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AC impedance studies on $LiFe_{5-x}Mn_xO_8$ ferrites

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ABSTRACT

A systematic investigation of AC impedance studies of Mn doped Lithium ferrites with composition formula, $LiFe_{5-x}Mn_xO_8$ (x = 0.0, 0.2, 0.4, and 0.6) has been undertaken. The materials were prepared by sol–gel method. Complex impedance data measured in the frequency range 200 Hz to 1 MHz at different temperatures was analyzed systematically. It has been observed that the magnitudes of real (Z') and imaginary (Z'') components of the impedance are found to decrease with increasing temperature. It is interesting to note that the relaxation time varies linearly with temperature. The Nyquist impedance plots of the present investigation clearly depicts the inherent phenomenon involved in conduction mechanism of Mn doped Lithium ferrites.

1. Introduction

The electrical properties of the spinel ferrites are in general affected by factors like method of preparation, cation substitutions, grain size etc. [1]. These materials have become an important class of magnetic materials due to their rich electrical and magnetic properties and attracted the attention of the scientific community for past few decades. The unusual combination of multifunctional activities makes them an excellent candidates for wide ranging applications including microwave devices, computer memories, transformers, magnetic recordings and magnetic switches [2–4].

The AC impedance spectroscopy is a powerful tool to understand the electrical behavior in ferrites and has been widely used for single crystals, poly crystals, and amorphous forms [5]. The AC impedance analysis gives an opportunity to study the electrical transport in detail by considering their resistive (real) and reactive (imaginary) components separately. The experimental data can be analyzed in terms of four possible complex formalisms such as the complex impedance (Z^*), the electric complex modulus (M^*), the complex admittance (Y^*) and the complex permittivity (ε^*) [6]. In fact, these physical parameters are interrelated as follows:

$$Z^* = Z' - Z'' \quad (1)$$

$$M^* = M' + jM'' = j\omega C_o Z^* \quad (2)$$

$$\varepsilon^*(\omega) = \varepsilon' - j\varepsilon'' = (M^*)^{-1} \quad (3)$$

$$Y^* = Y' + Y'' = (Z^*)^{-1} \quad (4)$$

where $Z' = |Z|\cos\theta$ and $Z'' = |Z|\sin\theta$ (Z' and Z'' are the real and imaginary components of impedance respectively), ω is the angular frequency ($2\pi f$), C_o the vacuum capacitance of the measuring cell and electrodes with an air gap in place of the sample, $C_o = \varepsilon_o/k$, here ε_o is the permittivity of free space and $k = l/a$, where l is the thickness and a is the area of the sample and finally, Y' and Y'' are the real and imaginary parts of admittance respectively.

It has been widely accepted that the ferrite materials synthesized via standard ceramic methods result faulty homogeneity, often secondary phases and require high sintering temperatures. Recently, it had been identified and explored that the soft chemical methods are best suitable method to prepare oxide materials in general and ferrites in particular. Since, these methods offer molecular level mixing of ingredient during the processing, the problem of faulty homogeneity, secondary phases and high processing temperatures can be avoided. Moreover, these chemical methods also recognized as technically feasible and commercially viable preparative techniques for oxide materials. In view of all these facts, citrate based sol–gel method has been used in present investigation.

In the present study, an efforts have been made to address electrical properties of sol–gel prepared $LiFe_{5-x}Mn_xO_8$ (x = 0.0, 0.2, 0.4, and 0.6) ferrites by analyzing their AC impedance data with varying frequencies at different temperatures and results of such an investigation are presented here.

