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EFFECT OF ADDITIVES ON THE MICROSTRUCTURE AND COMPLEX PERMEABILITY OF Ni-Zn FERRITES

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Polycrystalline nickel-zinc ferrites with the formula $Ni_{0.65}Zn_{0.35}Fe_2O_4 + x.\ Nb_2O_5 / V_2O_5$ where *x* values ranging from 0.0 wt% to 1.5 wt% in steps of 0.3 wt% have been prepared by conventional ceramic technique. The samples were sintered for 4 hours in air at 1250 °C in case of niobium containing ferrites and at 1210 °C in case of vanadium containing ferrites followed by natural cooling. The XRD analyses of the samples confirm single phase cubic spinel structures. Microstructures of the materials reveal that vanadium additions resulted in fine grain structures with grain sizes of 4.9 µm whereas niobium additions promoted grain growth with an increase in grain size from 5.7 µm to 13.2 µm when the niobium concentration is increased from 0.6 wt% to 1.5 wt%. Permeabilities of these ferrites exhibit stable frequency responses up to 2 MHz beyond which the real part decreases sharply and the imaginary part increases to have a peak in each case at the relaxation frequency. The results are explained in terms of the modifications in microstructures brought about by the niobium/vanadium additions.

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1. Introduction

Microstructure dependent ferrite properties such as permeability and permeability spectra depend heavily on composition, impurity levels and sintering conditions [1]. There have been many reports in establishing correlations between permeability and grain size [2-3]. Besides, the density and pore structure also play a vital role in determining the permeability of a ferrite. In order to influence the microstructural features, many efforts were made by several workers either by introducing small quantity of impurities or by altering the sintering schedules [4-5]. The essence of all these studies indicates that microstructures can be modified to desired levels by controlled additions of impurities.

Development of a high quality cost effective loss less high frequency ferrite material for power applications is an ever challenging aspect for investigation [6]. Important requirements for materials of this kind are high saturation magnetisation and low core losses. Core losses arise mainly from two sources, i.e., eddy current losses and hysteresis losses. Poly crystalline Ni-Zn ferrites find their utility for power applications at frequencies over 1 MHz because they have the advantage of curtailing eddy current loss component due to their higher electrical resistivities. In order to keep the other loss component at low, one must have higher magnetic permeabilities and fine microstructures. Hence, careful design of composition and optimum sintering schedule are necessary to obtain the desired properties that can push up the operating frequency of the material beyond 1 MHz.

Among all Ni-Zn ferrites, the composition that results highest room temperature saturation magnetisation, $Ni_{0.65}Zn_{0.35}Fe_2O_4$ is considered as basic composition for the present study. Since higher valent additions are reported to improve the core losses in Mn-Zn ferrites [7], it is aimed at studying with these additions of niobium and vanadium ions in the above Ni-Zn ferrite composition. This paper reports and discusses the effect of niobium and vanadium additions on the microstructure and microstructure related permeability and permeability spectra.

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2. Experimental details

Polycrystalline Ni-Zn ferrites with the formula $Ni_{0.65}Zn_{0.35}Fe_2O_4$ + x Nb_2O_5 / V_2O_5 where x values ranging from 0.0 to 1.5 wt% in steps of 0.3 wt% have been prepared by conventional ceramic technique. Sintering of the niobium containing samples was carried out at 1250 °C for 4 hours and those of vanadium containing samples at 1210 °C for 4 hours in air atmospheres followed by natural cooling. X-ray patterns of the samples confirm single phase cubic spinel structures. Characterisation of the samples was further done by measuring lattice constant, Curie temperature and saturation magnetization of the basic composition $Ni_{0.65}Zn_{0.35}Fe_2O_4$ which compare well with the respective parameters of the same composition reported earlier [8]. Micrographs are taken on fractured samples using Philips XL-50 microscope and permeability measurements are made on toroidal samples with 20 turns winding from 10 kHz to 10 MHz using HP 4192A Impedance Analyzer. Magnetisation measurements made by VSM and sintered density measurements by Archimedes principle are also given for the sake of in depth analyses of the results obtained.

3. Results and discussion

Values of sintered density, saturation magnetization and grain size for both niobium and vanadium doped systems are listed in Table 1. Though the sintering temperature is slightly lesser for vanadium doped samples, the undoped ferrite ended with slightly higher density for that system. All these three parameters showed little variation with dopant concentration in vanadium doped system, while they are marked by significant variations in niobium doped samples.

