Synthesis and Properties of Ni-Zn Nano Ferrite by Citrate Precursor Method for High Frequency Applications

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Abstract

Ni-Zn ferrite nanoparticles of the system, $Ni_{0.65}$ $Zn_{0.35}$ Fe_2 O_4, were synthesized by a soft chemical citrate precursor method. These nanoparticles were annealed at different temperatures from 400^0C to 1300^0C for improved crystallization. All the samples were then characterized by X-ray diffraction, Curie temperature and ponderometer techniques.The XRD patterns confirm spinel structures while the calculated volume density (4.5gm/cm3) and particle sizes, ranging from 27 to 135nm, increase with the increase in heat treating temperature.The resistivity of the ferrite is found to vary from (0.12×10^7 -6.28×10^8 Ω-cm) for different annealing temperatures andthe increase in the crystalline size leads to decrease in the resistivity for higher sintering temperaturesfrom 1000^0c.The value of saturation magnetization per unit mass have been observed to be 83emu/gm. for the sample annealed at 1100^0c, the highest value for Ni-Zn ferrites so far reported.The Curie temperature is observed to be the same for all the samples (385^0C) which is in close agreement with that of the reported.

Keywords: *Ni-Zn Ferrites, Nanoparticles, Citrate PrecursorsMethod, Crystalline size, Resistivity, Saturation Magnetization.*

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1. Introduction.

Ferromagnetic polycrystalline materials have been under intense research for so long due to their useful electromagnetic characteristics for a large number of applications like biomedical applications which need combined properties of high Saturation Magnetization and Biocompatibility.[1,2] The performance of these materials in their bulk form where the grain dimensions are in micrometer scales is limited to a few megahertz frequency [3 ,10] due to their higher electrical conductivity and domain wall resonance. However, the recent technological advances in electronics industry demand even more compact cores for work at higher frequencies [4].One way to solve this problem is by synthesizing the ferrite particles in nonmetric scales before compacting them for sintering. When the size of the magnetic particle is smaller than the critical size for multidomain formation, the particle is in a single domain state. Domain wall resonance is avoided, and the material can work at higher frequencies. Ferrite particles in Nano scales can be produced by soft chemical methods, such as co-precipitation, sol-gel and hydrothermal synthesis [5-7]. Among these methods, the citrate precursor method has been little reported [8]. . So it is chosen in the present study as the

conditions of synthesis in this method are highly controllable, simple, and further it provides homogeneous powders of highest yield and superior properties at temperatures close to 100^0C[8 ,9].This paper reports and discusses the results of synthesis and characterization of Ni-Zn ferrite nanoparticles with respect to the heat treating temperature.

2. Experimental Details

In the present study Nickle–Zinc ferrite samples with composition $Ni_{0.65}Zn_{0.35}Fe_2O_4$ have been prepared by Citrate precursor method. Nickle Nitrate, Zinc Nitrate,Iron Citrate and citric acid were taken as initial ingredients and are accurately weighed in stoichiometric proportions.An aqueous solution of Fe Citrate was prepared in distilled water. Nickle Nitrate and Zinc Nitrate were separately mixed with citric acid and a few drops of distilled water and heated at about 40^0C for half an hour to form the metal citrate complex. These solutions were then added slowly to the above prepared Fe citrate solution with constant stirring to avoid precipitation and obtain a homogenous mixture.The continuous mixing of this solution results a clear transparent brown colouredgel which decomposes at 100^0C and leads to the formation of a fine black powder. The powder thus obtained was made into pellets by adding 15% polyvinyl alcohol in small quantity as binder.A pressure of 4 ton/inch^2 was applied on all the pellets having a diameter20mm.All these pellets were then fired at various temperatures ranging from 400^0C-1300^0C in air for one hour in steps of 100^0C.Necessary Grinding of the pellets was done in order to remove the formation of any kind of oxide layer during sintering.

