the DC-resistivity as the function of temperature from room temperature to 300°C and it has been observed that the resistivity increases with the temperature, attains a maximum and then decreases with the increase in the temperature. The variation obtained is not much even at high temperature. The DC-resistivity of 1.32×10^8 Ωcm is obtained at room temperature and 1.41×10^7 Ωcm is obtained at 300°C for samples containing 34 vol% of Ni-Zn ferrite. A maximum of 1.61×10^8 Ωcm is obtained for the sample

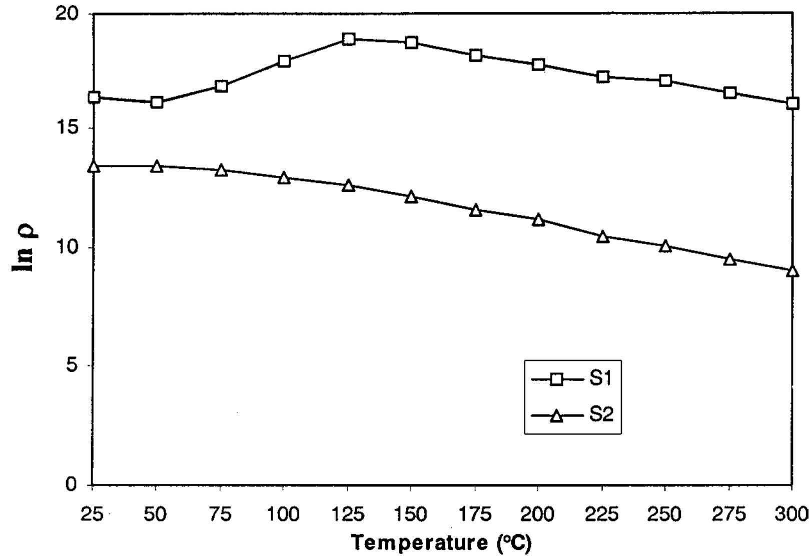

Figure 5 Variation of DC-resistivity as a function of temperature for $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite sintered at 1250°C.

containing 34 vol% Ni-Zn ferrite at 150°C. For the other sample containing 52 vol% Ni-Zn ferrite, the resistivity gradually decreases with the increase in the temperature up to 300°C. The resistivity observed at room temperature is 2.49×10^6 Ωcm and at 300°C is 1.32×10^4 Ωcm. From the Fig. 4 it is clear that the composite containing lower vol% of Ni-Zn ferrite have higher resistivity of the order of $\geq 10^8$ Ωcm. It is expected that the increase in the vol% of SiO_2 leads to increase the resistivity of the composite. The silica present in the composite acts as insulating agent for Ni-Zn ferrite grains increases the effective area of grain boundaries thus increases in resistivity of the composites. The decrease in resistivity is not much while increasing the temperature and it is maintaining even at high temperature. The value of resistivity also depends on concentration of zinc. Lower zinc content results in high resistivity. Verma *et al.* [18] and Satyanarayana *et al.* [19] reported high values of resistivity for Ni-Zn ferrites having lower zinc concentration.

Dielectric dispersion can be explained on the basis of space charge polarization which is a result of the presence of higher conducting phases (grains) in the insulating matrix (grain boundaries) of dielectrics, causing localized accumulation of charge under the influence of an electric field. Fig. 6 shows the variation in the dielectric constant as the function of frequency at room temperature. It is observed that the dielectric constant decreases with increasing frequency and Ni-Zn ferrite content. The maximum value of dielectric constant is obtained at 1 kHz. A steep fall of dielectric constant is observed for samples containing 34 vol% (S1) of Ni-Zn ferrite. The theoretical study shows that the dielectric constant (ε') and dielectric loss ($\tan\delta$) are inversely proportional to the angular frequency (ω) while the AC-electrical conductivity (σ_{AC}) is directly proportional to ω [20–22].

$$\sigma_{AC} = 1/\rho_{AC} = 4\pi\omega\, \varepsilon' \tan\delta$$

where π is a constant. The decrease in AC-electrical resistivity (ρ_{AC}) with the increase in frequency suggests that these results satisfy the above expression. Fig. 7 shows the variation in dielectric loss as the function

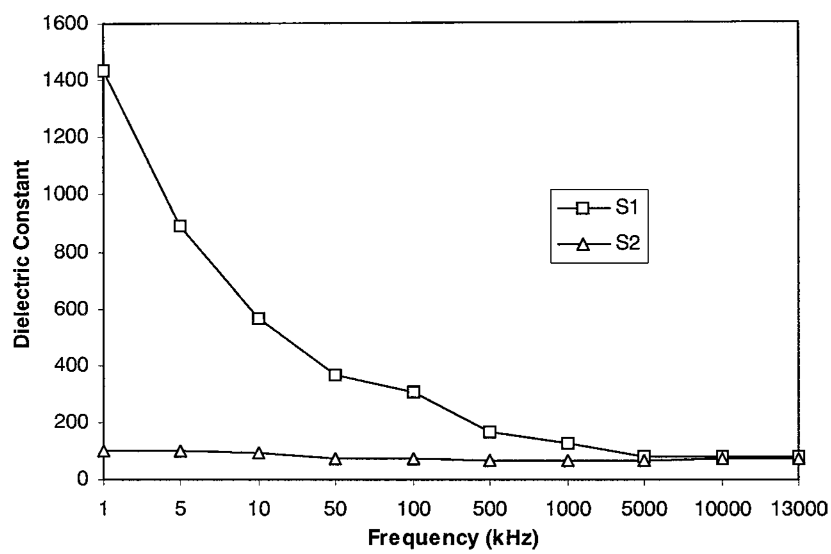

Figure 6 Variation of dielectric constant as a function of frequency for $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite sintered at 1250°C.

