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Low temperature processing of Mn–Zn nanoferrites

P. Mathur · A. Thakur · M. Singh

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Abstract $Mn_{0.4}Zn_{0.6}Fe_2O_4$ ferrite synthesized by coprecipitation method is investigated in the present work. D.C. resistivity is studied as a function of temperature and values upto 10^2 times greater than those for samples prepared by the conventional ceramic method are observed. It is found that resistivity decreases with increase in temperature. The initial permeability values are high as compared to those prepared by soft chemical route. Initial permeability is found to increase with increase in temperature. At a certain temperature, called the Curie temperature, it attained a maximum value, after which the initial permeability is found to decrease. Even at nanolevel, appreciable value of initial permeability is obtained. The particle size is calculated using Scherrer equation for Lorentzian peak, which comes out between 9 nm and 19 nm. Possible mechanisms contributing to these processes have been discussed.

Introduction

The performance of any ferrite is greatly influenced by its synthesizing technique [1–7]. The conventional ceramic method of preparation which involves solid state reaction between oxides at high temperature is cumbersome, time consuming and does not always result in pure reproducible product. Therefore, various non-conventional processing techniques [1–3], which are mainly solution techniques, are reported. In the present work, non-conventional preparation method, known as coprecipitation method, was used for preparation of Mn–Zn ferrite. Main advantages of this method are that it is inexpensive, time saving and results in superior properties of ferrites processed at much lower temperature. The absence of ball milling in this method leads to stoichiometric composition as there is no possibility of loss or gain of material during milling, as in case of conventional ceramic method. In the present work, the effects of temperature on structural, electrical and magnetic properties of $Mn_{0.4}Zn_{0.6}Fe_2O_4$ ferrite synthesized by coprecipitation method were considered.

Experiment

Mn–Zn ferrite of composition $Mn_{0.4}Zn_{0.6}Fe_2O_4$ was prepared by precipitation method. The materials used were manganese chloride (98% Merck, India), zinc chloride (96% Merck, India), iron (III) chloride (98% Merck, India) and sodium hydroxide (96% Merck, India). One molar solution of these materials was made with distilled water. About 70 mL sodium hydroxide was taken from one molar solution in approximately 1,760 mL of distilled water to have the concentration of 0.37 mol/L and heated to boiling. Manganese chloride, zinc chloride and iron (III) chloride were taken from their molar solution in accurate stoichiometric proportions. These solutions were poured as quickly as possible into boiling solution of NaOH under vigorous stirring produced by the glass mechanical stirrer (~500 rpm). Mixing is very important otherwise segregation of phases can take place. After coprecipitation, pH is set 12.5–13. Reaction vessel is covered with plastic cover to diminish evaporation of the solution. Reaction is continued for 30–40 min at temperature 90–100 °C under

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P. Mathur (✉) · A. Thakur · M. Singh
Department of Physics, Himachal Pradesh University, Shimla 171005, India
e-mail: at_phy_hpu@yahoo.co.in

vigorous stirring. Reaction vessel is cooled to ambient temperature and particles precipitate. Total volume is reduced to ~500 mL by aspiration of supernatant. Suspension is centrifuged in four beakers at 7,000 rpm for 10 min. Precipitate is washed with distilled water of ~900 mL and centrifuged once more in four beakers at 7,000 rpm for 10 min. The residue is dried and was calcinated in a box type furnace for 15 h at 200 °C at a heating rate of 200 °C/h to obtain a ferrite powder. This powder was mixed with 2% P.V.A. binder and pressed into pellets of 1.50 cm diameter and 0.20 cm thickness under pressure of 5 tons (1 ton = 1.016×10^3 kg) and rings of 1.5 cm outer diameter, 1.0 cm inner diameter and 0.20 cm thickness under a pressure of 3 tons. These samples were sintered in air at 500 °C at a heating rate of 250 °C/h and were subsequently cooled. The pellets were coated with silver paste to provide electrical contacts and the rings were wound with about 50 turns of 30 SWG enameled copper wire to form torroids. X-ray diffraction measurements were taken on a Rigaku Geiger Flex 3 kW diffractometer using CuK$_\alpha$ source. Initial permeability and loss factor were measured by using Agilent Technologies 4285A Precision LCR Meter. Resistivity as a function of temperature was measured by using Two-Probe method. Curie temperature was measured by using gravity method.

