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Preparation and characterization of nanosize $Mn_{0.4}Zn_{0.6}$ Fe_2O_4 ferrite by citrate precursor method

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Abstract

Syntheses of nanosize $Mn_{0.4}Zn_{0.6}Fe_2O_4$ particles from metal nitrate solution through citrate precursor method are reported. Soft ferrites have been prepared by a wet chemical process, known as the citrate precursor method, which involves the formation of citrate complexes of the constituent cations. The electrical and magnetic measurements on Mn–Zn ferrite have shown electrical resistivity higher by more than two orders of magnitude compared to that observed for sample prepared by conventional ceramic method and low magnetic losses, making these ferrites specially suitable for high frequency applications. The saturation magnetization, initial permeability and Curie temperature are found to be more in precursor method as compared with ceramic method because of uniformity and homogeneity in grains and smaller grain size in precursor method. Curie temperature and saturation magnetisation has shown initial increase and then decreases with sintering temperature. These changes in properties are explained on the basis of various theories and models.

Keywords: B. Grain size; C. Electrical properties; D. Ferrites; Saturation magnetization

1. Introduction

Properties of ferrites are known to be sensitive to the processing technique [1,2]. A small deviation in the compositional stoichiometry of the ferrite affects its properties greatly. Soft ferrites such as Mn–Zn, Ni–Zn and Mg–Mn are well known ferrites covering wide-ranging applications [3,4]. Manganese–zinc ferrites are technologically important materials because of their high magnetic permeability and low core losses. These ferrites have been widely used in electronic applications such as transformers, choke coils, noise filters, recording heads, etc. Ferrites are commonly produced by a ceramic process involving high temperature solid-state reactions between the constituent oxides/carbonates. The particles obtained by this process are rather large and non-uniform in size. These non-uniform particles, on compacting, result in the formation of voids or low-density area in the green compacts. On sintering, non-reproducible products in terms of their magnetic properties are obtained. In order to overcome difficulties arising out of the ceramic method, wet chemical method called citrate precursor method has been considered for production of homogeneous, fine and reproducible ferrites. One of the main considerations of high frequency performance of ferrites is the high eddy current losses, which prevent the interaction of the magnetic field with the ferrite component and hence impair device performance. These losses can be reduced by having a material of high resistivity. Electrical conductivity in Mn–Zn ferrite has been attributed to electron hopping [5] between the two valence states of iron, $Fe^{2+} \leftrightarrow Fe^{3+}$, on octahedral sites. Maintaining the $+3$ valence state of octahedral Fe ions is thus a prerequisite for achieving high resistivity.

2. Experiment

Manganese–zinc ferrite of composition $Mn_{0.4}Zn_{0.6}Fe_2O_4$ was prepared by citrate precursor method. The materials used were manganese nitrate (98%, Merck, Germany), zinc nitrate (96%, Merck, India), iron (III) Citrate (99%, Merck, Germany) and citric acid (99% Merck India). These materials were

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weighed accurately in stoichiometric proportions. Iron (III) citrate was dissolved in distilled water by warming at 40 °C. Citric acid was added to manganese nitrate and zinc nitrate separately until complete formation of metal citrate complex, transparent in colour was obtained. These solutions were then added to iron citrate solution slowly and with constant stirring, ensuring no loss of material. The precursor mixture was then heated at 40 °C with constant stirring to allow evaporation and to obtain a dried product that was in the form of a uniformly coloured brown transparent glass containing all the cations homogeneously mixed together at the atomic level. As there is no precipitation at any stage, the problem of segregation of phases, which normally occurs in some other wet chemical methods such as co-precipitation, did not occur in this material. The dried citrate precursor was calcinated in a box type furnace for 2 h at 500 °C at the rate of 250 °C/h to obtain a ferrite powder. This powder was mixed with 2%P.V.A. binder and pressed into pellets of 1.30 cm diameter and 0.15 cm thickness under a pressure of 10 tons ($1\ \text{ton} = 1.016 \times 10^3$ kg) and rings of 1.60 cm outer diameter, 0.95 cm inner diameter and 0.23 cm thickness, under a pressure of 5 tons. These samples were sintered in air at 900, 1000, 1100, 1200 and 1300 °C at a heating rate of 250 °C/h in a box type furnace and were subsequently cooled. The pellets were coated with silver paste to provide electrical contact and the rings were wound with about 50 turns of 32 SWG enameled copper wire to form toroids. Saturation magnetisation was measured by using a vibrating sample magnetometer (EC&G PARC Model 155). DC resistivity was measured by two-probe method using Keithley electrometer (model 610) with current measuring capability down to 10^{-13}A. The Curie temperature, T_c, of the ferrite was obtained by a simple set up described by Soohoo [6]. X-ray diffraction measurements were taken on a Rigaku Geiger Flex 3 kW diffractometer using CuK_α source. Dielectric constant, ϵ', Initial permeability μ_I' and loss factors (ϵ'' and μ_I'') were measured by using Hewlett Packard LCR Meter Bridge model 4275A.