The Nano ferrite has been subjected to X-ray powder diffraction (Joint committee on powder Standard (JCPDS) and Curie temperature techniques to obtain experimental lattice constant and curie temperature values.It is known that these parameters are independent of micro structure and dependent on composition.Experimentally observed parameters of composition $Ni_{0.65}Zn_{0.35}Fe_2O_4$ in nano form are compared with those of the reported values of the same composition in bulk form and found in good agreement.

3.Results and Discussion

XRD patterns of all the samples of $Ni_{0.65}$ $Zn_{0.35}$ Fe_2 O_4 annealed at different temperatures from are shown in Fig (3.1-3.7) from 400^0C-1300^0 C The samples exhibit all the peaks indicative of single phase spinel crystal structure with increased crystalalinity with the increase in annealing temperature. The increase in sharpness of XRD peaks with the increase in annealing temperature indicates the growth in crystallite size. The calculated value of lattice constant(8.375) for the said composition has been estimated to be in good agreement with that of the reported [2] and the observed value of lattice constant remains unchanged with annealing/sintering temperatures as shown in fig [3].

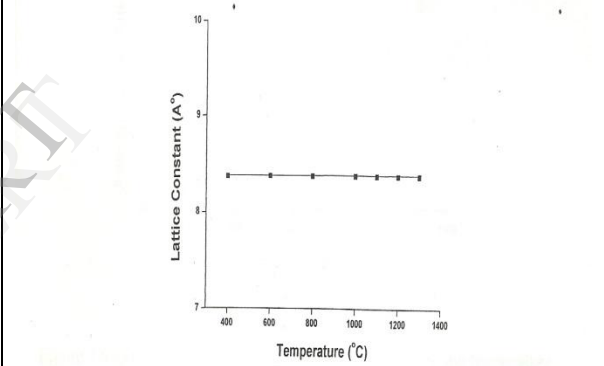


Fig 3.Lattice constant versus annealing/sintering temperature

The average crystalline size D has been calculated from the experimentally observed broadening of intense (311) peak of x-ray Diffraction pattern and the Scherrer Equation. The gradual increase in thevalue of average crystalline size from 27nm[10] has been noticed with increase in temperature upto800^0C followed by a steep rise in the value for further increase in temperature [12].This rise in the value of the crystalline size may be attributed to the rapid grain growth that occurs at higher sintering temperatures as shown in fig (3.8).