Table 1. Sintered density, saturation magnetization and grain size data of $Ni_{0.65}Zn_{0.35}Fe_2O_4 + x\, Nb_2O_5/V_2O_5$.

.	Sintered density, g/cm^3		Ms, emu/g		Grain size, μm	
wt%	Nb_2O_5	V_2O_5	Nb_2O_5	V_2O_5	Nb_2O_5	V_2O_5
0.0	4.910	4.921	73.5	78.5	-	4.9
0.3	4.717	4.939	78.3	78.0	-	4.9
0.6	4.796	4.903	79.2	78.3	5.7	4.9
0.9	4.992	4.896	78.2	77.9	7.3	4.9
1.2	4.865	4.900	77.7	77.1	9.7	4.9
1.5	4.771	4.872	78.3	75.5	13.2	7.8

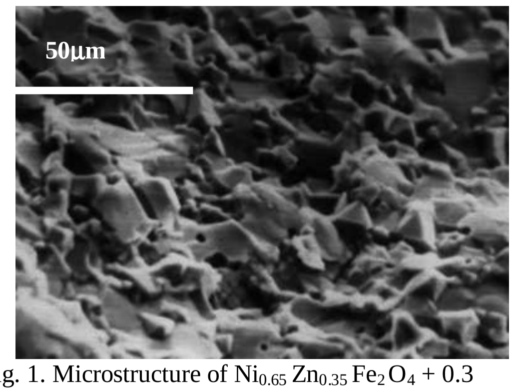

Fig. 1. Microstructure of $Ni_{0.65}Zn_{0.35}Fe_2O_4$ + 0.3 wt% Nb_2O_5 (intergranular bridges to complete).

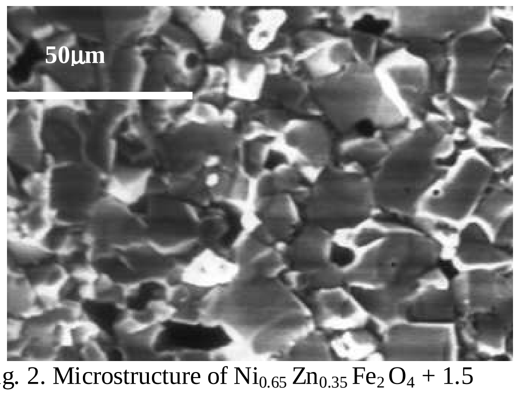

Fig. 2. Microstructure of $Ni_{0.65}Zn_{0.35}Fe_2O_4$ + 1.5 wt% Nb_2O_5 (grain size=13.2 μm with open pores).

Niobium additions initially, perhaps due to under firing, inhibited densification process, but once these ions enter lattice and dissolve in the matrix the densification enhances with increase in niobium concentration till 0.9 wt%. Beyond this concentration, the density has been observed to decrease. These results are complemented by the microstructures of the corresponding samples as shown in Figs. 1 and 2. Typical microstructures for two different niobium concentrations of 0.3 wt% and 1.5 wt% respectively are shown in the figures. The intergranular bridges with discontinuous grain growth in the microstructure of 0.3 wt% concentration reveal that the densification process is yet to be completed. Subsequent concentrations promoted grain growth as evidenced by the increase in grain size from 5.7 µm at 0.6 wt% concentration to 13.2 µm at 1.5 wt% concentration. Despite this increase in grain size, particularly at higher doping levels, the sintered density is decreased mainly because of the increased grain boundary phase at these concentrations. The deeply extended grain boundaries with pore size of approximately 1.3 µm in the microstructure of Fig. 2 provide evidence for the decreased densities.

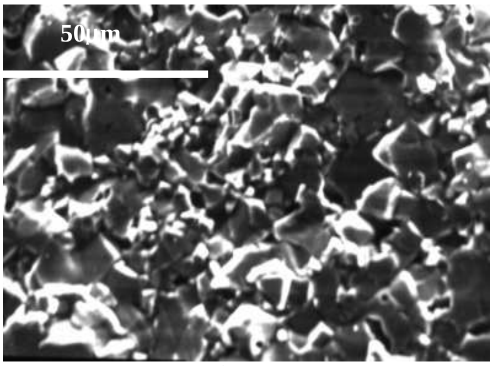

Fig. 3. Microstructure of $Ni_{0.65}Zn_{0.35}Fe_2O_4$ + 0.6 wt% V_2O_5 (grain size=4.9 µm with open pores).