2. Experimental

2.1. Synthesis

Polycrystalline samples with compositional formula, $LiFe_{5-x}Mn_xO_8$ (x = 0.0, 0.2, 0.4, and 0.6) were prepared by sol–gel method. Highly pure and analytical grade Li_2CO_3, $Mn(CH_3COO)_2{\cdot}4H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, HNO_3 and citric acid were used as

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initial ingredients. In the first step, Li_2CO_3 has dissolved in appropriate amount concentrated nitric acid to make a clear water soluble compound. The other ingredients, $Fe(NO_3)_3{\cdot}9H_2O$ and $Mn(CH_3COO)_2{\cdot}4H_2O$ were also dissolved in deionized water separately and finally, all these transparent solutions mixed together to form a nitrate mixture. The nitrate mixture solution was converted into citrate solution by adding 1:1 ratio of the citric acid to the metal atoms present in the composition. To promote the reactants faster and active, the pH of the solution was adjusted in between 6.5 and 7.5 by adding dilute ammonia solution. Due to poly-hydroxy nature of the citric acid, the entire solution will become viscous during a continuous heating at ~60 °C and vigorous stirring on hot plate with magnetic stirrer for about 10–12 h. During the process, a homogeneous solution was attained and a subsequent removal of entire water content in the solution, and as a result highly viscous solution was formed. A gelating reagent, ethylene glycol was added in a molar ratio of 1:1.2 to the metal atoms present in the compound. Further heating at temperatures ~160–180 °C for 2–3 h, yields a porous material (dried gel) consisting of some residue of reagents. During the process of heating, at one particular stage the ignition will start with self-propagating combustion and the material becomes a puffy porous mass by exhausting the residue in the form of gases. This powder form was considered as-synthesized powder. The obtained porous powders were ground in agate mortar. This ground powders were heated at 300 °C in small amounts in an Electric Bunsen burner to remove the excess citrates and ethylene glycol present in the compound. This precursor was heated at 500 °C temperature for 2 h in a muffle furnace so as to get the final product. All these steps are sequentially presented in a flow chart given in Fig. 1. The prepared ferrite powders was mixed with an appropriate amount of 2 wt.% poly vinyl alcohol (binder) and the granulated powders was uniaxially pressed at a pressure of 4000 kg cm^{-2} to form the pellets. The specimens were sintered at 1050 °C for 4 h in air atmosphere.

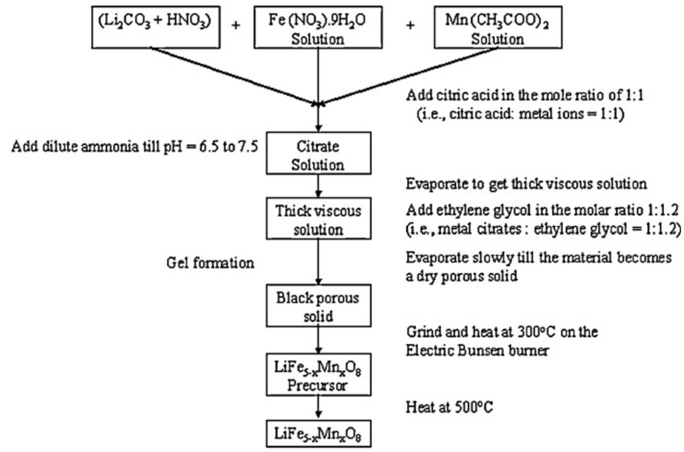

Fig. 1. Flow chart showing the sol–gel method of preparation of $LiFe_{5-x}Mn_xO_8$ ferrites.

2.2. Characterization

The phase purity and crystal structure of the material were confirmed by X-ray diffraction (XRD) measurements (by Panalytical X-pert pro system) with Cu-Kα