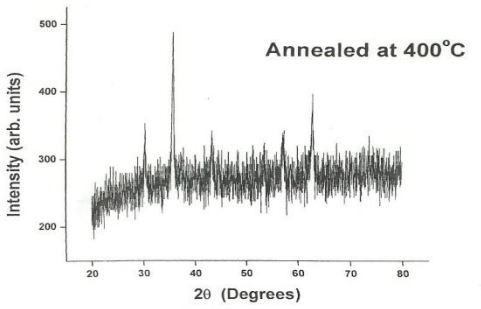


Fig 3.1 X-ray diffraction patterns of Ni Zn ferrite annealed at 400^0C

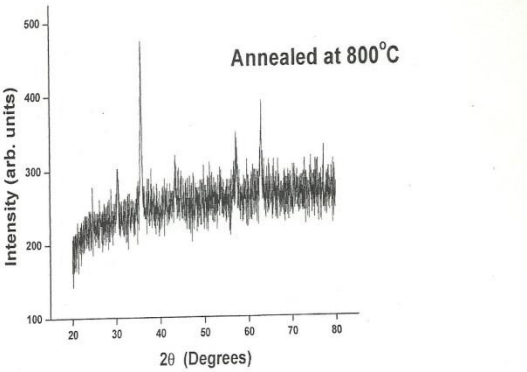


Fig 3.3 X-ray diffraction patterns of Ni Zn ferrite annealed at 800^0C

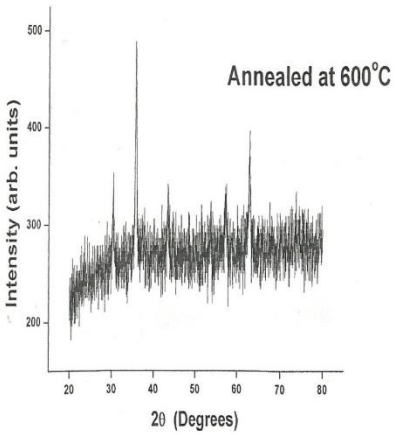


Fig 3.2 X-ray diffraction patterns of Ni Zn ferrite annealed at 600^0C

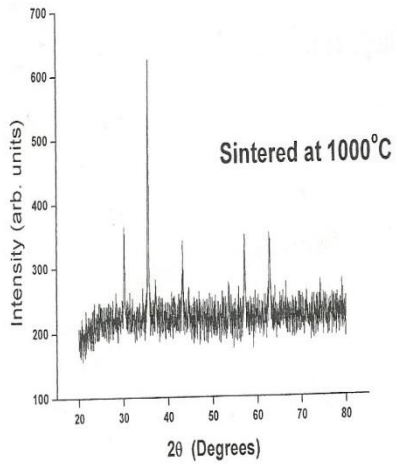


Fig 3.4 X-ray diffraction patterns of Ni Zn ferrite annealed at 1000^0C

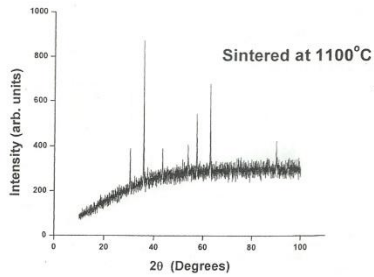


Fig 3.5 X-ray diffraction patterns of Ni Zn ferrite annealed at 1100^0C

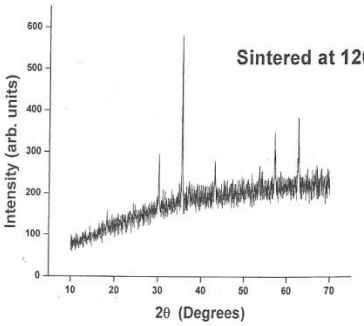


Fig 3.6 X-ray diffraction patterns of Ni Zn ferrite annealed at 1200^0C

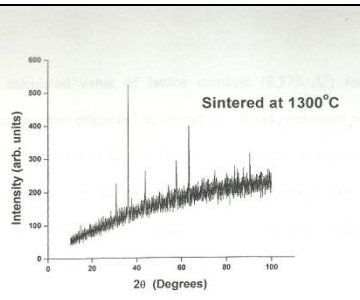


Fig 3.7 X-ray diffraction patterns of Ni Zn ferrite annealed at 1300^0C

The bulk density of the samples was determined and the observed variation in volume density of Ni-Zn ferrite samples is shown in fig (3.9).As the annealing /sintering temperatures increases gradually from 400^0c -1300^0c, aslow increase in density is noticed upto 1100^0C followed by a steep rise beyond 1100^0c.The variations are explained on the basis of the presence of normally available pores and cracks during the formation of a ceramic material.As the firing temperature of the ceramic material increases, the existing available pores, voids and cracks will gradually vanish resulting in the formation of smaller grains.At higher sintering temperatures these smaller grains grow into bigger grains by reducing the number of grain boundaries, thereby enhancing the volume density.The measured value of density at 1300^0c has found to be in good agreement with that of the bulk counterpart[8, 9].

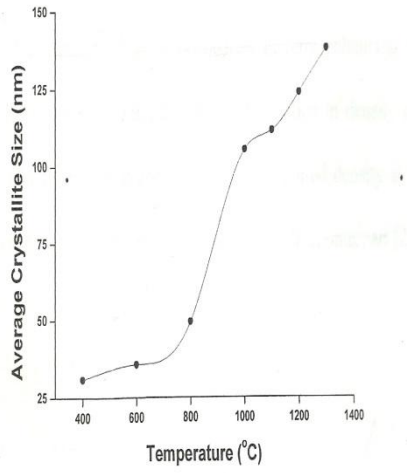


Fig 3.8 Average Crystalline size as a function of processing temperature.