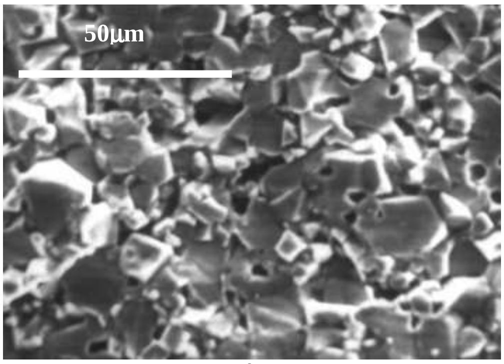

Fig. 4. Microstructure of $Ni_{0.65}Zn_{0.35}Fe_2O_4$ + 1.5 wt% V_2O_5 (grain size=7.8 µm with closed pores).

Vanadium additions, due to their low melting point, seem to promote densification even at 0.3 wt% concentration. Simultaneously, it may melt and form a liquid film at grain boundaries and thereby inhibits the grain growth [9]. This argument holds good for the whole range of concentrations supported by the fine and uniform microstructures and consistent grain size of 4.9 µm for these samples, except for the sample with 1.5 wt% vanadium concentration. Typical microstructure of 0.6 wt% niobium doped sample is shown in Fig. 3. If V_2O_5 is over doped, it leads to a rapid grain growth in which pores would be trapped within the grains as evidenced by the microstructure, as shown in Fig. 4, of this sample.

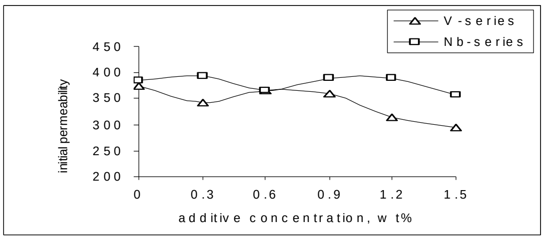

Fig. 5. Variation of initial permeability, μ_i with additive concentration, x at 10 kHz of the system $Ni_{0.65}Zn_{0.35}Fe_2O_4 + x\,Nb_2O_5/V_2O_5$.

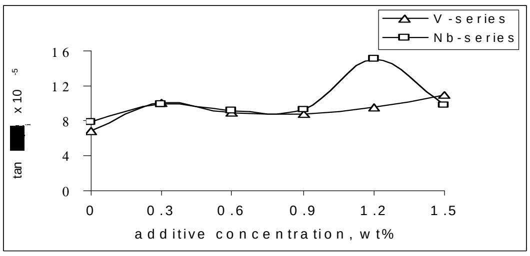

Fig. 6. Variation of tan δ/μ_i with additive concentration, x at 1 MHz of the system $Ni_{0.65}Zn_{0.35}Fe_2O_4 + x\,Nb_2O_5/V_2O_5$.

Variation of initial permeability with additive concentration at 10 kHz for both niobium and vanadium doped systems is shown in Fig. 5. The initial permeability values of niobium doped samples exhibit slight variation except for two samples. The lower value at 0.6 wt% concentration is further verified by making measurements again and this may be attributed to lower grain size of that sample. Whereas, the lower value of initial permeability at 1.5 wt% concentration, despite the large grain size of this sample, may be understood in terms of its pore filled microstructure and low sintered density. Similarly, the permeability values in vanadium doped samples can also be explained by the microstructural changes brought about by the addition of vanadium ions in these ferrites. Because of its low melting point, the vanadium oxide melts at grain boundaries and initially acts as grain growth inhibitor. Usually at low doping levels, the vanadium ions penetrate in the lattice inducing slow modifications of the microstructures marked by fine grains and grain boundary melts as secondary phases. These imperfections tend to pin the domain walls from bulging, thereby having bad influence on the magnetic performance of the ferrite. At higher concentrations, because of the rapid grain growths as described earlier, the grain size increases and also, besides grain boundary phases, a large number of small closed pores are being trapped inside the grains. These pores and secondary phases have demagnetizing influences and lower the magnetization as well as permeability [10]. The observed lower values of permeability and magnetization at higher concentrations of vanadium doped samples are in agreement with the above considerations.

Variation of relative loss factor, tan δ/μ_i with additive concentration at 1 MHz for both niobium and vanadium doped systems is shown in Fig. 6. The variations show similar trends in both the systems except for one concentration at 1.2 wt% for niobium series. The magnitude of the tan δ/μ_i values has been observed to be in good order, but the trends contrary to expectations are not declined to the required levels. This may be explained as follows: Since the basic composition in the present study is a high room temperature saturation magnetization ferrite among the entire Ni-Zn series, the niobium or vanadium additions in that system have not shown much improvement in magnetization. Also, the sintered densities and the microstructures of these ferrites due to their secondary phase imperfections and porosities contributed very little to improve the initial permeability. As a result, the relative loss factor has been observed to be slightly more for the doped samples compared to the undoped samples in both the systems. However, optimum sintering schedule in combination with minor compositional modifications in these ferrites to push up resonances would provide better tan δ/μ_i values at least up to few megahertz.

