Effect of Sintering Conditions on Magnetic Properties of Nanoparticle Mn–Zn Ferrite Synthesized with Nitrilotriacetate Precursor Method

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EFFECT OF SINTERING CONDITIONS ON MAGNETIC PROPERTIES OF NANOPARTICLE Mn—Zn FERRITE SYNTHESIZED WITH NITRILOTRIACETATE PRECURSOR METHOD

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Nitrilotriacetate precursors have been used for synthesis of oxide materials. High permeability Mn—Zn ferrite with general formula \( \text{Mn}_2\text{Zn}_{1-x}\text{Fe}_2\text{O}_4 \) where \( x = 0.3/0.35/0.4/0.45/0.5/0.55/0.6/0.65/0.7 \) were prepared using this novel method. Formation of cubic spinel structure was confirmed by XRD, which also provided information on formation of fine particle material. The magnetic properties of these materials were investigated after sintering the same at 950°C, 1150°C, 1250°C and 1350°C in nitrogen atmosphere and at 1050°C in air and were found to be interesting.

Keywords: Nitrilotriacetate; hydrezinium; nanoparticle; sintering; hysteresis; domain.

1. Introduction

Research in nanomaterials is growing at a dramatic pace since reduced dimensions in the nanometer range alter the properties of the materials. This has opened up enormous possibilities to meet the challenges in different fields like electronics, optoelectronics, medicine, biotechnology, engineering, defense, information technology, etc. Production of efficient devices with new technology can save tremendous amounts of energy, decrease their size and increase efficiency.

Ferrofluids is a relatively new class of magnetic materials, consisting of magnetic nanoparticles colloidalily dispersed in a carrier liquid, exhibit both fluid and magnetic properties. This gives rise to the numerous unusual fundamental phenomena as well as to interesting applications. One of their promising applications is as liquid heat carriers in different heat-exchange devices as well as in devices for...
magnetocaloric energy conversion. Such systems may require ferrofluids with high thermomagnetic coefficients. However, the most widely used ferrofluids with the magnetite nanoparticles do not satisfy these requirements. Therefore the development and synthesis of special temperature-sensitive magnetic nanoparticles for ferrofluids is of great interest. Among the different temperature-sensitive magnetic materials, Zn containing spinel type ferrites $\text{Me}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ are important substances in which variation of content of initial components (Zn substitution degree $1-z$) allows to change their magnetic parameters$^2,3$ in a wide range of values. This helps to obtain materials exhibiting different thermomagnetic coefficients. Moreover, Zn containing ferrites can be obtained in the form of ultra fine particles by using different chemical methods$^4$ such as coprecipitation method, different precursor methods, sol–gel method, hydrothermal synthesis,$^5$ mechanochemical processing, etc.$^6,7$ Among different Zn substituted ferrites Mn–Zn ferrites are preferred due to their lower Curie temperatures and high magnetization, which lead to rather high thermomagnetic coefficients. Crystalline and magnetic properties of bulk Mn–Zn ferrites are well-known. However, properties of ferrite nanoparticles significantly differ from those of a bulk material. Therefore a detailed study of conditions of synthesis and their influence on properties of Mn–Zn ferrite nanoparticles is necessary. Magnetization measurements of these nanoparticles under different conditions may shed some light on the regularities of behavior of their magnetic parameters.

In the present work for synthesis, precursor method which yields ferrites at low temperature with good homogeneity is employed. The samples were characterized using standard techniques. Half-level width of the maximum peak was substituted in Scherrer’s formula to obtain the average size of particles. Samples sintered at different temperatures and environment were then studied for their magnetic properties. The result of this study is quite fascinating.

2. Sample Preparation

The samples were prepared by mixing aqueous solution of metal salts in stoichiometric quantities and aqueous solution of dihydrazinium nitrilotriacetate. Nitrilotriacetate hydrazinate precursor of mixed metal ions, so formed in solution, was obtained in dry form and ignited. Autocombustion of dry product results in formation of mixed oxides. As the mixed oxides are produced at low temperature, the particle size obtained is small. The mixed oxide samples in powder form were subjected to chemical analysis, XRD, IR spectroscopy and SEM. The percentage yield, X-ray diffraction pattern, IR pattern, and the lattice constant confirm the formation of mixed ferrites. The broadening of XRD peaks indicates formation of fine particle material. The fine powdered samples were then pressed into pellets of dimension 1 cm diameter and thickness, ranging between 2 mm and 3 mm for further investigations.
3. X-Ray Powder Diffraction

X-ray powder diffraction allows identification of crystalline structure of the samples. X-ray powder diffraction patterns were obtained on the automated Rigaku and Siemens diffractometer, Cu-Kα radiation source with the wavelength $\lambda = 1.54183 \text{ Å}$ was used for the purpose.

A typical X-ray powder diffraction pattern obtained for Mn–Zn ferrite fine particle powder (Mn$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$) is shown in Fig. 1. Widening of peaks is related to the size of crystallites. The mean diameter of particles was determined from the measurements of the widening at half height using Scherrer’s formula. The mean diameter of the particles calculated was found to vary from 4.46 nm to 25.276 nm.

From the experimental values of $\theta$, “a” the lattice constant was calculated using standard method. The values obtained are in good agreement with the reported values. The decrease in the lattice constant with increase in Zn concentration $(1-x)$ may be attributed to the replacement of small size Fe$^{3+}$ ions by large size Zn$^{2+}$ ions in the tetrahedral site. Fe$^{3+}$ has an ionic radius of 0.63 Å whereas Zn$^{2+}$ has an ionic radius of 0.78 Å.