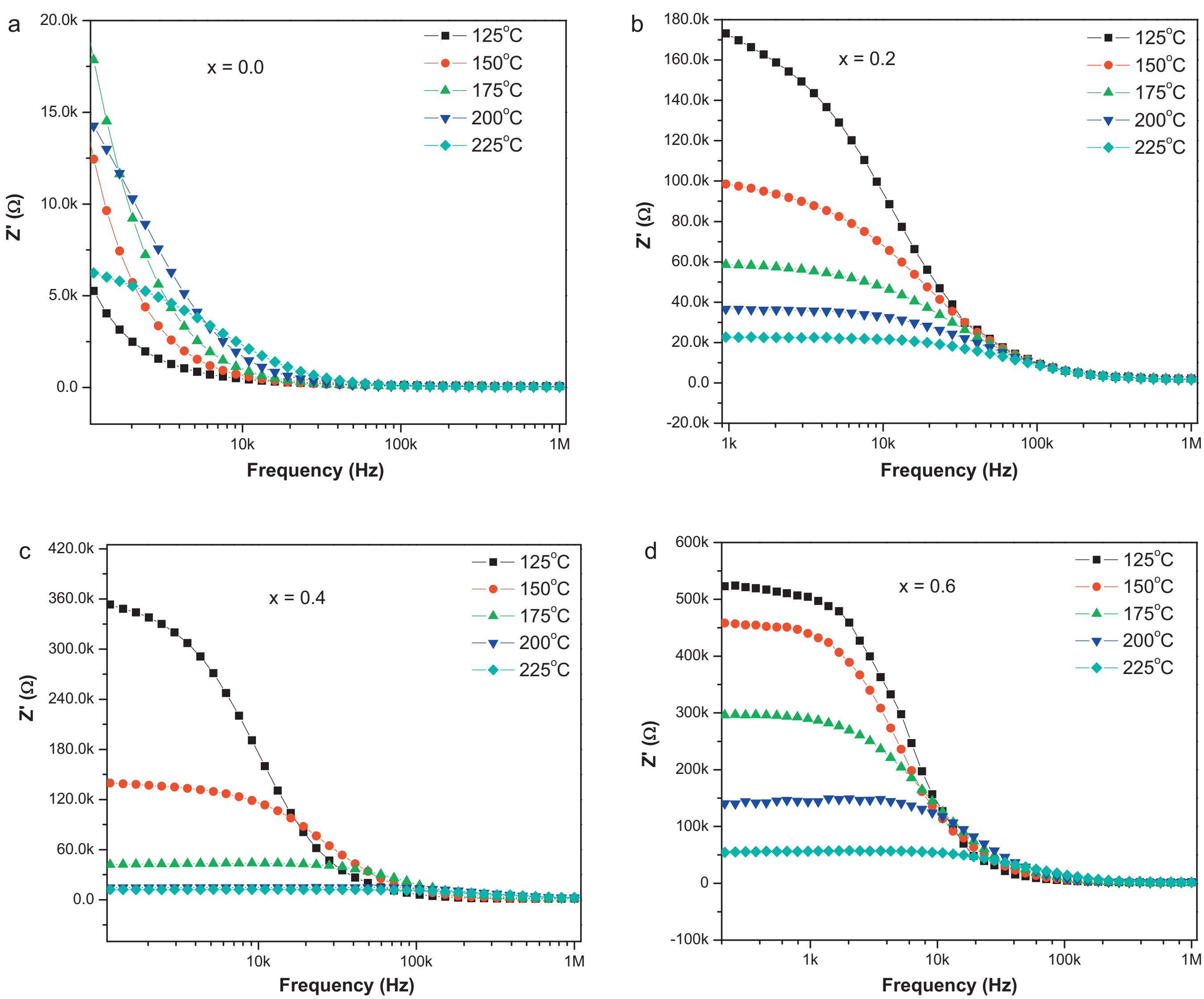

Fig. 2. (a–d) Variation of Z' with frequency of $LiFe_{5-x}Mn_xO_8$ ferrites at different temperatures.