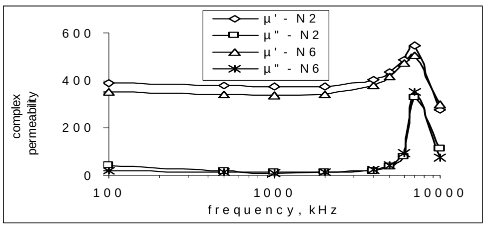

Fig. 7. Variation of real and imaginary parts of initial permeability for 0.3 wt% and 1.5 wt% concentrations of $Ni_{0.65}Zn_{0.35}Fe_2O_4 + x\,Nb_2O_5$.

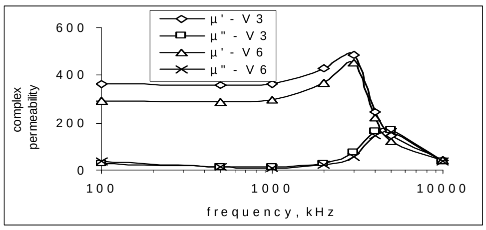

Fig. 8. Variation of real and imaginary parts of initial permeability for 0.6 wt% and 1.5 wt% concentrations of $Ni_{0.65}Zn_{0.35}Fe_2O_4 + x\,V_2O_5$.

The variations of real and imaginary parts of initial permeability for both niobium and vanadium doped systems are shown in Figs. 7 and 8. The samples exhibit fairly stable response up to a few megahertz, beyond which the real part of the permeability decreases rapidly while the imaginary part exhibits a peak related to relaxation phenomena [11]. Interestingly, the frequency at which the dispersion takes place has been observed to be higher for higher permeability samples in these systems. Further, the imaginary part of the permeability in either of the systems has not been marked by broad peaks as was normally the case with relaxation. Phase difference between the applied field and magnetization of the ferrite occurs normally due to the damping of either spin motions or domain walls. If there is no damping, the imaginary part is zero for all frequencies except at relaxation frequency. But, magnetic relaxations appear as μ' decreases with increasing frequency and μ'' has a maximum near the relaxation frequency. The μ'' in both niobium and vanadium doped samples in the present study is not marked with maximum values good enough for relaxation. Then, if the permeability relaxation phenomena in ferrites can not be solely explained as a superposition of domain wall motion and spin rotation, it may well be related to the behaviour of the electromagnetic waves within the core [12]. This had been well demonstrated in earlier case [13] as a resonance due to sample dimensions in Mn-Zn ferrites. Thus, the effects of both relaxation due to damping of spins and domain walls and resonance due to sample dimensions are responsible for the observed behaviour of permeability spectra in these ferrites.

4. Conclusions

Pentavalent niobium additions in nickel-zinc ferrites initially inhibited densification process. As the doping level is increased, it enhances densification up to 0.9 wt% concentration and then the density decreases again. The microstructures of niobium added samples reveal that the lower concentrations of niobium do not promote grain growth under the given sintering conditions. However, increased additions of niobium promotes grain growth and the grain size increases; but the microstructures at higher concentrations are marked by large grains with deeply extended inter granular pores and secondary phase imperfections. The initial permeability values of these samples closely follow the microstructures.

Vanadium added nickel-zinc ferrites seem to have produced better densities due to the low melting point of vanadium pentoxide. Because of this melting, these ions form a thin grain boundary film, which impedes grain growth; thus the grain size is observed to be invariable throughout except for the sample with 1.5 wt% concentration. Over addition of vanadium for this sample brings in rapid grain growth with higher grain size and large number of small closed pores inside the grains in its microstructure. Initial permeability variation with composition for these samples is also closely followed by their microstructures.

Frequency responses of real and imaginary parts of permeability have been stable up to a few megahertz and beyond this frequency the real part is experienced a sudden fall in both the systems. Since the imaginary part does not exhibit maximum values at relaxation frequency in either of the systems, the behaviour of complex permeability dispersion is explained as a combined effect of both relaxation due to damping of spin motions and domain walls and resonance due to sample dimensions.

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