4. Scanning Electron Microscopy (SEM)

Pictures of samples taken on Scanning Electron Microscope, Fig. 2, shows surface morphology of unsintered Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ sample and when pellets of the same sample are sintered in nitrogen atmosphere.
5. Infra-Red (IR) Absorption Spectroscopy

Infra-red (IR) absorption spectroscopy allows us to identify the spinel structure as well as the presence of certain types of chemical substances adsorbed on the surface of particles. IR spectra of dried samples were recorded in the wave range of 4000-200 cm\(^{-1}\).

(1) \(\text{Me}_T \longrightarrow \text{O} \longrightarrow \text{Me}_O\) stretching vibration 600-550 cm\(^{-1}\),
(2) \(\text{Me}_O \leftrightarrow \text{O}\) stretching vibration 450-385 cm\(^{-1}\),
(3) \(\text{Me}_T \leftrightarrow \text{Me}_O\) stretching vibration 350-330 cm\(^{-1}\),

where O is oxygen, \(\text{Me}_O\) is metal in the octahedral site and \(\text{Me}_T\) — in the tetrahedral site. The metal–oxygen absorption bands (1) and (2) are characteristically
pronounced for all spinel structures and for ferrites in particular. The band (3) is less intensive than bands (1) and (2). Sometimes it merges with the band (2) and gives one wide band at 420–330 cm\(^{-1}\) as seen in the absorption spectra, Fig. 3.

Comparison of the IR-spectra of samples taken for different values of “x” as well as comparison of the same with Mn–Zn ferrite treated at high temperature allows understanding of the product structure transformations. The chemical compositions were confirmed by chemical analysis, EDS studies were carried out on Joel Model 840 (SEM) to confirm the composition and to determine percentage content of Mn, Zn, Fe and O.

6. Magnetic Properties

Sample preparation for measurements:

(i) The fine powders were pressed into pellets of the size 10 mm in diameter and thickness ranging between 2 mm and 3 mm were used for measurements. Saturation magnetization, AC susceptibility measurements, and Curie temperature measurements were made for the powdered sample.

(ii) Five sets of pellets were then sintered in the furnace at 950°C, 1050°C, 1150°C, 1250°C and 1350°C in nitrogen atmosphere for 3 h and were allowed to cool at a natural cooling rate. The pellets were then used for making similar measurements as in (i).

(iii) Another set of pellets were sintered at 1050°C for 24 h in air. There was no control over heating rate as well as cooling rate of the sample. Measurements on these samples were then made as in (i).
Saturation magnetization curves, Fig. 4, show a high value for $M_s$ equal to 75.9 emu/g for unsintered Mn$_{0.55}$Zn$_{0.45}$Fe$_2$O$_4$ sample whereas profiles of all sintered samples show maxima for Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ sample. The maximum saturation magnetization values for sintered samples are lower, as compared to the fine particle unsintered sample. The highest being 72.44 emu/g observed for sample sintered at 1350°C. Samples sintered in air at 1050°C show very low values for saturation magnetization.

Curie temperature for samples in nano phase were found to be size dependent. A high $T_c$ of 750 K and a low $T_c$ of 380 K were observed for samples with particle size varying between 25.276 nm and 4.464 nm. For samples sintered in N$_2$ atmosphere, the Curie temperature was found to decrease with increase in sintering temperature. In both cases Curie temperature was found to change with change in concentration of Zinc in the sample, Fig. 5.

The AC susceptibility curves obtained for unsintered samples in Fig. 6 are typical to curves obtained for fine particle ferrite. The density of the samples in Fig. 7 was found to depend on concentration of Zinc in the sample, the sintering temperature and at large on the grain size of the sample. The highest density was
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Fig. 5. Curie temperature with concentration of Zn$_{1-x}$ in Mn$_x$Zn$_{1-x}$Fe$_2$O$_4$.

Fig. 6. Ratio $X_T/X_{300}$ as a function of temperature for Mn$_{0.7}$Zn$_{0.3}$Fe$_2$O$_4$ and Mn$_{0.7}$Zn$_{0.7}$Fe$_2$O$_4$.

obtained for samples sintered at 1350°C in N$_2$ atmosphere. The hysteresis losses indicated in Fig. 8 are quite low and are found to depend on concentration of Zinc. There was only a marginal increase in the hysteresis loss for samples sintered in N$_2$ atmosphere.
7. Results and Conclusion

- The precursor method employed yields nanoparticle ferrites.
- The nanomaterial produced by this method shows high values of saturation magnetization\(^6\) both in nano phase as well as in the bulk mode when sintered at 1350°C without addition of any additives.
- Mn–Zn Ferrite being a soft ferrite, the Curie temperature ranges from 500 K to 300 K for materials which are prepared by conventional ceramic method. The
samples prepared by the present method gives a higher Curie temperature which ranges between 750 K to 380 K for materials in the nano phase and are found to depend on particle size. The same varies from 520 K to 320 K in bulk mode when the samples are sintered at 1350°C in N₂ atmosphere. Sintering of sample changes the microstructure which increases grain size there by reducing total surface area of the sample. Curie temperatures for samples sintered at 950°C are higher than those obtained for samples sintered at 1350°C. This indicates strong dependence of Curie temperature on particle size.

- It has been reported that the values of saturation magnetization decreases with decrease in particle size. However, such a variation was not observed for the samples prepared using nitrilotriacetate precursor method.
- The preparative conditions could be monitored more carefully for tailor-made particle size and clustering of particles could be overcome by providing more energy to the particles after decomposition.