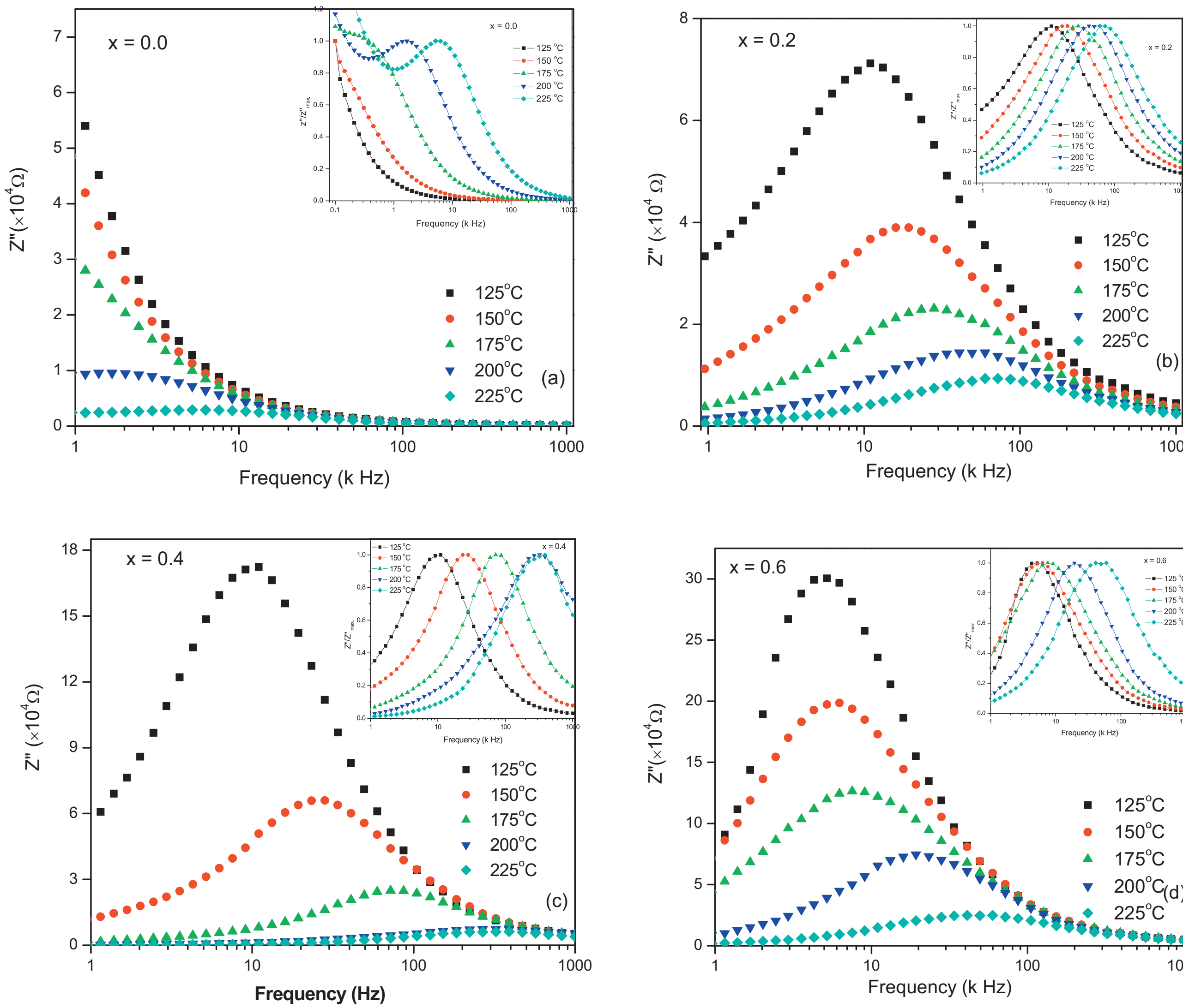

Fig. 3. (a–d) Variation of Z'' with frequency of $LiFe_{5-x}Mn_xO_8$ ferrites at different temperatures.

as a radiation source at room temperature. AC impedance measurements were preformed on fine polished pellets painted with silver paste by using AutoLab PGSTAT-30 frequency impedance analyzer. The measurements were carried out over a frequency range 200 Hz to 1 MHz at different temperatures. The relaxation time has been deduced from the corresponding frequency of the peak values by using the relation $\omega_{max}\tau_z = 1$, where, the relaxation time $\tau_z = 1/(2\pi f_{max})$, and the conductivity of the samples has been calculated using the $\sigma = l/RA$ relation, where, l is the thickness, A denotes the surface area and R is the resistance of the sample.