Result and discussion

X-ray diffraction pattern of the ferrite sample pre-sintered at 200°C and sintered at 500°C are shown in Figs. 1 and 2. The observed diffraction lines were found to correspond to those of standard pattern of Manganese ferrite with no extra lines, indicating thereby that the samples have single-phase spinel structure and no unreacted constituents were present in these samples. Lattice constant ''a'' for the samples sintered at 200°C and 500°C were calculated from the observed ''d'' values and found to be 8.318 Å and 8.329 Å, respectively. The peak becomes sharper with increase in sintering temperature. The particle size of the samples has been estimated from the broadening of the X-ray diffraction peaks using the Scherrer equation [8] for Lorentzian peak:

$$\mathrm{d} = \frac{0.9\lambda}{(w - w_1)\cos\theta}$$

where d is the grain diameter, w and w_1 are the half intensity width of the relevant diffraction peak and the instrumental broadening, respectively, λ is the X-ray wavelength and θ is the angle of diffraction. The average particle size was found to be between 9 nm and 19 nm, which is due to lack of domain magnetic structure in the samples [9].

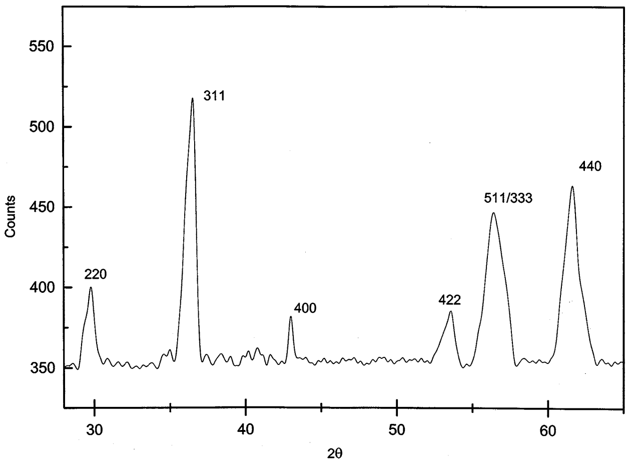

Fig. 2 XRD of $Mn_{0.4}Zn_{0.6}Fe_2O_4$ sintered at 500°C

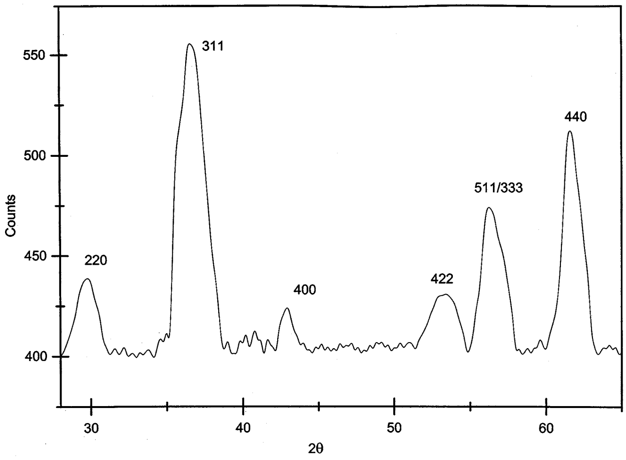

Fig. 1 XRD of $Mn_{0.4}Zn_{0.6}Fe_2O_4$ sintered at 200°C

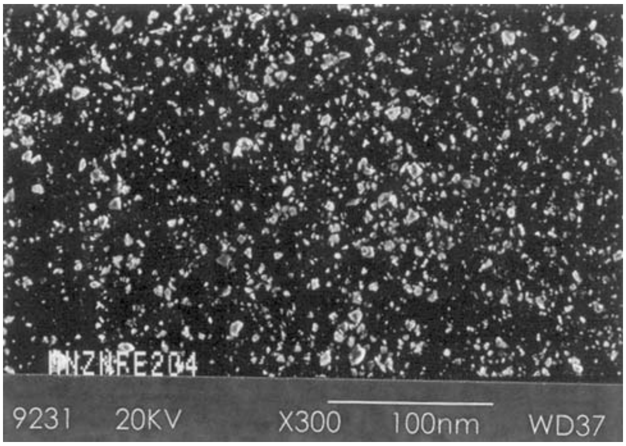

Fig. 3 Scanning Electron Micrograph of $Mn_{0.4}Zn_{0.6}Fe_2O_4$ sample sintered at 500°C

Figure 3 shows Scanning Electron Micrograph of the sample sintered at 500°C, which is in good agreement with the theoretical XRD results.