References
High permeability of low loss Mn–Zn ferrite obtained by sintering nanoparticle Mn–Zn ferrite

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Abstract
Nanoparticle ferrite having general formulae Mn x Zn 1-x Fe 2 O 4 with x = 0.35/0.40/0.45/0.55/0.60/0.65 were prepared using nitrilotriacetate precursor method. Production of fine grain size material at low temperature is the unique feature of this method. Bulk Mn x Zn 1-x Fe 2 O 4 ferrite material produced by sintering nanoparticles 950/1050/1150/1250/1350 °C progressively in nitrogen atmosphere showed high values for initial permeability. Scanning electron microscopy and transmission electron microscopy were especially employed in order to elucidate the microstructure and understand the dependence of permeability and relative loss factor on the material grain size.

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Keywords: Magnetic materials; Sintering; Magnetic properties; Electrical properties

1. Introduction
A tremendous surge in research on nanomaterials and bulk materials produced from nano-sized grains has been observed in the last few years since these materials are to shape the future advanced technology. The demand for high performance and miniaturization of electronic devices is on rise. This exclusively needs soft magnetic materials as its basic component. Soft ferrite material is extensively used in inductors, transformers, antenna rods, loading coils, deflection yokes, choke coils, recording heads, magnetic amplifiers, electromagnetic interference (EMI), power transformer and splitter applications, which forms a basic requirement in high technology areas. Mn–Zn ferrite material adequately suits these demands. Nano sized Mn–Zn grains are also found to be of great use in medical applications. For high performance the permeability and resistivity of this materials needs to be increased. An important parameter for high performance is small grain size Drofenik et al. [1], Inaba et al. [2]. Power ferrites should have low power loss characteristics under driving conditions. Low power loss Mn–Zn ferrites demands uniformly sized grains of high-fired density. Currently electronic modules are becoming smaller and lighter, the power supplies must likewise be reduced. The core loss, consisting of hysteresis loss, eddy current loss and residual loss, vary considerably with operating frequency and magnetic flux density. These losses can be reduced by production of material with uniform microstructure. This type of material facilitates better domain wall movements, as they are free from lattice defects, pores and impurities. Along with this low mechanical stress, low magneto crystalline anisotropy and low magnetostriction are also essential.

The factors responsible for controlling the grain size of the material are the method of preparation and conditions at preparation. Ferrite materials prepared using precursor method which is a solution technique produces material with improved microstructure Verma et al. [3]. In the present work a novel nitrilotriacetate precursor method is used for preparing compositionally and structurally perfect fine particle Mn–Zn ferrite. This method results in the samples exhibiting low magnetic and electrical losses as

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compared to those prepared by the conventional ceramic and other wet chemical methods. Fine particle Mn-Zn ferrite material synthesized using precursor method has a unique advantage of producing the material at very low processing temperature. These nanoparticles, when sintered in nitrogen atmosphere, using suitable sintering profile, show high values for permeability and low relative loss. Occurrence of phase transitions while sintering is also observed for these materials.

2. Experimental

Mn–Zn ferrite samples in form of ultra fine powders having general formula Mn\textsubscript{x}Zn\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{4} with x = 0.35/0.4/0.45/0.5/0.55/0.6/0.65 were synthesized using nitrilotriacetate precursor method as in Tangsali et al. [4]. XRD patterns for the samples were obtained on micro-computer controlled Siemens D-500 X-ray diffractometer and X-pert PRO PANalytical Philips diffractometer using CuK\textalpha (\lambda = 1.5406 Å). FTIR absorption spectra for all the samples were recorded on Shimadzu FTIR 8900 spectrometer. Estimation of metal ions was carried out by titrimetry. Estimation of Mn, Zn, Fe and O by EDAX was carried out using JEOL Model 840(SEM). Average grain size estimation was done with the help of Scherrer Formula. SEM photographs of prepared samples were obtained on JEOL Model 840(SEM), which provided the surface morphology of the material under investigation. TEM photographs were taken on Philips model CM200 with resolution 0–23 nm with an electron beam of 200 KeV Transmission electron Microscope to confirm formation of ultra fine particle size of the samples and to know grain size of unsintered and sintered samples. The fine powders were pressed into torroids of height ranging between 3–4 mm with inner and outer diameters of 1 and 2 cms, respectively by application of 75 kN pressure for 3 min. The torroids were sintered at 950/1050/1150/1250/1350°C in nitrogen atmosphere for 3 h in a progressive manner. The heating and cooling rate was fixed at 5°C/min during each sintering. Permeability measurements were carried out after each temperature sintering. A winding of 100 turns of super enameled doubly insulated copper wire of guage 33 was done on each torroid to carry out initial permeability (\mu\textsubscript{i}) and loss factor measurements as a function of temperature and frequency. Inductance values were recorded starting from room temperature to 500°C with a frequency variation from 50 Hz to 1 MHz using HP 4284A precision LCR meter.
SEM and TEM photographs of the sintered samples were recorded to obtain the information on grain size development of the sintered samples.

