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A comparative study of electric properties of nano-structured and bulk Mn–Mg spinel ferrite

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Abstract

A series of nano-sized particles of $Mn_{1-x}Mg_xFe_2O_4$ (x = 0.0, 0.1, 0.2 and 0.25) have been synthesized by co-precipitation method. The effect of Mg-substitution on structural and dielectric properties is reported in this paper. X-ray diffraction analysis for both nanosize and bulk samples revealed the nanocrystalline nature in the prepared ferrite samples. The crystallite size increases from 3–6 nm in nanosamples to 63.9–85.5 nm in bulk samples. The dielectric properties for all the samples have been studied as a function of frequency in the range 10–10^5 Hz at different temperatures. Dielectric properties such as dielectric constant (ε') dielectric loss (ε''), dielectric loss tangent ($\tan\delta$) and ac conductivity have been studied for the investigated samples as a function of frequency. The data indicated that, the dielectric constant and the loss factor values of our former are ten orders of magnitude than those of the later. The low dielectric behavior makes ferrite materials useful in high frequency applications.

Keywords: Mg–Mn nanoferrite; Bulk ferrite; Dielectric constant; ac conductivity

1. Introduction

Ferrites constitute an important group of magnetic materials with a wide range of applications due to their magnetic properties and low dielectric loss [1,2]. Spinel ferrites of chemical formula (MFe_2O_4) play a significant role in microwave control components such as circulators, isolators and phase shifters. Nanostructured materials are now being studied intensively due to their novel physicochemical properties. Mg–Mn ferrites were considered as the most versatile ferrites due to their high resistivity and low eddy currents for high frequency application. Microstructure and magnetic properties of Mg–Mn ferrites are highly sensitive to composition, sintering conditions, grain size, type, and amount of additives, impurities and the preparation methodology [3,4]. Among different ferrites, magnesium ferrite ($MgFe_2O_4$) enjoys a special attention because of its vast applications in high-density recording media, heterogeneous catalysis, adsorption, sensors and magnetic technologies [5]. Mg ferrite may be used also in lower requirement television yokes and fly-back transformers because of the lower cost of Mg and because its higher resistivity that eliminates the need for taped insulation between yoke and winding. Moreover, Mg ferrite may be used in conjunction with other divalent ions (Mn) in higher frequency applications for resistivity reasons; where for high frequency applications the permeability drops off due to the great increase in losses, and to avoid that Mg–Mn or other higher resistivity ferrites are the materials of choice. It is well known that low eddy current losses even at microwave frequencies are some of the characteristic properties of Mg–Mn ferrites.

In recent years, worldwide researchers, because of their interesting physical and chemical properties compared to their counterpart bulk materials [6], have extensively studied nanosize materials. Magnesium ferrites are a commercially important material and have been widely used as magnetic materials [7,8].

The electrical properties are important for ferrites and composites containing mixed ferrites, not only from the application point of view but also from the fundamental point of view [9]. Evaluation of ac electrical conductivity reveals a wealth of information as regards the usefulness of these

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materials for various applications. Moreover the study of ac electrical conductivity sheds light on the behavior of charge carriers under an ac field, their mobility and the mechanism of conduction [10].

It is known that, magnetic nanoparticles are also used extensively in the field of biomagnetics for a broad range of applications, such as drug delivery [11–13], cell labeling and sorting [14], magnetic resonance imaging, sensing [15] as well as therapeutic applications [12,16] such as and ac magnetic field-assisted cancer therapy.

Among these, fine ferrites made of oxides of manganese, magnesium and iron have been of interest due to their applications in various fields. Manganese–magnesium ferrites and low losses and these materials extensively used in microwave devices, computer memory chips, magnetic recording media and, fabrication of radio frequency coils, transformers cores and rod antennas [17,18,5,19].