3. Result and discussion

X-ray diffraction pattern of the ferrite sample sintered at 1200 °C is shown in Fig. 1. The observed diffraction lines were found to correspond to those of standard pattern of Manganese ferrite with no extra lines, indicating thereby that all the samples have single phase spinel structure and no unreacted constituents were present in these samples.

Variation of DC resistivity of $Mn_{0.4}Zn_{0.6}Fe_2O_4$ ferrite with different sintering temperatures prepared by citrate precursor technique is shown in Fig. 2. The DC resistivity decreases from 90×10^6 ohm-cm to 19×10^6 ohm-cm, when sintering temperature of the sample was increased from 1000 to 1200 °C which is about 10–100 times more than that of ceramic ferrite. This observation is of significant importance as it makes these ferrites suitable for high frequency applications where eddy current losses become appreciable. The higher values of DC resistivity is because of stoichiometric compositions, better crystal structures and the improved microstructures obtained by citrate precursor method.

Grain size is another important contributing factor to the resistivity of the sample. Samples sintered at low temperatures possess smaller grain size. Sample with small grains consists of more number of grain boundaries. The grain boundaries are the regions of mismatch between energy states of adjacent grains and hence act as 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 smaller grains, thus keeping iron in the Fe^{3+} state [7]. Therefore, the sample sintered at low temperature is found to exhibit higher resistivity as compared to ceramic ferrite.

The variation of dielectric constant (ϵ') with frequency at different sintering temperatures is shown in Fig. 3. The value of dielectric constant decreases continuously with increasing frequency and the observed variations for the sample show systematic behaviour. The dispersion of dielectric constant is maximum for 1000 °C. This behaviour is mainly governed by the resistivity of the sample. Therefore, the dielectric constant is affected by the following factors:

1. There is an inverse proportionality between resistivity and dielectric constant [8].
2. There is an increase in homogeneous dielectric structure when the sintering temperature is increased.

This decrease in dielectric constant with increase in frequency is a normal dielectric behaviour and observed by Rezlescu and Rezlescu [9]. The dispersion at 1000 °C may be explained on the basis of available ferrous ions on octahedral sites. As a consequence, it is possible for these ions to be polarized to maximum possible extent. Further, as the frequency of externally applied electric field increases gradually, although the same number of ferrous ions is present in the ferrite material, the dielectric constant (ϵ') decreases. This reduction occurs because beyond certain frequency of applied electric field, the electronic exchange between the ferrous and ferric ions i.e. $Fe^{2+} \leftrightarrow Fe^{3+}$ cannot follow the alternating field.