3. Results and discussion

Fig. 2(a–d) shows the variation of real part of impedance (Z') with frequency at different temperatures. It is clear from the figures that at lower temperatures, the value of Z' decreases with increasing frequency up to certain value and for further increase and becomes almost constant. The decrease in Z' with the increasing frequency may be attributed to the space charge polarization effect in the material. In fact, this phenomenon has been further verified by observing the coalesced behavior of real part of high frequency impedance for all measured temperatures. The decrease of Z' with increasing temperature clearly depicts the importance of single relaxation process in the materials, which results in the enhancement of AC conductivity. In fact, the present results are in good agreement with reported ones for similar ferrites [7–9].

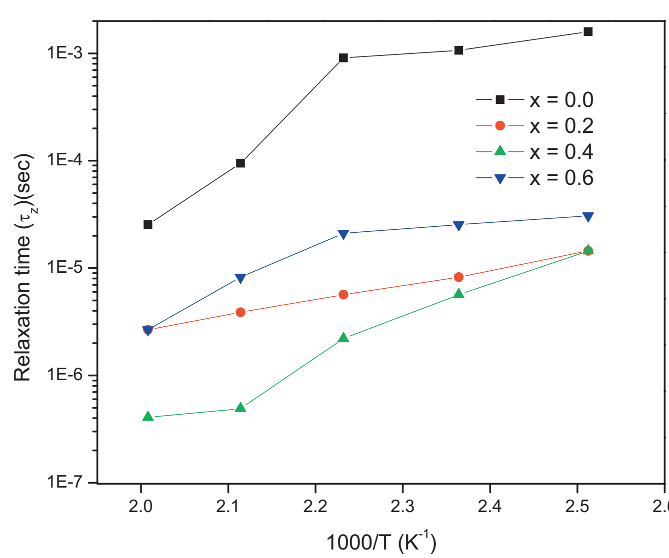

Fig. 4. Relaxation time versus inverse of temperature for $LiFe_{5-x}Mn_xO_8$ ferrites.