In recent years, nanocrystalline ferrites have attracted much interest because of their unusual magnetic properties and their promising technological applications. The bulk properties of ferrites change as their dimensions are changed to nanoscale [20]. The properties of ferrites are very sensitive to the processing techniques. The co-precipitation method offers a synthesis route for the production of ferrite, which is uniform and non-aggregated [21]. In literature, as far as the authors know, a comparative study of the ac electrical properties of substituted Mg–Mn nano-structured ferrites – prepared by co-precipitation method – and their bulk counterparts has not been reported yet. Hence, due to the technological importance of Mg–Mn ferrites, the present work aims to perform such a study.

The goal of this paper is compare the structural and the electrical properties due to the evaluation of the ac conductivity values, loss factor and dielectric values in $Mn_{1-x}Mg_xFe_2O_4$, $x = 0.0, 0.1, 0.2$, and 0.25 nano and bulk ferrite and carry out the frequency and temperature variation studies on these samples.

2. Experimental

Nano-sized particles of $Mn_{1-x}Mg_xFe_2O_4$ ($x = 0.0$, 0.1, 0.2 and 0.25) were previously prepared by co-precipitation method; where the raw materials of $Fe(NO_3)_2{\cdot}9H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$ and $Mg(NO_3)_2{\cdot}6H_2O$ were mixed in their respective stoichiometry. The precipitation was carried out using drop wise of NaOH solution under constant stirring. The pH of the solution was constantly monitored as the NaOH solution was added. The reactants were stirred until a pH level of 11–12 was reached. The precipitate was washed by double distilled water many times to remove NaCl. Finally, drying at room temperature was performed and the particles had been characterized by X-ray diffraction analysis to be sure of the formation of the ferrite.

In the present work a part of those samples was sintered at 1200 °C for 4 h to obtain bulk samples via increasing the particle sizes, then X-ray diffraction analysis has been performed again for the bulk counterparts. The ac conductivity, the dielectric constant (ε') and dielectric loss factor ($\tan\delta$) of the two sets of samples (nano-structured and bulk) were measured by complex impedance technique using a lock-in amplifier (Model SR 510 Stanford Research Systems) in the frequency range 10–10^5 Hz at different temperatures. In the experimental setup [22] a small resistor R is connected in series with the sample. The current is then given by ($I = V_R/R$) where V_R is the drop voltage on R. The lock-in amplifier is used to measure simultaneously the voltage V_R, the frequency of the applied voltage f and the phase difference between the applied ac voltage V and V_R. From those readings ac conductivity, dielectric function and loss factor could be calculated at different frequencies and temperatures.

3. Results and discussion

The XRD patterns of as-prepared manganese–magnesium ferrite nano and bulk ferrite samples $Mn_{1-x}Mg_xFe_2O_4$; $0 \leq x \leq 0.25$ were measured and the results indicated that, the crystallite size of the nanosize samples increases ranging from 3 to 6 nm whereas for the bulk samples increases from 63.9 to 85.5 nm.

Figs. 1 and 2 display the ac conductivity as a function of frequency at different temperatures for nano and bulk samples respectively. It can be seen that in general the conductivity of bulk samples has greater values than the corresponding nanostructure samples. This is expected and acceptable according to Koops model [23], due to the suggestion that, a simple model for a ferrite sample that, two resistors and two capacitors are needed in order to build up a two-pole (equivalent circuit) having a finite value of dc resistance and showing the typical loss factor versus frequency curve with one hump which had been found with his materials. This model is justified if the ferrite sample is assumed to be consisted of well conducting grains separated by layers of lower conductivity called grain boundaries. According to this model, it is expected that the nano-samples will have smaller grains and larger ratio of grain boundaries to grain areas, i.e. larger areas of more resistive regions. It is known that the grain boundaries are the region of mismatch between the energy states of adjacent grains and hence act as a barrier to the flow of electrons [21]. Therefore, larger areas of grain boundaries lead to lower values of conductivity as found in the studied samples. Moreover, the ac conductivity increases with increasing temperature in both types of samples ensuring the semiconducting nature of the samples; besides it increases with increasing frequency. In other words the frequency is acting as a pumping force to the charge carriers between different localized states and these charge carriers participate in the conduction process. The conductivity decreases as x increased in case of nanoferrite samples due to statistical redistribution of Fe^{3+} ions among A and B sites together with the existence of a very small amount of Fe^{2+} which is responsible for the conduction mechanism. As the Mg content increases, the probability of the valence exchange (Mn^{3+}, Mn^{2+}) is lowered which contributes to the higher resistivity values.