The variation of dielectric loss factor (tan δ_ϵ) and imaginary part of dielectric constant (ϵ'') are shown in Figs. 4 and 5, respectively. It can be seen that dielectric loss factor and the imaginary part decreases with increasing frequency, but tan δ_ϵ shows a slight increase

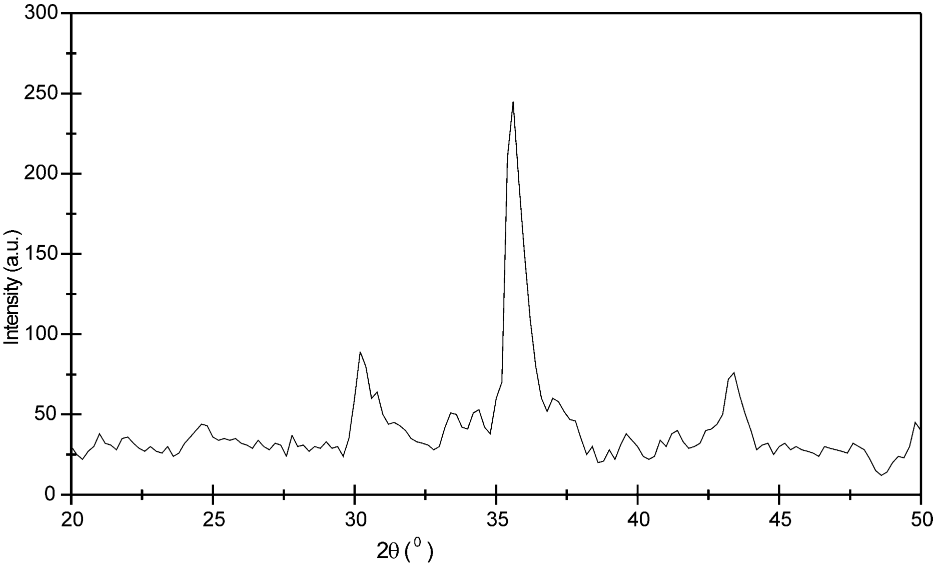

Fig. 1. XRD pattern of $Mn_{0.4}Zn_{0.6}Fe_2O_4$ sintered at 1200 °C.