3. Results and discussion

3.1. X-ray analysis

Formation of single-phase cubic spinel structure of \( \text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4 \) with \( x = 0.35/0.40/0.45/0.55/0.60/0.65 \) was confirmed with the help of XRD patterns obtained for all the samples under investigation. Fig. 1 shows a typical XRD pattern obtained on Siemens X-ray diffractometer using \( \text{CuK} \alpha (\lambda = 1.5406 \text{ Å}) \) radiation for the sample \( \text{Mn}_{0.65}\text{Zn}_{0.35}\text{Fe}_2\text{O}_4 \). The values of lattice parameters determined using Bragg’s law shows a smooth decrease in the lattice constant as the concentration \( (1-x) \) of zinc is increased. The lattice constant \( "a" \) for \( \text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4 \) (8.479 Å) reduces smoothly to (8.455 Å) for \( \text{Mn}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4 \) as Zn-concentration is increased. This decrease could be easily explained on the basis of the ionic radii of Fe and Zn ions. \( \text{Fe}^{3+} \)-ions with radius (0.63 Å), which are smaller, are replaced by Zn-ions with radius of (0.78 Å) which are larger, as the concentration of Zn is increased in the sample.

3.2. IR analysis

Analysis of IR spectra gives the information about product structure transformation as well as a presence of certain types of chemical substances adsorbed on the surface of particles. The metal oxygen absorption bands at 600–550 and 450–385 cm\(^{-1} \) are characteristically pronounced for all spinel structures and for ferrites in particular. The band 350–330 cm\(^{-1} \) is less intense and sometimes it merges with the band 450–385 cm\(^{-1} \) giving a single wide band at 420–330 cm\(^{-1} \). Fig. 2 shows two broad bands at 600–550 cm\(^{-1} \) and 420–330 cm\(^{-1} \) for all the samples.

Fig. 4. Variation of initial permeability with temperature for samples \( \text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4 \) sintered at: (a) 950°C; (b) 1050°C.
3.3. Particle size determination

The particle size estimates of as prepared samples were done using three different tools. Particle size calculations through Scherrer formulae based on XRD peak widening showed formation of ultra fine particle material with average grain size in the range of 10–80 nm and are found to depend on Zn concentration in the sample. The average particle size of the samples as seen from TEM photographs Fig. 3(a) and (b) are in excellent agreement with the particle size estimates made using Scherrer Formula. The average particle size of the as prepared samples seen from TEM photographs is about 10 nm.

3.4. Chemical analysis

Estimated percentage contents of the elements Mn, Zn, Fe and O carried out with the help of EDS analysis of all the samples (Table 1 for Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$) are in good agreement with the theoretical estimated values thus confirming the preservation of stoichiometry [5].

3.5. Permeability and loss factor

Initial permeability ($\mu_i$) is an important magnetic parameter, which decides the suitability of a ferrite for particular application. It is technologically important extrinsic magnetic property, which is influenced by the microstructure, which in turn depends upon the method of preparation. The initial permeability is dependent on grain size, density and porosity of the material (Goldman [6]). Temperature dependence of initial permeability is a very important factor to be considered in designing any magnetic component.

The initial permeability ($\mu_i$) was calculated from the formulae

$$L = 0.0046 N^2 h \ln(OD/ID)$$

Fig. 5. (a) The variation of initial permeability with temperature for the sample Mn$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$ sintered at different temperatures; (b) Variation of maximum value of initial permeability with sintering temperature for Mn$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$. 
where $L$ is inductance in Henry, $N$ is the number of turns of copper wire on torroid, $h$ is height of the core in metres, OD is outer diameter of torroid in metres, and ID is the inner diameter of torroid in metres.

The variation of permeability with the temperature for the samples sintered at 950 and 1050°C is shown in Fig. 4 (a and b). It is observed that initial permeability increases slowly, reaches peak value at a certain temperature and drops gradually to zero at Curie temperature. The maximum in initial permeability corresponds to the point of zero anisotropy field (Standley [7]). The increase in permeability with temperature is due to the fact that the anisotropy decreases faster with temperature than the saturation magnetization.

The variation of initial permeability with temperature for the sample Mn$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$ sintered at 950, 1050, 1150, 1250 and 1350°C is as shown in Fig. 5(a). The drops are observed near Curie temperature and a high value of initial permeability 25,472 at 150°C for frequency 50 Hz obtained for sample Mn$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$ sintered at 1050°C is much higher than the reported values. Samples Mn$_{0.35}$Zn$_{0.65}$Fe$_2$O$_4$, Mn$_{0.60}$Zn$_{0.40}$Fe$_2$O$_4$ and Mn$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$ when sintered at 950°C shows very low room temperature permeabilities (Fig. 4(a)) where as sample Mn$_{0.40}$Zn$_{0.60}$Fe$_2$O$_4$ shows high value of 2753 and the sample Mn$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$ shows a value of 13,831 for room temperature permeability. However, the overall permeabilities for this sample are found to increase as the

Fig. 6. SEM photographs of Mn$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$ sintered in nitrogen atmosphere for 3 h at: (a) 950°C; (b) 1050°C; (c) 1150°C; (d) 1250°C and (e) 1350°C.
temperature increases. Room temperature permeability values (Fig. 4(b)) are drastically changed when the same samples are sintered at 1050°C. Mn$_{0.40}$Zn$_{0.60}$Fe$_{2}$O$_{4}$, Mn$_{0.45}$Zn$_{0.55}$Fe$_{2}$O$_{4}$ and Mn$_{0.55}$Zn$_{0.45}$Fe$_{2}$O$_{4}$ show very low values whereas Mn$_{0.60}$Zn$_{0.40}$Fe$_{2}$O$_{4}$ shows higher value of $\mu_r$ and the sample Mn$_{0.65}$Zn$_{0.35}$Fe$_{2}$O$_{4}$ shows highest room temperature value for $\mu_r$, which is higher than 10,000.