The conductivity of the sample with $x = 0$ bulk sample show very low values at $T = 330$ and 307 compared with other samples due to the high resistivity of the $MnFe_2O_4$ at room temperature. And also the $x = 0.0$ sample is just Mn ferrite

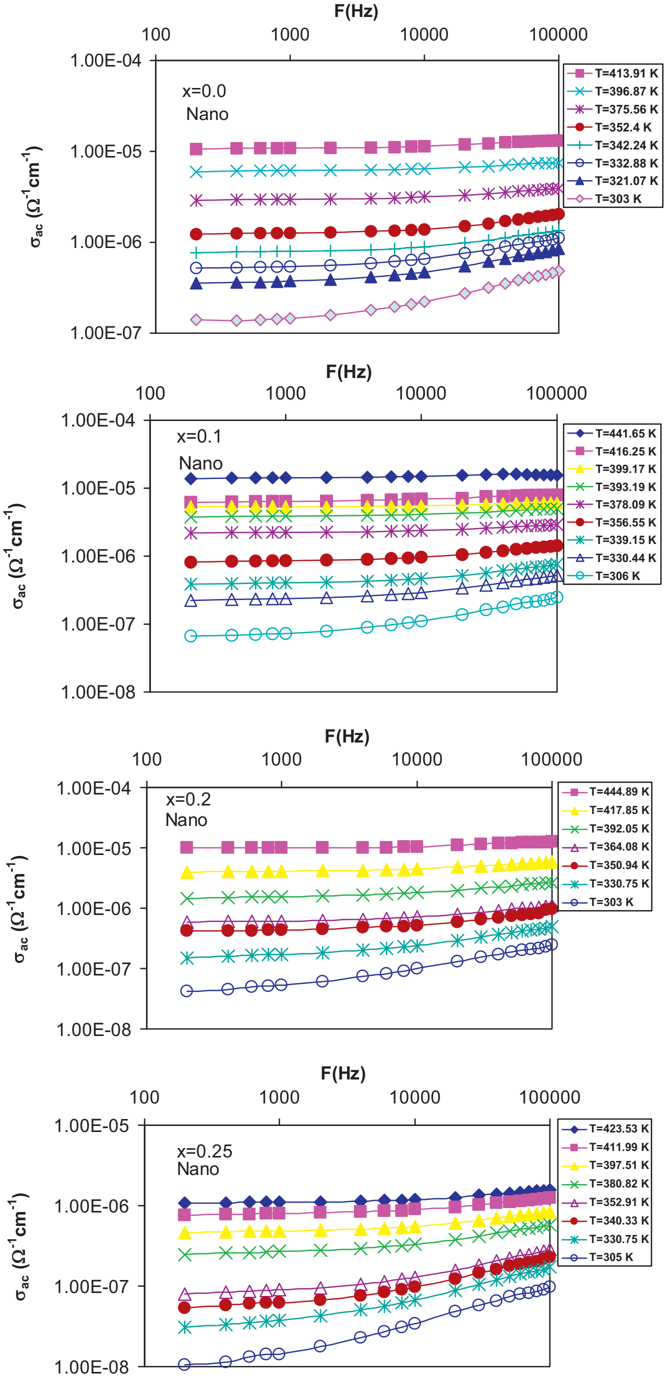

Fig. 1. The ac conductivity as a function of frequency at different temperatures for nano samples.