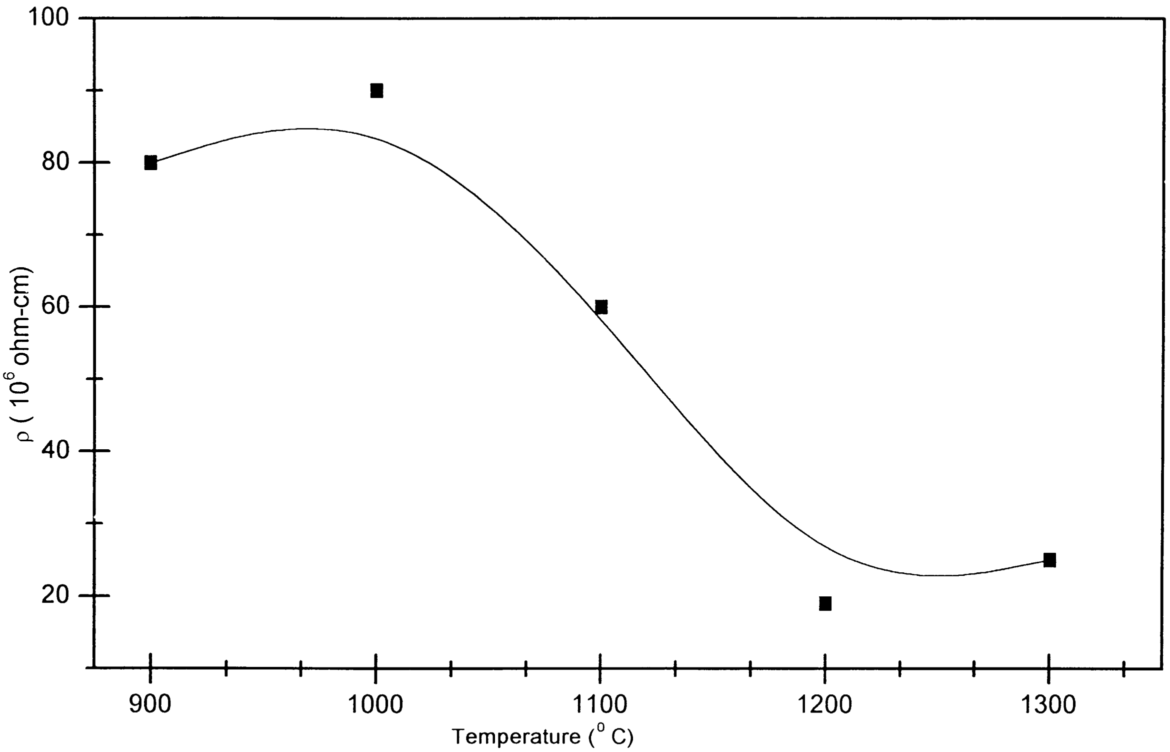

Fig. 2. Variation of DC resistivity (ρ) with sintering temperature for $Mn_{0.4}Zn_{0.6}Fe_2O_4$.

at higher frequencies. A qualitative description of this increase in tan δ_ϵ can be given as, Iwauchi [10] pointed out, that there is a strong correlation between the conduction mechanism and dielectric behaviour of ferrites. The conduction in ferrites is considered as due to hopping of electrons between Fe^{2+} and Fe^{3+}.

The variation of saturation magnetisation, $4\pi M_s$, as a function of the sintering temperature is shown in Fig. 6. It indicates that saturation magnetisation increases for increase in temperature from 900 to 1200 °C and then decreases. The cation distribution in $MnFe_2O_4$ ferrites is given by:

$$(Mn^{2+}_{0.8}Fe^{3+}_{0.2})[Mn^{2+}_{0.2}Fe^{3+}_{1.8}]O^{2-}_4$$

Sawazky et al. [11] have shown that canted spin structure is present in $MnFe_2O_4$ where the Y-K angle is equal to 48°. At sintering temperature upto 1200 °C,

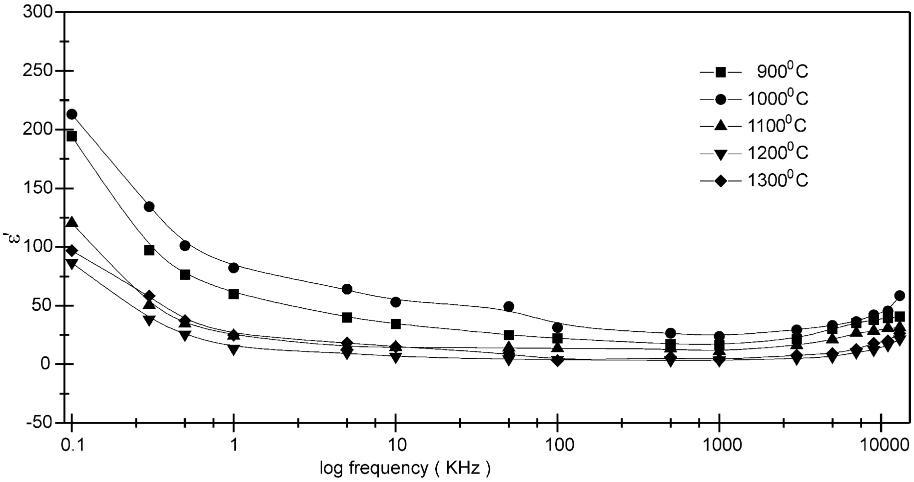

Fig. 3. Variation of dielectric constant ε' with log frequency of $Mn_{0.6}Zn_{0.4}Fe_2O_4$ at different sintering temperatures.