The variation of initial permeability, μ_i, with frequency at different temperatures was measured and shown in Fig. 4. The trends in the value of μ_i with frequency were same at different temperatures. There is decrease in the value of μ_i with increasing frequency upto 8 MHz and a significant rise is observed at high frequencies. Initial permeability, μ_i, is found to be high as the sample is formed at low temperature and the grain size is found to be small and uniform, which results in single domain structure with uniform magnetization [9]. The resonance peak, which occurs when the frequency of applied field equals the Larmor precession of electron spins, could not be observed in the present technique. The main reason is that, as the grain size becomes smaller and uniform, the resonance character vanish [10]. Similar trend of results was found by Rado et al. [11–13] and Snoek [14]. The other reason for the absence of resonance peak may be as they probably lie beyond the measurable frequency range. The variation of initial permeability with frequency can be understood on the basis of Globus model [15, 16]. According to this model, relaxation character, $(\mu_i - 1)^2\ f_r$ = constant, where μ_i is the static initial permeability and f_r is the relaxation frequency. It follows from this equation that dispersion frequency is expected to be lower for specimen of higher permeability. At nanolevel, initial permeability of 480 is a good value. The initial permeability, μ_i, is found to be high as compared to that observed in ferrite prepared by soft chemical route [4].

The variation of initial permeability, μ_i, with temperature at different frequencies is shown in Fig. 5. The initial permeability, μ_i, is found to increase with increase in temperature at all the frequencies, as is expected. At a temperature of 475 K, called the transition temperature, T_d, it attains a maximum value, after which there is a decrease in initial permeability. This temperature was found in accordance with the Curie temperature, T_c (475 K), obtained from the gravity method. The Curie temperature is the temperature above which the thermal agitation overcomes the alignment of magnetic moments and causes the material to become paramagnetic. It is typical of most magnetic materials that initial permeability, μ_i, increases with rising temperature to a peak value just below the Curie temperature, T_c and decreases to μ_o above Curie temperature [17]. The sharp drop in the initial permeability at the Curie point [18] indicates a good homogeneity in composition for the coprecipitation method.

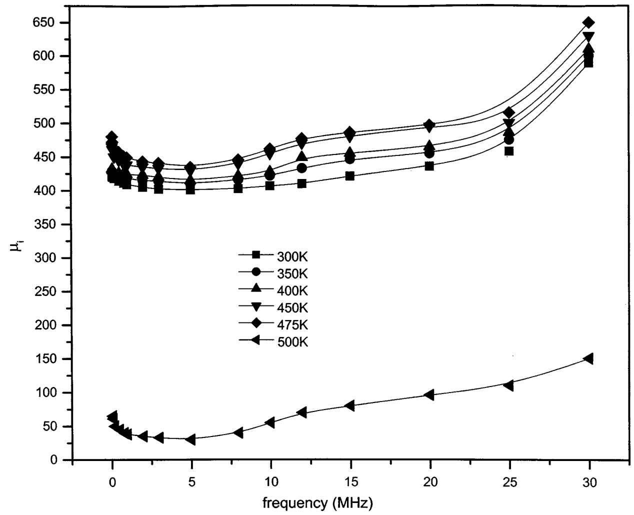

Fig. 4 Variation of initial permeability, μ_i, with frequency at different temperatures

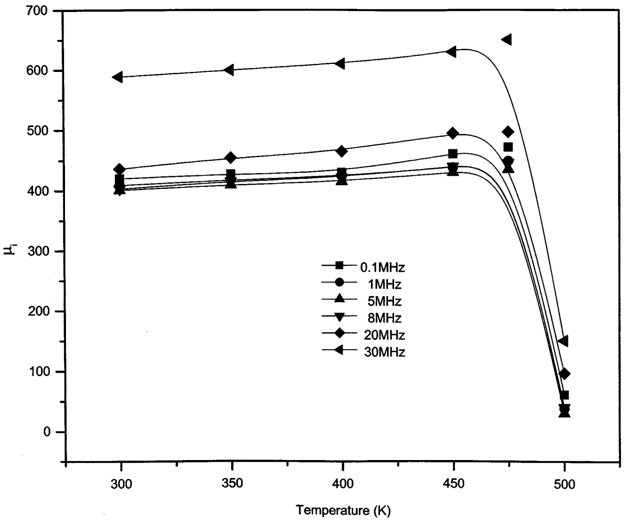

Fig. 5 Variation of initial permeability, μ_i, with temperature at different frequencies

The variation of permeability loss factor, tan δ_μ, with frequency at different temperatures is given in Fig. 6. As can be seen, the values are of order 10^{-2}–10^{-3} for different frequencies. These values are about the same and in some cases are of an order of magnitude lower than those for the specimens prepared by soft chemical route [14]. The variation of tan δ_μ with frequency showed identical behaviour for all the specimens.