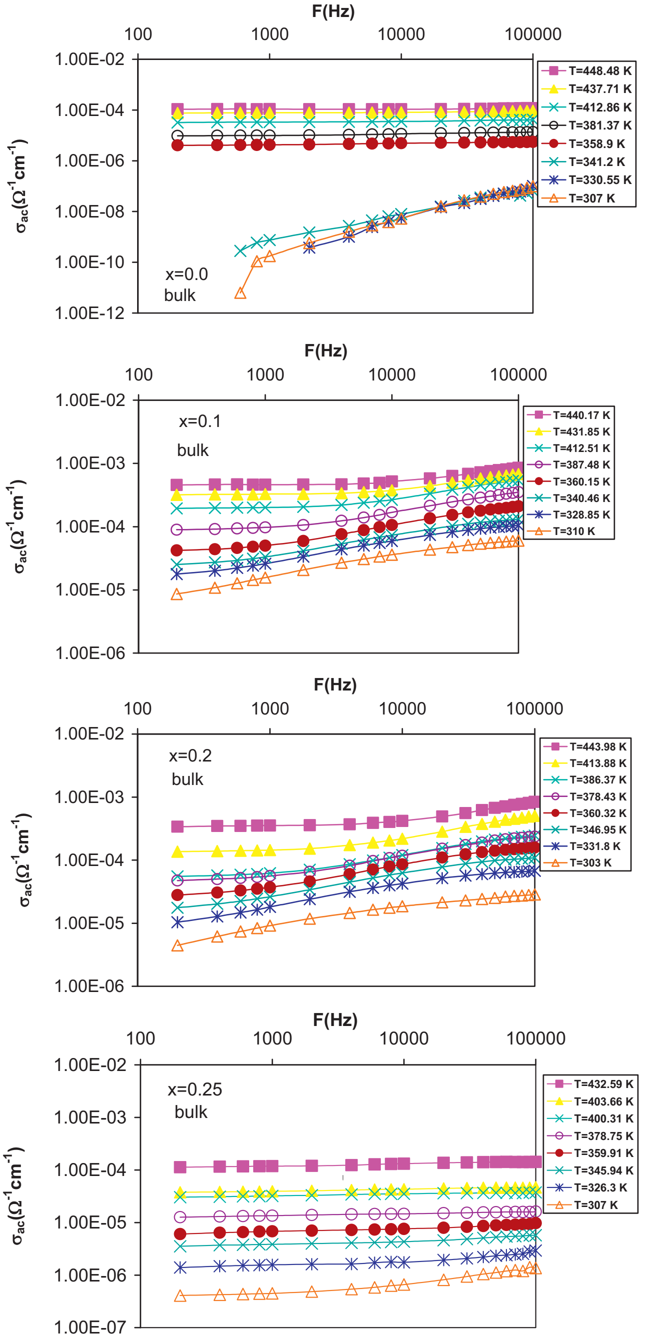

Fig. 2. The ac conductivity as a function of frequency at different temperatures for bulk samples.

without any Mg content and it is known that the n-type charge transfer in Mn ferrite is due to the hopping of electrons between Fe^{2+} and Fe^{3+} ions according to: $Fe^{3+} + e \leftrightarrow Fe^{2+}$, while p-type charge transfer between Mn^{2+} and Mn^{3+} ions exists according to: $Mn^{2+} + h \leftrightarrow Mn^{3+}$ [24]. In other words, in the studied sample of $x = 0.0$, both types of charge carriers take part in the conduction process, and since it is well known that the contribution of p-type charge carriers to conductivity is more pronounced at high temperatures, therefore this explains the observed increase in conduction values after the temperature is raised enough to manifest the contribution of p-type charge carriers. Also, there is a sharp increase in conductivity with increasing frequency in that sample at room temperature which may be due to electrode polarization, where there is a virtual capacitor between the sample and the electrode; its impedance effect diminishes as the frequency increases.