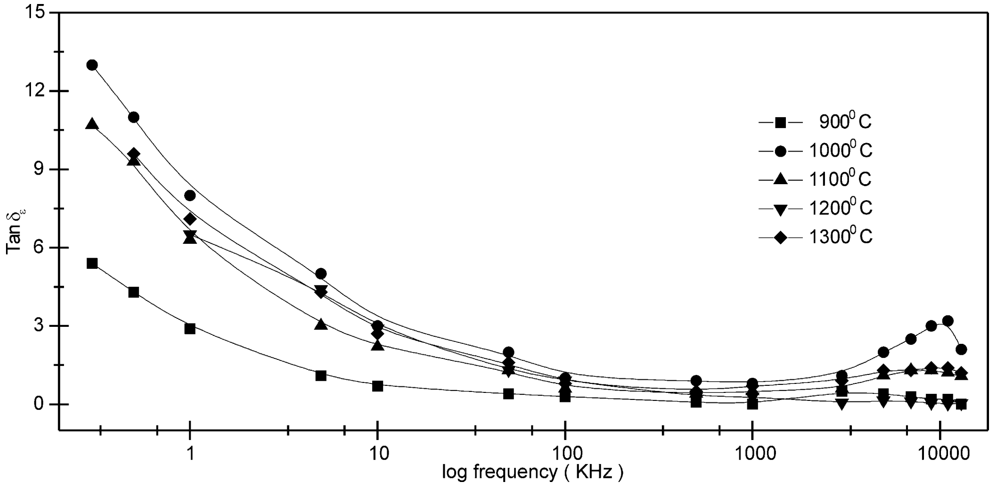

Fig. 4. Variation of dielectric loss factor (tan δ_ε) with log frequency at different sintering temperatures for $Mn_{0.4}Zn_{0.6}Fe_2O_4$.

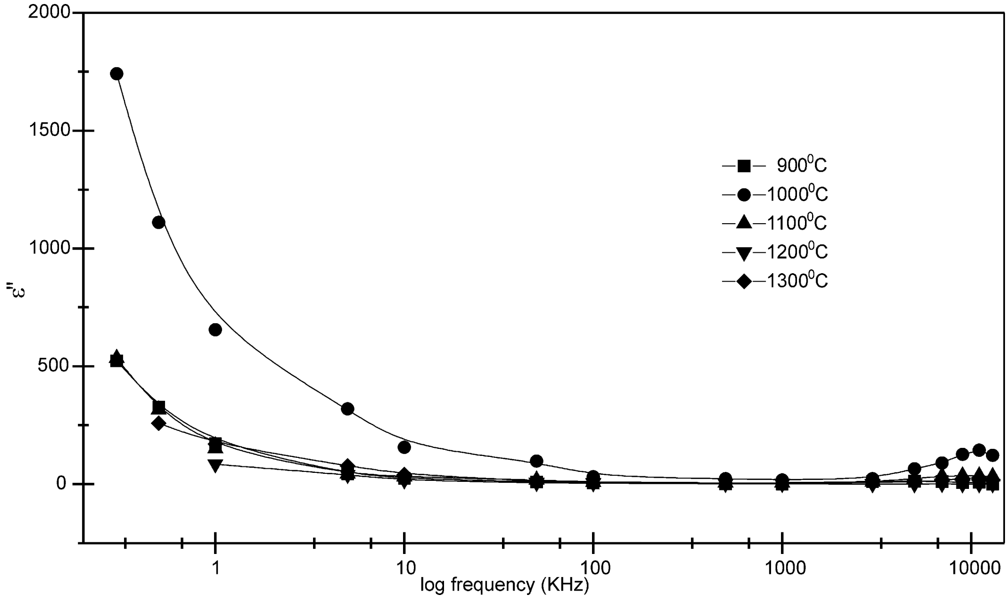

Fig. 5. Variation of imaginary part of dielectric constant (ε'') with log frequency at different sintering temperatures.