All these samples show broad peaks followed by a gradual fall near Curie temperature as usual. For samples sintered at 950°C the curie temperatures is beyond 250°C whereas for samples sintered at 1050°C the Curie temperature lies between 100 and 500°C. Fig. 5(b) shows variation of maximum values of $\mu_r$ with sintering temperature for sample Mn$_{0.45}$Zn$_{0.55}$Fe$_{2}$O$_{4}$. The variation of maximum value of the permeability for the sample is found to show a peak at 1050°C and a fall followed by a rise at sintering temperature 1350°C. This behavior and the initial permeability trends observed in Fig. 4(a) and (b) and Fig. 5(a) and (b) can be related to the existence of different crystalline phases which the samples undergoes at different sintering temperatures. This is evident from the SEM and TEM photographs depicted in Figs. 6 (a—e) and 7.

The initial permeability of high permeability material depends to a large extent on mobility of the Bloch's domain walls. To obtain high permeability it is important to reduce the crystalline anisotropy and the magnetostriiction. Ferrites in particular are burdened with magnetic imperfections. Voids in bodies that are not completely densified, non-magnetic inclusions are the factors, which give, rise to internal magnetostatic energy. The stable domain configuration in a material is always such is to minimize this energy. The loss that occurs is proportional to imperfections of materials as well it's anisotropy, both crystalline and strain. High permeability may be expected in polycrystalline material that are homogeneous, dense and have composition that has very low value of anisotropy. Anisotropy is temperature dependent property. Effect of this depends on the composition. The anisotropy in Mn–Zn ferrite is highly dependent on the material composition. For some compositions of Mn–Zn anisotropy takes negative value at room temperature, increases monotonically with temperature to zero at Curie temperature whereas for certain combinations of Mn–Zn it takes a negative value increases to zero, takes a positive value and decreases to attain a zero value at Curie temperature. This behavior is strongly reflected in the initial permeability of the material. The initial permeability rises to maximum at both zero anisotropy points with a saddle corresponding to the temperature at which anisotropy has a maximum positive value [9], Verma et al. [8]. Well-adjusted sintering conditions support the design of microstructure and resulting magnetic properties of the sample. SEM micrographs Fig. 6 (a—e) shows the morphology of sample Mn$_{0.45}$Zn$_{0.55}$Fe$_{2}$O$_{4}$ sintered at 950, 1050, 1150, 1250 and 1350°C, respectively.

The sample sintered at 950°C Fig. 6(a) shows a more compact microstructure with well-developed grains, however the existence of non-magnetic voids is also large. The density of the sample is 2587 Kg/m$^3$. The samples sintered at 1050°C (Fig. 6(b)) shows larger polycrystalline grains with less non-magnetic voids and a density of 3200 Kg/m$^3$. The sample exhibits a high value of permeability. The samples sintered at 1150°C (Fig. 6(c)) shows formation of well developed crystals and has a density of 3983 Kg/m$^3$. The anisotropy for this sample is expected to be higher due to blocking of domain wall movement and the strain isotropy, which is a result of increase in lattice stress. The sample sintered at 1250°C shown in Fig. 6(d) appears to possess a very high value of anisotropy and magnetostriiction compared to other samples. This appears to be a stage with substantial magnetic imperfections and poor grain growth. The sample has a density of 3867 Kg/m$^3$. A different crystalline phase with fewer imperfections is obtained for sample sintered at 1350°C (Fig. 6(e)). The density of this sample is found to be 3925 Kg/m$^3$.

The microstructures show different crystalline phases which are responsible for variations in anisotropy and domain wall movement in the sample. Fig. 7 confirms the existence of polycrystalline phase in the sample sintered a 1050°C, which is one of the factors for enhancing th permeability value of the sample.

The ratio tan $\delta$ to $\mu_r$ known as relative loss factor (rlf) plotted against frequency as shown in Fig. 8(a) and (b). It observed that for some samples the value of rlf rapid decreases as the frequency is increased whereas it remain extremely low for most of the samples for all sintering temperatures. The rlf is found to depend on compositon and microstructure of the sample, which is decided
sintering profiles of the sample. In the present work the rlf values obtained range from $10^{-2}$ to as low as $10^{-6}$, in the frequency range of 50 Hz–1 MHz.

4. Conclusions

The materials prepared by sintering nanomaterial Mn–Zn ferrite prepared using nitrilotriacetate precursor method yield high performance materials. The samples are found to show high permeability and low loss, which are essential parameters for any present-day electronic and electromagnetic applications. The permeability and loss depends on the various factors such as stoichiometry, density and grain size. For electromagnetic application of ferrites it is necessary that the rlf values should be as low as possible over a large frequency range. The rlf values of the samples under investigation are found to be much lower.

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References


Effect of sintering conditions on resistivity of nanoparticle Mn–Zn ferrite prepared by nitrilotriacetate precursor method

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Abstract Mn–Zn spinel ferrites are most important class of magnetic materials owing to their high saturation magnetization, high permeability, low loss and interesting applications in various fields. The magnetic as well as electrical properties of these ferrites depend on relative distribution of cations at different sites, grain size, sintering conditions as well as preparative conditions. Nanoparticle Mn–Zn ferrite material having general formula MnₓZn₁₋ₓFe₂O₄ with x = 0.35/0.4/0.45/0.5/0.55/0.6/0.65 were synthesized using nitrilotriacetate precursor method and characterized using standard techniques. The resistivity measurements of all these samples were carried out after sintering the same in nitrogen atmosphere at 1,050 °C/1,150 °C/1,250 °C/1,350 °C, respectively. High resistivity values obtained for the system of materials would provide a low eddy current loss material for wide ranging applications in electronics and telecommunications. Semiconductor like behavior of the material with resistivity variation over large range of temperature is ideal characteristic essential for materials in sensor applications.