Figs. 3 and 4 show the real part of permittivity function or the dielectric constant ε' as a function of frequency at different temperatures for nano and bulk samples respectively. It is clear that, the values of ε' decrease with increase in the frequency

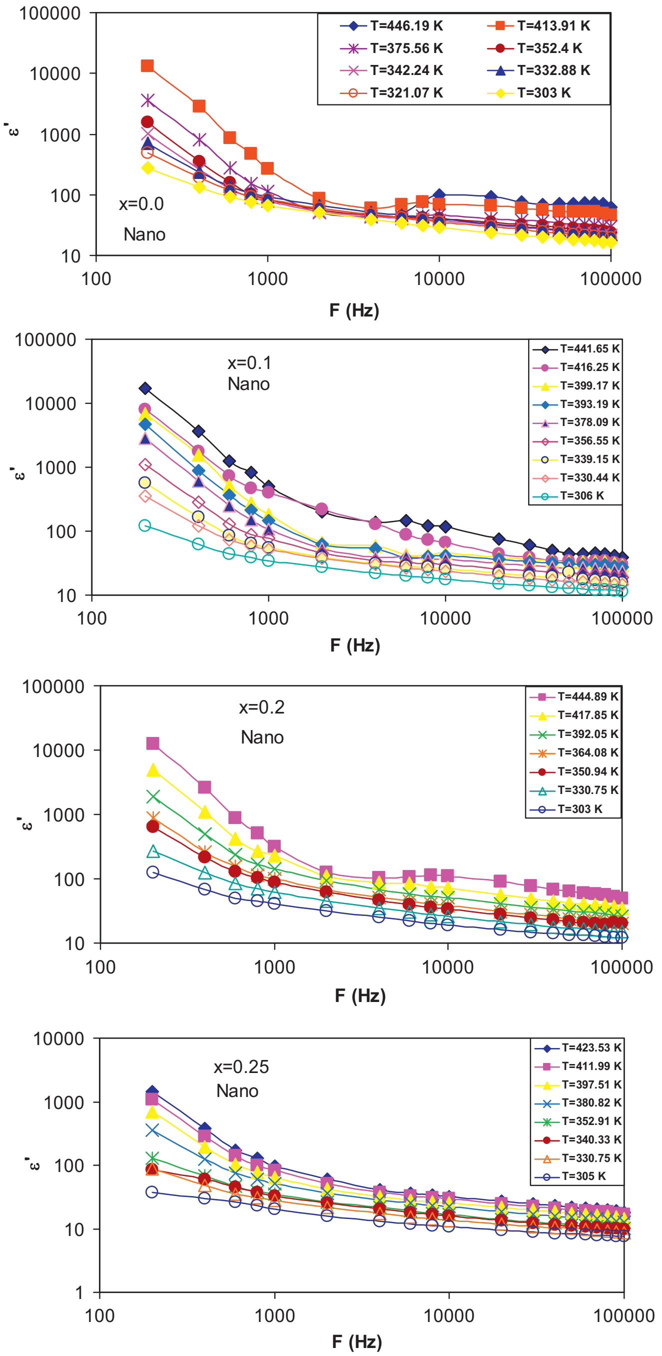

Fig. 3. The dielectric constant ε' as a function of frequency at different temperatures for nano samples.