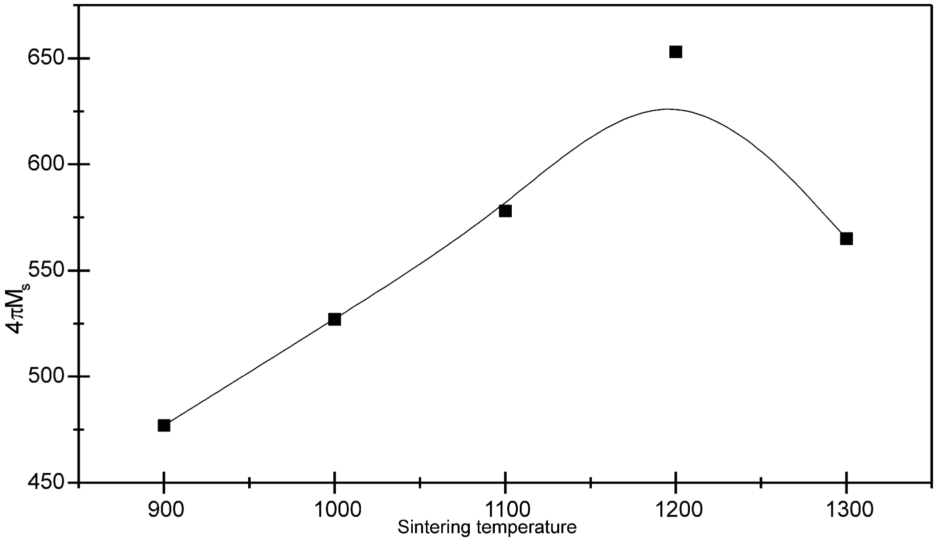

Fig. 6. Variation of saturation magnetisation 4 πM_s with sintering temperature.

Zn^{2+}, being diamagnetic in nature, preferentially go to octahedral site. As the observed saturation magnetisation M_s, increases, it indicates that the canting angle (Φ), at B site decreases due to the presence of Zn^{2+} ions, yielding higher value of M_s given by:

$$M_s = M_B \cos\Phi - M_A$$

When the sintering temperature is increased, these ions occupy B site by replacing Zn^{2+} ions and drifting some of the Fe^{3+} ions from the B to the A site. The observed increase in saturation magnetization, M_s, with increase in sintering temperature implies that spin ordering gradually changes from Yafet-Kittel Type to Neel type. Saturation magnetisation in the citrate precursor technique is found to be comparatively high as compared to ceramic technique. This is because in the precursor technique grain size becomes uniform, increasing the magnetic ion density and lowering the porosity [12] due to which magnetic moment per unit volume increases.

The variation of Curie temperature, T_c, with sintering temperature is shown in Fig. 7. The observed values are in close agreement with the reported values, thus further conforming the formation of $Mn_{0.4}Zn_{0.6}Fe_2O_4$by citrate precursor method. It can be seen that Curie temperature of the ferrite increases with increase in sintering temperature from 900 to 1200 °C and then decreases. This increase can be explained from the fact that as the sintering temperature is increased to 1200 °C, the grain size becomes more uniform. This helps Zn^{2+} ions to change spin ordering from Yafet-Kittel to Neel type. Since the energy required to offset the antiparallel spin alignment in Neel type is more than that required in Y-K type order, it results in an increase in Curie temperature. Another factor contributing to increase in Curie temperature is lattice contraction. Lattice contraction increases the overlapping of the orbitals, thus, strengthening the AB

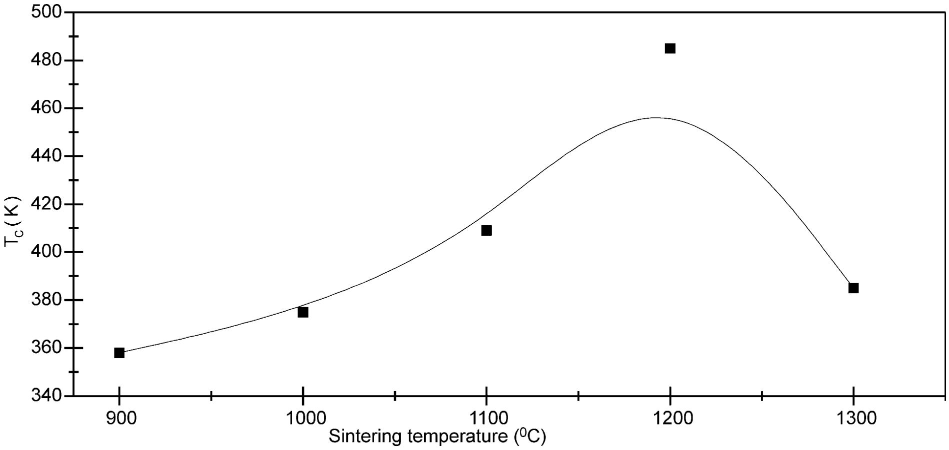

Fig. 7. Variation of Curie temperature (T_C) with sintering temperature for $Mn_{0.4}Zn_{0.6}Fe_2O_4$.