Introduction

Research in nanomaterials is on growth as the reduced grain dimensions drastically alter the properties of materials. Nano sized magnetic oxides are becoming important materials due to their unique micro magnetic properties such as superparamagnetism, magneto optic, magneto caloric effect, colossal and giant magnetic resistance etc. These materials are useful in a variety of applications in the electronic industry due to their high permeability, high saturation magnetization, high resistivity and low loss as these formed the key impediments in downsizing of transformer cores deflection yokes, antenna rods in the world of miniaturization. The most important parameter for high performance is small grain size. Resistivity of bulk Mn–Zn Ferrite obtained by sintering ultra fine particle Mn–Zn ferrite...
material is different from the one obtained by sintering material prepared by conventional methods like ceramic method and other wet chemical methods which yields large particle size. The performance of these materials is greatly influenced not only by its composition but also by the method of preparation and conditions at preparations. These factors are responsible for controlling the grain size of the material. The power loss per unit volume $P_V$ for a Mn–Zn ferrite material can be divided into the hysteresis loss $P_H$, the eddy current loss $P_E$, and the residual loss $P_R$. The eddy current loss is dependent on the resistivity of the sample. The eddy current loss is given by $P_E = cL^2B_m^2f^2/\rho$; $f$ is frequency, $L^2$ is equal to the $A$ dimension of the circuit, $B_m$ is the maximum flux density, $\rho$ is the electrical resistivity of the bulk, and $c$ is a coefficient related to the dimension of the circuit of the eddy current. Eddy currents in the core are related to material microstructure as the parameter $L^2$ may be replaced by $D^2$ the average diameter of the individual grains [1, 2].

Fine particle Mn–Zn ferrites were synthesized using nitrilotriacetate precursor method. Samples were characterized using standard techniques. The resistivity of the bulk material obtained on sintering the nanoparticles at different temperatures was found to be very high which can account for sizable reduction in eddy current losses.

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**Experimental**

Mn–Zn ferrites samples in form of ultra fine powders having general formula $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ with $x = 0.35/0.4/0.45/0.5/0.55/0.6/0.65$ were synthesized using nitrilotriacetate precursor method [3]. The advantage of this method is that it produces nanoparticle Mn–Zn Ferrite material at much lower temperature. The decomposition of the complex precursor takes place at around 250 °C, which proceeds via auto-combustion method. XRD pattern for the samples were obtained on microcomputer controlled Siemens Diffractometer using Cu Ka ($\lambda = 1.54183$ AU). FTIR absorption spectra were recorded Shimadzu FTIR 8900 Spectrometer. Estimation of metal ions was carried out by titrimetry. Analysis for estimation of Mn, Zn, Fe and O by EDAX was also carried out by using Joel Model 840(SEM). Average grain size estimation was done using Scherrer Formula. TEM photographs were taken on Philips model CM200 Transmission electron Microscope with resolution 0–23 nm to confirm formation of ultra fine particle size of the samples. SEM photographs of sintered samples were obtained on Joel Model 840(SEM), which gave information on the microstructure of the materials under investigation. Fine powders of $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ were pressed into pellets of the size 10 mm diameter and of thickness ranging between 2 and 3 mm under a pressure of 75 KN applied for 3 min. Four sets of pellets were sintered in nitrogen atmosphere at temperatures, 1,050, 1,150, 1,250 and 1,350 °C, respectively, for 3 h by setting heating and cooling rate at 5 °C per minute. The pellets were silver painted on either side for establishing good Ohmic contacts with the electrodes. Resistivity measurements on these samples were then made using standard two-probe method.

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**Results and discussion**

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A typical XRD pattern obtained for the sample is shown in Fig. 1. Similar patterns were recorded for all the samples. The $d$ values, 20 values and the values of lattice constants $a$ calculated from these was verified and is found to be in excellent agreement with reported values. Formation of cubic spinel structure was thus confirmed by XRD data analysis. The particle size of these fine powders, as calculated from Scherrer formula using XRD data, was found to range between 10 and 80 nm.

![XRD pattern](image)

**Fig. 1** XRD pattern obtained for as prepared powdered sample Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$

Analysis of IR spectra gave the information about product structure transformation. The study of far-infrared spectrum is an important tool to get information about the positions of the ions in the crystal through the crystal's vibrational modes [4]. It also helps in identifying the spinel structure as well as a presence of certain types of chemical substances adsorbed on the surface of particles. In the IR spectra of the mixed oxides the following vibrations, with a corresponding wavenumber are possible.

\[
\text{Me}_1 - \hat{\text{O}} - \text{Me}_0 \text{ stretching vibration } 600 - 550 \text{ cm}^{-1}
\]  

(1)

\[
\text{Me}_0 - \hat{\text{O}} \text{ stretching vibration } 450 - 385 \text{ cm}^{-1}
\]  

(2)

\[
\text{Me}_1 - \text{Me}_0 \text{ stretching vibration } 350 - 330 \text{ cm}^{-1}
\]  

(3)
where O is oxygen, Me$_0$ is metal in the octahedral site and Me$_T$ in the tetrahedral site. The metal–oxygen absorption bands (1) and (2) are pronounced for all spinel structures and essentially for ferrites. Usually the band (3) is less intense than bands (1) and (2), and sometimes found to merge with the band (2) resulting in a single wide band at 420–330 cm$^{-1}$. In the IR absorption spectra recorded for the powdered samples (Fig. 2), two broad bands (1) and (2) are observed in addition to a small narrow less intense third band in the range 350–330 cm$^{-1}$ that has almost merged with band (2).