With the increase in temperature from 300 K to 500 K, dc resistivity is found to decrease from 33×10^6 Ωcm to 4×10^6 Ωcm as shown in Fig. 7. This value is about 10–100 times more than that of ceramic ferrite. This property makes these ferrites suitable for high frequency applications where eddy current losses become appreciable. The higher values of dc resistivity are because of stoichiometric compositions, better crystal structures and the improved nano-structures obtained by coprecipitation method.

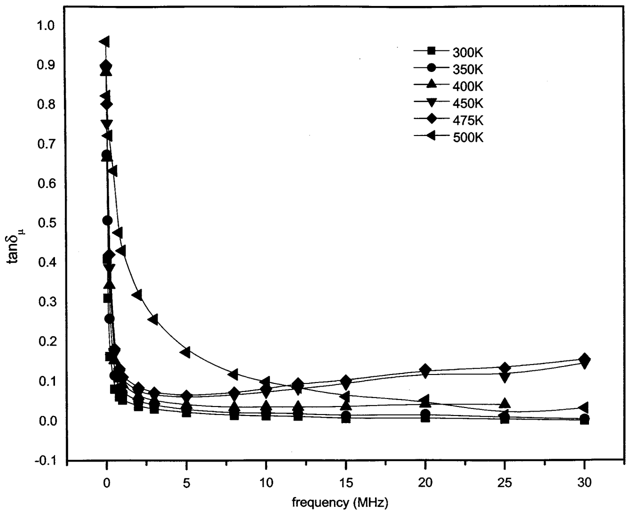

Fig. 6 Variation of permeability loss factor, tan δ_μ, with frequency at different temperatures

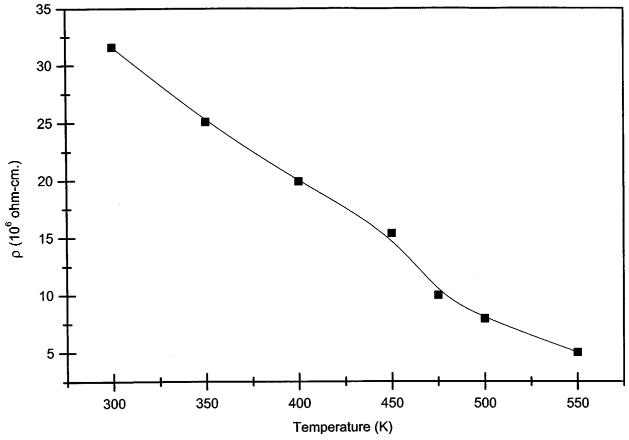

Fig. 7 Variation of dc resistivity with temperature

Samples sintered at low temperature possess small grain size [4]. Sample with small grain consists of more number of grain boundaries. The grain boundaries are the region of mismatch between the energy states of adjacent grains and hence acts barrier to the flow of electrons. Another advantage of small grain size is that it helps in reducing Fe^{+2} ions as oxygen moves faster in small grains, thus keeping iron in Fe^{+3} state [19]. Therefore, sample sintered at low temperature is found to exhibit high resistivity as compared to ceramic ferrite.

Hence, it is concluded that the initial permeability, μ_i, is a sensitive function of ambient temperature. It attains a maximum value at Curie temperature, T_c. In this method, we were successful in achieving high resistivity, which was about 10^2 times more as compared to conventional method. Appreciable value of initial permeability was obtained at low temperature and permeability loss factors were also found remarkably low. Coprecipitation technique is an effective and convenient route to synthesize nanocrystalline Mn–Zn ferrite particles because there is no requirement for a calcination process at high temperature. The synthesized powder has high activity due to its nanosized particle size. Ferrite powder can be sintered at 500°C and possesses a fine-grained microstructure. The low temperature sintered Mn–Zn ferrite has good electromagnetic properties, which makes this material suitable for commercial applications.

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