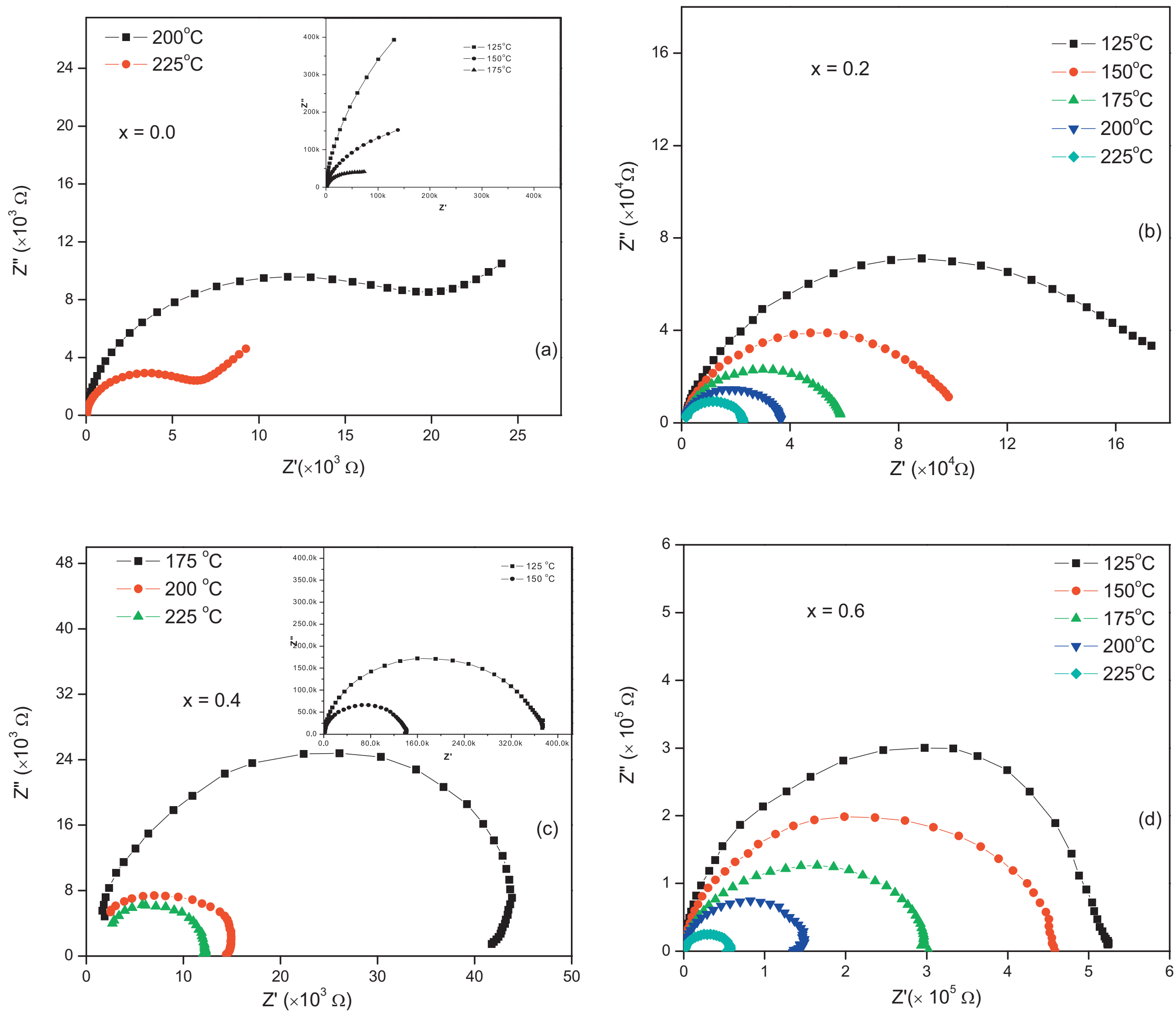

Fig. 5. (a–d) Variation of Z'' with Z' of $LiFe_{5-x}Mn_xO_8$ ferrites at different temperatures.

It is well known that the space charge behavior of charge carriers depends on the frequency. In order to make deeper understanding of this space charge effect and the relaxation processes, the variation of imaginary part of impedance with frequency at different temperatures have been studied and the results are shown in Fig. 3(a–d). It is observed from the figures that the Z'' values are showing maximum values at peak (Z''_{max}) for the temperatures 125–225 °C except for the composition $x = 0.0$. This is a clear indication of the existence of relaxation effects and also changes in the bulk resistance of the materials. At low temperatures, the low conductivity and high impedance values are observed with a broad peak above the particular temperature, which is different for different frequencies. Further, it is noticed from the figure that the peak Z''_{max} found to shift to higher frequency side with increasing temperature and this indicates the multiple relaxation process in the materials. The decrease of the values of Z'' maxima with increasing temperature (Fig. 3a–d) reveals the decrease in the resistance of materials. Further, coalescing of all of these curves (Fig. 3a–d) at higher frequencies mimics the reduction of space charge polarization with increasing frequency [10].