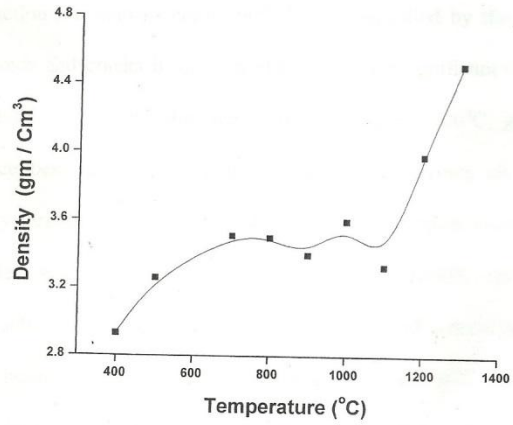


Fig. 3.9 Variation of density as a function of sintering temperature.

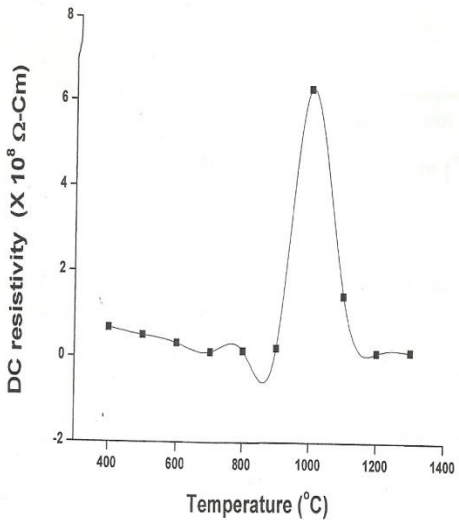


Fig. 3.10 Variation of DC resistivity as a function of sintering temperature.

Dc resistivity of the ferrite samples was measured.Fig (3.10) shows the variation of dc electrical resistivity of Ni-Zn ferrite as a function of annealing/sintering temperatures.As the temperature increase from 400^0 C-1300^0 C ,the resistivity has been observed to remain constant upto 900^0C and thereafter rises sharply for 1000^0c and falls to its initial value at higher sintering temperatures. The dc resistivity is found to be (0.12×10^7 - 6.28×10^8 Ω - cm) has been observed to be less than that of reported[15 ,16] for the Ni-Zn nanoferrite processed through the same method and found to be higher than that of the bulk with the same composition [10]. Resistance decreases with increasing temperature, thus demonstrating semiconducting properties of spinel type. The Activation energies for all the samples have been calculated form the log of resistivity versus 1/T plots(fig3.11), found to increase with increasing annealing/sintering temperatures.The activation energies in the present work are observed to be higher than those(0.1-0.4ev) normally reported in literature[15]for Ni-Znbulk ferrites prepared by the conventional ceramic process.The Activation energy 0.54ev obtained for a particle 0f 130nm sintered at 1300C in in close agreement with the reported [1] through the same process.

Conduction mechanism below 900^0c may be controlled by the presence ofpores, voids and cracks in the material and their insignificant changes with temperature.With increasing temperature at about 1000^0C,grain growth takes place besides minimizing the defects which favours an increase in resistivity through the generation of nano grains with more number of grain boundaries.In addition, considerable amount of zinc loss[19, 20]may exist at higher sintering temperatures resulting in cation vacancies and unsaturated oxygen ions, to enhance the conductivity and hence the activation energies.The Activation Energies in the present work are observed to be higher than those (0.1-0.4ev) normally reported in literature[11] for the one prepared by conventional ceramic process. The excess electrons on oxygen then bond with the neighbouring$Fe3^+$ ions in the spinel lattice due to electro static interaction giving rise to Fe^{2+}. The overall charge balance is restored by oxygen loss from the sample.Formation of Fe^{2+} ions depends on the amount of zinc loss from the sample, which in turn depends on the sintering temperature of the ferrite .Higher the sintering temperature greater is the possibility of Fe^{2+}formation.All these above

effects contribute to the observed variations in dc resistivity and Activation energy with temperature.