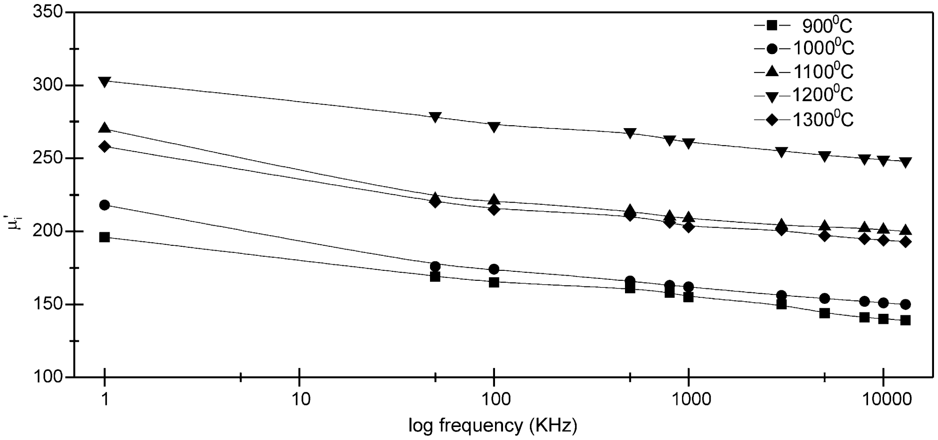

Fig. 8. Variation of initial permeability μ_i' with log frequency of $Mn_{0.6}Zn_{0.4}Fe_2O_4$ at different sintering temperatures.

interactions, which in turn increases the Curie temperature. The value of Curie temperature obtained in the citrate precursor method is found to be slightly higher as compared with ceramic technique. This is due to higher density of the magnetic ions, in citrate precursor ferrite, of low porosity, which require more energy to offset the antiparallel spin alignment.

The variation of initial permeability (μ_I') with frequency at different sintering temperatures is shown in Fig. 8. The initial permeability (μ_I') which is flux induced in the material at very low fields arises as a result of reversible movement of domain walls [13]. Greater the number of domain walls, higher is the permeability. The permeability in present case is found to be higher than that in ceramic technique [14–16]. The main reason for this increase is that the grain size in precursor technique is smaller and more uniform than that in ceramic technique. Smaller grains contain greater number of domain walls, which leads to an increase in permeability [17] in citrate precursor technique. The resonance peaks, which occur when the frequency of applied field equals the Larmor precision of electron spins, could not be observed in the present technique. The main reason for absence of resonance in the present work is that, as the grain size becomes uniform in citrate precursor technique, the resonance character vanishes [18]. A similar trend of results was found by Rado et al. [19–21] and Snoek [22] in ceramic technique. The other reason for the absence of resonance peaks may be as they probably lie beyond the measurable frequency range used in this work. It can be seen that initial permeability decreases with increase in frequency and increases with increase in temperature. The variation of initial permeability with frequency can be understood on the basis of Globos model [23,24]. According to this model, relaxation character, $(\mu_i - 1)^2 f_r = \text{constant}$, 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.