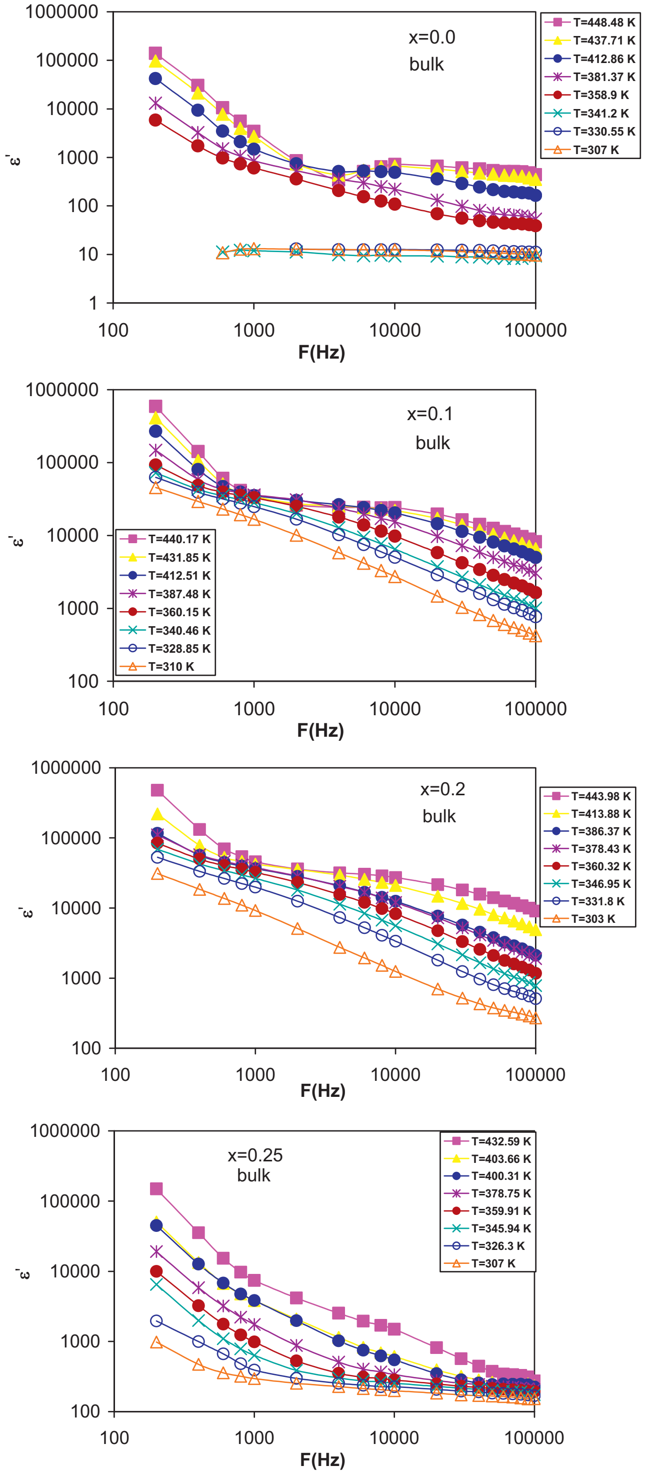

Fig. 4. The dielectric constant ε' as a function of frequency at different temperatures for bulk samples.

while increase with increasing temperature in agreement with several investigators [25–30]. Generally, the dispersion of ε' can be explained on the basis of the interfacial polarization due to the inhomogeneous dielectric structure of ferrites – as discussed above (Koop's model) – where the high observed values at low frequencies are due to the accumulation of charge carriers at the boundaries between the conductive grain regions and the highly resistive grain boundary regions. Whereas, at high frequencies, those charges cannot follow the variation of the field and therefore their contribution to the polarization ceases. Also it can be seen that ε' increases with increasing temperature which attributed to the fact that the interfacial polarization is governed by the number of charge carriers. With the increases in temperature, the number of charge carrier increase leads to enhanced build up of space charge polarization and hence increase the dielectric constant [10]. Finally, in the comparison between the bulk and nano-structured samples, it can be easily observed that, the dielectric constant values of our former are ten orders of magnitude greater than the later. This is because the main contributor to the dielectric constant value in ferrites is the interfacial polarization which is tightly correlated to the conduction process therefore the same above explanation of increasing conductivity with increasing grain size is valid in the case of dielectric constant. An evidence of the correctness of this assumption is the observed behavior of ε' in the sample of $x = 0.0$ at the lowest three temperatures too.