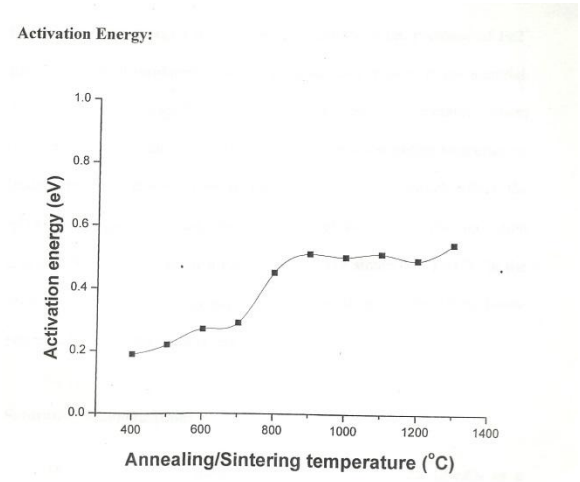
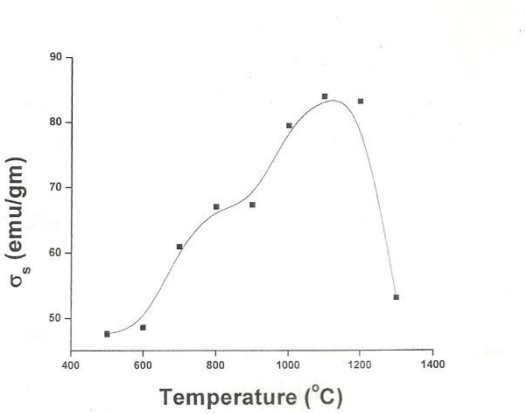


Fig 3.11 Variation of Activation energy with Sintering Temperature.

The saturation magnetization of the samples was measured by the pendulum(ponderometer) method at the saturating field of 2 kilo gaussas described by Rathenav and Snoek.The variation of saturation magnetization increase gradually with increasing of sintering temperatures upto 1100^0c and there after decreases sharply with further rise in temperature.It is amazing in the present work that the value of saturation magnetization per unit mass has been observed to be 83 emu/gm. for the sample annealed at 1100^0c, the highest value for the Ni-Zn so far reported [13 ,14].The observed lower values of saturation magnetization fig (3.12) in case of samples annealed at low temperatures are attributed to the absence of exchange interaction between the nano grains.The observed decrease in the saturation magnetization in the samples sintered beyond 1100 ^{0}c may be due to the volatilization of Zn from the material leading to the formation of vacancies and lattice defects.



3.12 Variation of Saturation Magnetization as a function of sintering temperature.

Table1. Comparision among various parameters in Nano and Bulk Ni – Zn ferrite of studied composition.

Parameter	Observed value in Nano $Ni_{0.65}Zn_{0.35}Fe_2O_4$	Reported in Literature in Bulk $Ni_{0.65}Zn_{0.35}Fe_2O_4$
Density	4.5 gm /cm^3	4.8 gm/cm^3
DC Resistivity	6.28 X 10^8 Ω- cm	4.5 X 10^3 Ω-cm
Saturation Magnetization	83 emu/gm.	77 emu/gm.
Curie Temperature	$385^o \pm 5^o$C	390^0C

Conclusions

In conclusion, the observed results of the materials under investigation are analyzed to the following conclusions:

1. X-ray diffraction patterns confirm that the synthesis of
2. fully crystalline Ni-Zn ferrite nanoparticles can be successfully done at lower temperatures.
3. The Estimated Lattice Parameter was observed to be independent of the sintering temperature.
3. The sudden rise in the crystalline size and Density at 1000^0c was due to the diffusion of nano particles at higher temperatures
4. The Activation Energy and the Dc Resistivity of the ferrite is higher than those of the conventional solid state ceramic route.The increase in the resistivity is due to the presence of more grains and grain boundaries in the sample.
5. The decrease in the value of Saturation magnetization per unit mass coupled with the reasonable value of dc resistivity make this composition suitable for high frequency core applications.

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