![Fig. 2 IR spectra obtained for as prepared powdered sample Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$](image)

The grain size of the sample as seen from TEM photograph of Fig. 3 is in excellent agreement with values obtained for particle size using Scherer formula. Preservation of stoichiometry was confirmed on analyzing the EDS results.
The density values of the samples (Table 1) are found to show abrupt changes on changing sintering temperature from 1,050 to 1,350 °C. The density of sintered Mn$_x$Zn$_{(1-x)}$Fe$_2$O$_4$ ferrite material where $x = 0.65, 0.6, 0.45$ and $0.4$ is found to be high when sintered at 1,150 and 1,350 °C whereas these values are low when these samples are sintered at 1,050 and 1,250 °C. The density for sample with $x = 0.55$ is found to increase with sintering temperature whereas the same is observed to be lower for sample with $x = 0.35$ sintered at 1,350 °C. Although density depends on the concentration of Mn in the sample the present unusual behavior observed in the density may be attributed to the existence of phase transitions which occur during the crystal formation process while sintering, as evident from SEM photographs depicted in Fig. 4. The investigation on fine structure of Mn$_x$Zn$_{(1-x)}$Fe$_2$O$_4$ ferrite clearly indicates the influence of sintering conditions on the grain growth [5], density of the sample and crystalline phase of the sample [6]. The unusual trend in the density values is also observed in the resistivity trends of the samples. Figure 5a–d shows plots of log $\rho$ v/s $1,000/T$ (K) for Mn$_x$Zn$_{(1-x)}$Fe$_2$O$_4$ ferrite. A semiconductor like general behavior is seen for all the samples as the samples undergo a second order ferrimagnetic to paramagnetic phase transition. Although the trends depend on the concentration of Mn in the sample these are more strongly dependent on the sintering temperature of the sample.

Resistivity values at 300 K are seen to vary between $3.789 \times 10^7$ ohm-cm and $1.898 \times 10^8$ ohm-cm for samples sintered at 1,050 °C the highest and the lowest being observed for Mn$_{0.35}$Zn$_{0.65}$Fe$_2$O$_4$ and Mn$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$, respectively. A considerable variation in the resistivity is observed for samples sintered at 1,150 °C. The resistivity at 300 K is found to vary between $7.5 \times 10^8$ ohm-cm and $2.832 \times 10^8$ ohm-cm with the highest for Mn$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$ sample. These values are found to be much lower for samples sintered at 1,250 °C and are found to range between $2.285 \times 10^6$ ohm-cm and $6.08 \times 10^6$ ohm-cm. A large variation in the resistivity values is observed for samples sintered at 1,350 °C both at 300 K and at higher temperatures with the highest being $1.624 \times 10^9$ ohm-cm for Mn$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ at 300 K. It may be seen that large variations in resistivity at 300 K are observed for samples sintered at 1,150 and 1,350 °C. This may be due to formation of definite small grain shapes with high resistive boundaries in between any nearby neighbors and is evident from the SEM photographs (b) and (d) of Fig. 4.

Table 1 Table showing density of unsintered samples and density of samples sintered at 1,050, 1,150, 1,250 and 1,350 °C

<table>
<thead>
<tr>
<th>Mn Conc. ($x$)</th>
<th>Unsintd. density (g/cc)</th>
<th>Sintd. 1,050 °C density (g/cc)</th>
<th>Sintd. 1,150 °C density (g/cc)</th>
<th>Sintd. 1,250 °C density (g/cc)</th>
<th>Sintd. 1,350 °C density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>2.3941</td>
<td>3.1825</td>
<td>4.1127</td>
<td>4.0287</td>
<td>4.1824</td>
</tr>
<tr>
<td>0.6</td>
<td>2.7779</td>
<td>3.6226</td>
<td>3.7624</td>
<td>3.6477</td>
<td>4.0999</td>
</tr>
<tr>
<td>0.55</td>
<td>2.696</td>
<td>3.7536</td>
<td>3.9285</td>
<td>3.9909</td>
<td>4.1401</td>
</tr>
<tr>
<td>0.45</td>
<td>2.396</td>
<td>3.2007</td>
<td>3.9833</td>
<td>3.8674</td>
<td>3.9251</td>
</tr>
<tr>
<td>0.4</td>
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<td>3.5169</td>
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<td>3.5923</td>
<td>3.7124</td>
</tr>
<tr>
<td>0.35</td>
<td>3.0324</td>
<td>3.7512</td>
<td>4.0987</td>
<td>4.2953</td>
<td>3.9222</td>
</tr>
</tbody>
</table>