Figs. 5 and 6 illustrate the loss tangent (tan δ) as a function of frequency at different temperatures for all the investigated samples. It can be seen that, almost all samples exhibit maxima. The maxima shift to higher frequencies with increasing temperature. Generally, these peaks were explained in literature also due to the strong correlation between the conduction mechanism and the dielectric behavior in the spinel ferrites as pointed out by Iwauchi [31]. The conduction mechanism in the present samples is almost always explained according to hopping process. In this case, a maximum in the dielectric loss tangent is observed when the frequency of the hopping charge carriers is

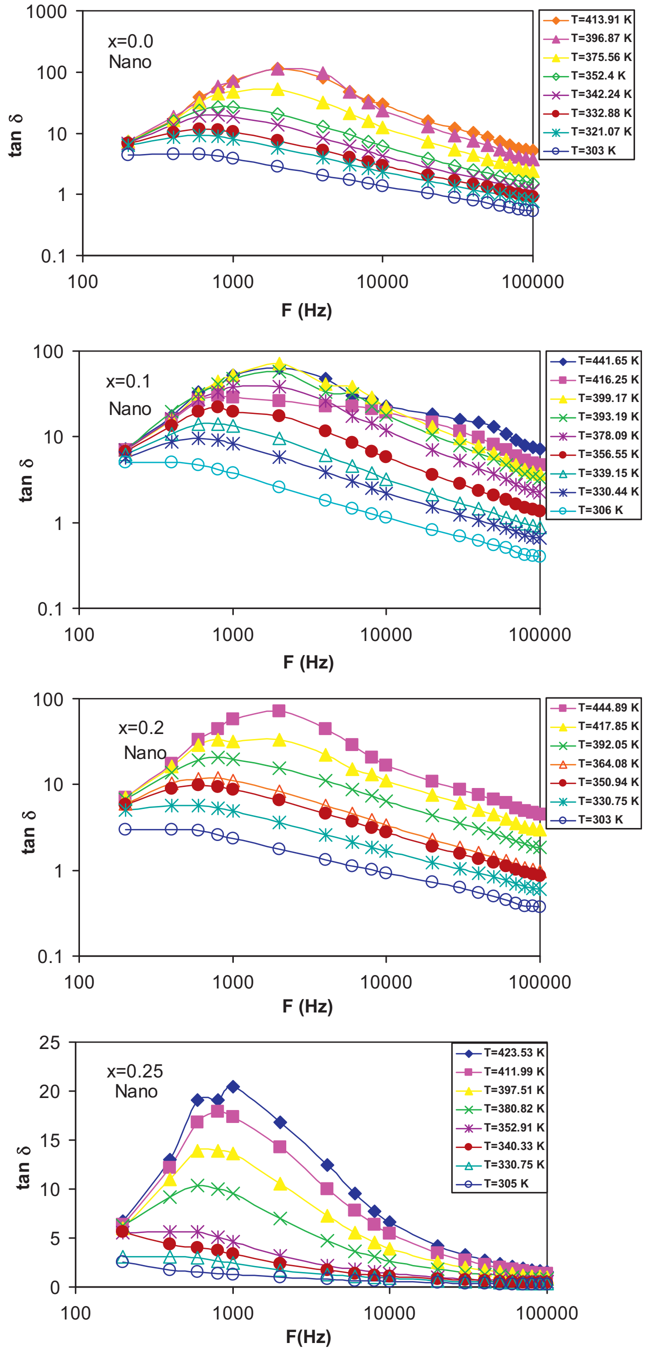

Fig. 5. The loss tangent (tan δ) as a function of frequency at different temperatures for nano samples.