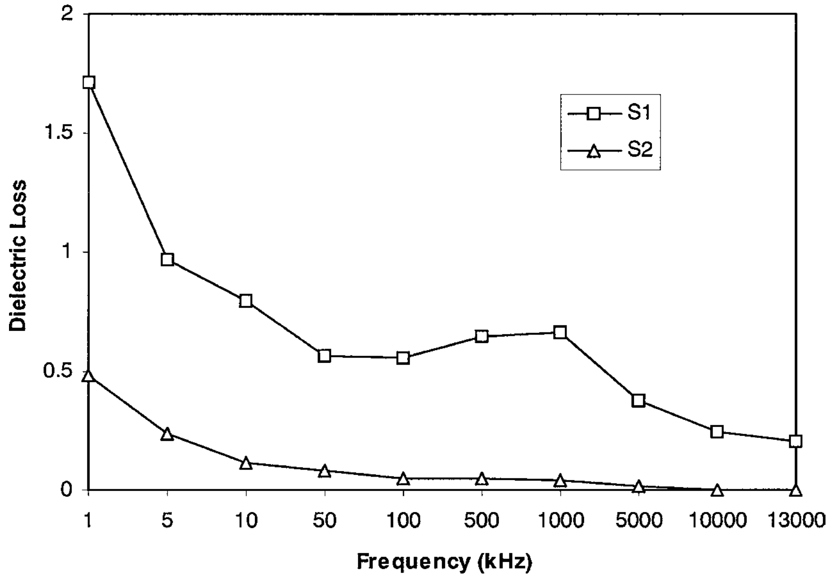

Figure 7 Variation of dielectric loss as a function of frequency for $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite sintered at 1250°C.

of frequency. The dielectric loss arises due to lag of the polarization behind the applied alternating electric field and is caused by the impurities and imperfections in the crystal lattice. It is observed that the dielectric loss decreases with increase of frequency. Both the dielectric constant and dielectric loss decrease as the frequency increases. Density plays an important role in the variation of dielectric constant. Higher porosity and low density results in lower dielectric constant and dielectric loss. It can be seen from the dielectric loss curve that they are frequency dependent.

The microstructure was analyzed by scanning electron microscope for fractured surfaces of the samples sintered at 1250°C. The photographs are shown in Fig. 8. The fracture surfaces of the sintered samples show the presence of Ni-Zn ferrite grains of 1–2 μm size are embedded in the silica matrix.

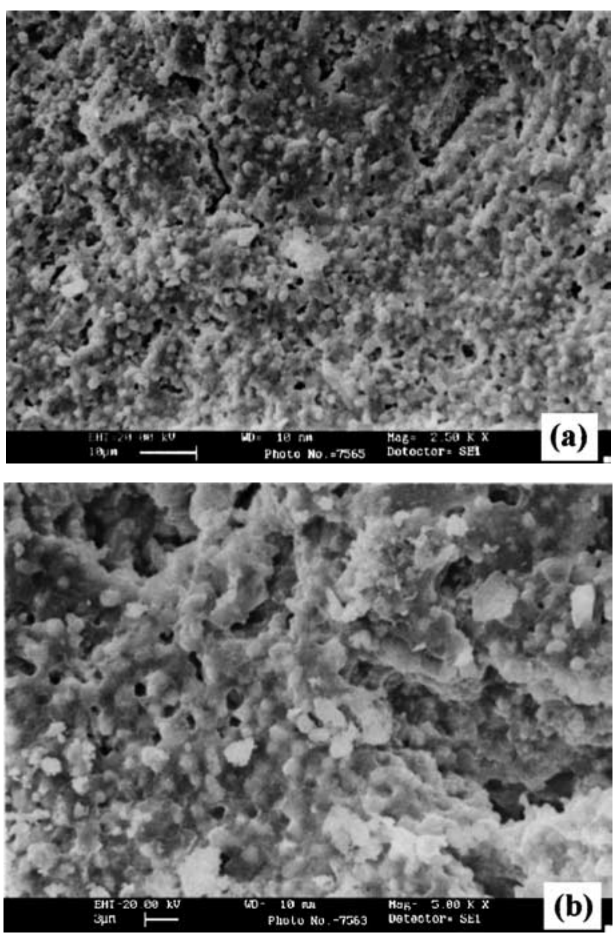

Figure 8 Microstructure photographs (a and b) of fracture surfaces of $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite sintered at 1250°C.

4. Conclusions

The $Ni_{0.8}Zn_{0.2}Fe_2O_4$/silica composite were prepared by sol-gel technique for two different vol% of Ni-Zn ferrite. The samples were sintered at 1250°C and characterized into physical, electrical and magnetic properties. An agreeable permeability value is obtained which makes these composites effective at high frequencies. High resistivity is obtained even at high temperature. The dielectric constant and dielectric loss decrease as the frequency increases exhibiting the normal behavior of ferrites. The Ni-Zn ferrite grains of 1–2 μm size are found in the silica matrix. The results obtained in the present investigation thus show better quality ferrites, which can be used at high frequencies and at high temperatures.

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