The variation of the permeability loss factor ($\tan \delta_\mu$) and imaginary part of permeability (μ_I'') with frequency are shown in Figs. 9 and 10, respectively. The permeability loss factor ($\tan \delta_\mu$) is required to be low for high frequency use of ferrites. It can be seen that $\tan \delta_\mu$ and μ_I'' decrease with increasing frequency and show identical behaviour at all the

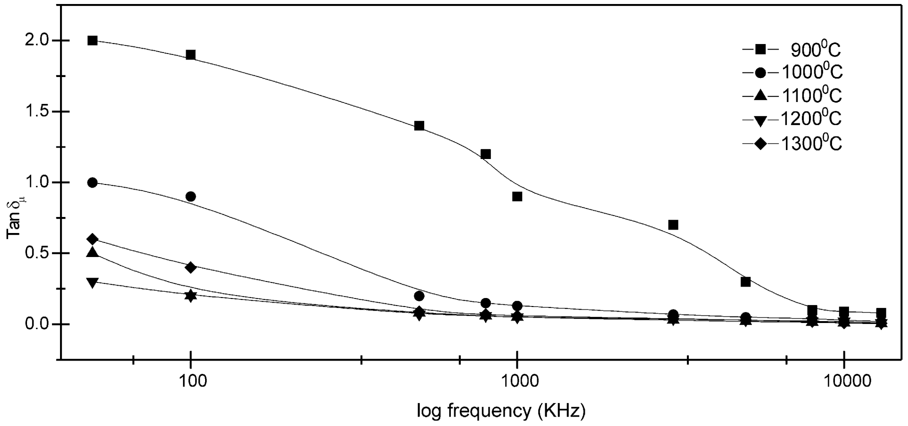

Fig. 9. Variation of permeability loss factor ($\tan \delta_\mu$) with log frequency at different sintering temperatures.

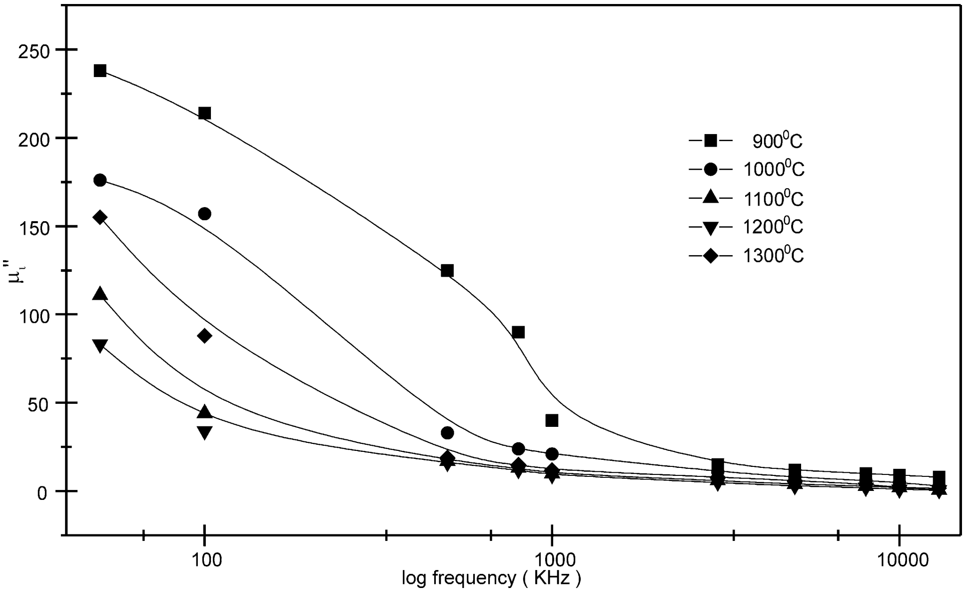

Fig. 10. Variation of imaginary part of initial permeability (μ_i'') with log frequency at different sintering temperatures.

sintering temperatures. These values are about the same and in some cases are of the order of magnitude lower than that of the conventionally prepared technique [22]. The low losses are a result of appropriate control of chemical composition and microstructure of ferrite. Since at a sintering temperature 1200 °C initial permeability is high and loss factor is low, the result of present investigation may be used to select an appropriate composition $Mn_{0.4}Zn_{0.6}Fe_2O_4$ at sintering temperature 1200 °C.

Hence, it is concluded that Mn–Zn ferrite prepared by citrate precursor technique results in better magnetic and electrical properties than ceramic technique. The main advantage of this method lies in lowering the permeability and dielectric losses at sintering temperature 1200 and 1000 °C, respectively.

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