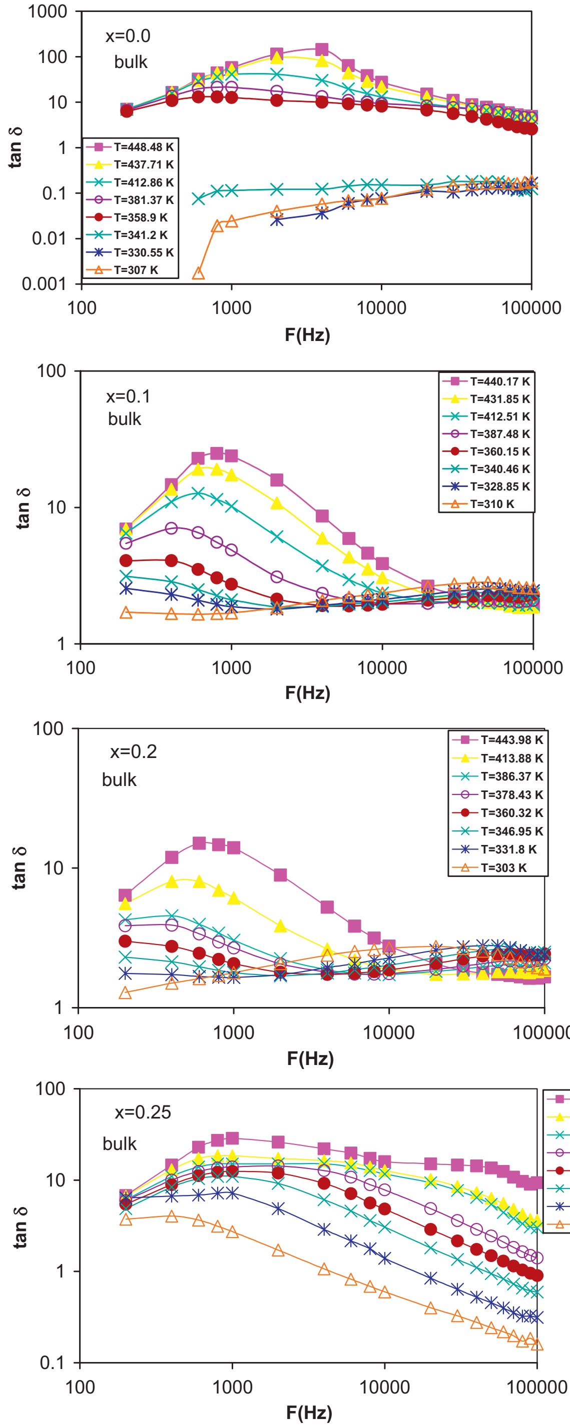

Fig. 6. The loss tangent (tan δ) as a function of frequency at different temperatures for bulk samples.

approximately equal to the external electric field frequency [10]. Comparing the bulk and nano-structured samples it can be also observed that the loss tangent values of the former are ten orders of magnitude greater than the later as mentioned before.

4. Conclusions

Mg–Mn nanoferrites ($x = 0$, 0.1, 0.2, and 0.25) were prepared by the co-precipitation method. The crystallite size increases from (3–6 nm) to (63.9–85.5 nm) after sintered at 1200 °C with increase in Mg-content. The conductivity as a function of temperature reveals the semiconducting nature of all samples. In general, the conductivity values of bulk samples have greater values than the corresponding nanostructure samples. The co-precipitation prepared samples are found to exhibit lower values of the dielectric constant and losses as compared to those obtained in ferrites prepared by the conventional ceramic method. In the same time, dielectric constant and loss decreases rapidly with increasing frequency, and then reaches a constant value.

The dielectric constant and the loss factor values of the former are ten orders of magnitude than those of the later. The loss factor ($\tan\delta$) of all the investigated samples exhibits maxima at the supposed frequency of hopping electrons.

Hence much lower dielectric constants obtained for the ferrites are used in the applications at high frequencies as microwave absorbers.

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