**Fig. 4** SEM photographs of Mn$_{0.45}$Zn$_{0.55}$Fe$_2$O$_4$ sintered in nitrogen atmosphere for 3 h at (a) 1,050 °C, (b) 1,150 °C, (c) 1,250 °C and (d) 1,350 °C.
In ferrites electron conduction mechanisms have been studied by many investigators and reviewed by Klinger et al. [7]. Various models were proposed; however, the thermally activated hopping model is found to be more appropriate in explaining qualitatively the electrical behavior of Mn–Zn ferrites. In the hopping process the additional electron on a ferrous (Fe$^{2+}$) ion requires little energy to move to an adjacent (Fe$^{3+}$) on the equivalent lattice sites (B sites). In presence of the electric field, these extra electrons hopping between iron ions give rise to the electrical conduction. Therefore, any change in the (Fe$^{2+}$) ion content in the spinel ferrite lattice and/or the distance between them is crucial to the intrinsic resistivity of Mn–Zn ferrite grains, including the intrinsic grain boundaries. If the introduction of another cation into the lattice causes a change in the valency distribution on the B sites, then the number of electrons potentially available for transfer will be altered. On the other hand, the incorporation of foreign (addition of impurity) ions can change the distance between the B lattice sites, which is crucial for the conduction mechanism. Thus, the formation of an intrinsic grain boundary in doped samples by the segregation of aliovalent ions must increase the resistivity. This gives rise to polycrystalline Mn–Zn ferrite with non-ferrimagnetic grain boundary, ferrimagnetic outer grain region and ferrimagnetic conductive...
core. Thus the contribution to the bulk resistivity may be considered as resistivity contribution coming from three different regions. To establish a relation between the Power loss due to eddy currents and the average grain diameter a hypothetical brick wall model is applied. As per the model each layer can be represented by a resistance-capacitance (R–C) lumped circuit of high Ohmic layers. When the resistivity of the bulk is much lower than the grain boundary layers, the equivalent circuit of the ferrite can be represented by a series of lumped R–C circuits of the grain boundary layers [2].

As the samples under investigation are sintered from Nanoparticle Mn–Zn ferrite in a reducing atmosphere with no additives there is no possibility of formation of high resistivity ferrimagnetic outer grain boundary. Thus the total contribution should come only from the non-ferrimagnetic grain boundaries and ferrimagnetic conductive core. It is evident from Fig. 4 that due to phase transitions samples sintered at 1,150 and 1,350 °C show small grain sizes with large non-ferrimagnetic grain boundaries more over the total surface area of the sample also increases due to formation of fine crystals which results in high resistivity for the samples. The samples sintered at 1,050 and 1,250 °C do not show formation of perfect crystals or small grain shapes which results in low surface area and less high resistivity non-ferrimagnetic grain boundaries which accounts for low value of resistivity at 300 K for this samples as compared to samples sintered at 1,150 and 1,350 °C. The resistivity values obtained are much higher as compared to the reported resistivity values of $10^{5}$ ohm-cm [8, 9].

Conclusion

The present investigations on the resistivity of the Mn–Zn ferrite developed by sintering nanoparticle Mn–Zn ferrite, prepared by nitritoltriacetate precursor method in an inert atmosphere, show existence of phase transitions thus contributing to amazingly high electrical resistivity in comparison to the reported values. This is a very important parameter in minimizing the eddy current losses in power applications. It is evident that the material prepared by sintering nanomaterial Mn–Zn ferrite not only gives low loss material but also produces material with small grain size with large surface area as the grain growth is suppressed due to phase transitions. This feature can have remarkable effect on the other properties of the material. The semiconductor like behavior of the resistivity shown by this material makes it a favorable material for sensor applications.

References


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   [CrossRef] [ChemPort]

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Papers Presented at National/International conferences:

1. "Fine Particle Magnetic Ferrite Material From Sulphite – Hydrazinate Based Precursors"

2. Preparation and Characterization of Nanoparticle Ferrite from Sulphite-Hydrazinate based Precursors


4. “Magnetic properties of nanoparticle Mn-Zn ferrite synthesized with Nitrilotriacetate precursor method” was presented in the workshop New Frontiers in Chemistry organized by Dept. of Chemistry, Goa University, Feb 2003.


7. “Effect of sintering conditions on electric properties of nanoparticle Mn-Zn Ferrite synthesized with Nitrilotriacetate precursor method” was accepted for oral presentation in IUMRS-ICA-2004, International conference in Asia organized by Material Research society- Taiwan held in Nov.2004.


15. “Preparation and Characterization of Nanoparticle Mn-Zn spinel ferrite using Microwave induced decomposition” has been accepted for poster presentation in APCOT-2006, International conference in Asia organized by Asia-Pacific Conference of Transducers and Micro-nanotechnology at Singapore to be held in June 2006.

16. “High performance ultra loss nanoparticle Mn-Zn ferrite material prepared by nitrilotriacetate precursor with induced microwave combustion” presented in the Indo-Australian symposium on nanomaterials and nanotechnology, held in IISc, Bangalore from 31-1 April 2006.
17. "Preparation and Characterization of nanoparticle Mn-Zn spinel ferrite using Microwave induced decomposition" has been accepted for poster presentation in Nano-2006, Eighth International conference on nanostructured materials to be held in August 2006 in IISc. Bangalore.


19. “Magnetic properties of nanoparticle Mn$_{0.67}$Zn$_{0.33}$Fe$_2$O$_4$ spinel ferrite prepared by microwave induced combustion”, presented at International conference on Advanced Nanomaterials 2007 organized by Indian Institute of Technology Powai, Mumbai, held in Jan 2007.

**List of publications refereed Journals**


6. “Magnetic properties of nanoparticle Mn$_{0.67}$Zn$_{0.33}$Fe$_2$O$_4$ spinel ferrite prepared by microwave induced combustion” Journal of Nanoscience and Nanotechnology (in review).