It is believed that the space charges developed in the sample may also affect the relaxation processes. In view of this fact, the normalized imaginary part (Z''/Z''_{max}) of impedance with varying frequency at different temperatures have been analyzed and are shown in the inset of Fig. 3. At all the measured temperatures, value of (Z''/Z''_{max}) parameter is found to exhibit a peak with a marginal asymmetric nature. The relaxation time (τ_z) of dipole relaxation as a function of temperature has been plotted as log τ_z versus 1000/T and shown in Fig. 4. Relaxation time represents the local effects of mobile charge carrier and the intrinsic properties of material [11]. The relaxation time basically gives an estimate of the dynamics of the electrical relaxation process occurring in the material. The higher the value of τ_z, the slower is the electrical relaxation process and vice versa [12]. It is clear from the figure that the relaxation time of dipoles is found to decrease with increasing temperature [13]. The log τ_z versus 1000/T plots indicate a non-linear variation over the range of temperature in the present investigation. This may be related to the presence of multiple relaxation process in the material with a distribution of relaxation time [12].

Generally, the space charges are created in the material due to the disparity in concentration and inhomogeneity of the applied field, which hinders the fast recombination of the charge carriers [14]. Therefore, the space charges present in the samples might be trapped well in the grain boundary and grain–electrode interfaces. In a complex impedance plane, grain, grain boundary, grain–electrode effects appear as semicircles. The lower frequency

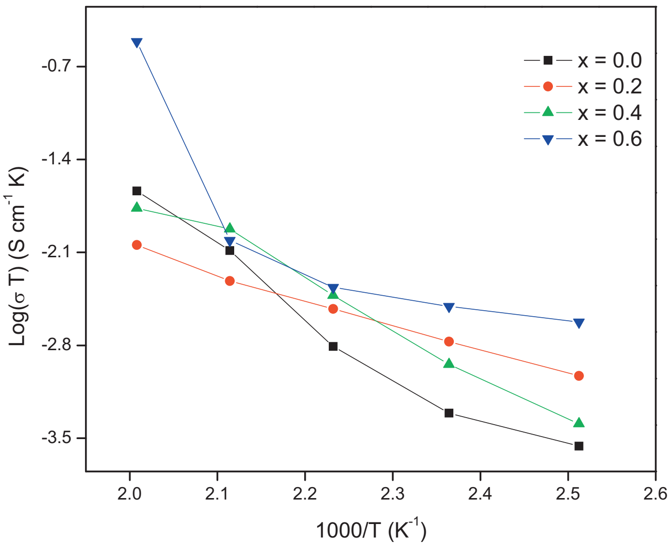

Fig. 6. Electrical conductivity versus inverse of temperature for $LiFe_{5-x}Mn_xO_8$ ferrites.

arc corresponds to the grain boundaries, while the high frequency arc represents the grain.

Figs. 5 and 6 show the complex impedance (Nyquist) plots and conductivity ($\log\sigma$) versus $1000/T$ of samples of the present investigation. The variation of Z'' with Z' has been shown at different temperatures and each point on the plot represents a particular frequency over wide range of measured frequencies. Fig. 5 shows that the shape of Nyquist plots is temperature dependent and as the temperature increases to a certain value, the curves attain larger curvature and become perfect semicircles [15,16]. All these semicircles merge and terminate on the real impedance axis at higher frequency side. This indicates the presence of only bulk resistance for these samples and the grain boundary resistance is negligibly small as no second semi-circle is observed. The absence of the series resistance in the equivalent circuit model for the sample further supports the observed result [17]. All the semicircles start on the real impedance axis at the lowest frequency [16]. It is observed that the low frequency side of semi-circle is shifting towards lower values on real impedance axis with increasing temperature. This behavior of Nyquist plots is the characteristic feature of conducting nature of the samples and as a result the absence of series capacitance in the equivalent circuit representation is envisaged. It is noticed that the radius of semi-circles decreases with increasing temperature indicates the decrease in relaxation time. The bulk resistance of the sample at any particular temperature can be obtained from the low frequency intercept of the semi-circle in the Nyquist plots [17]. Generally, different types of dipoles contained in the material are characterized by their own relaxation time. Therefore, the Nyquist plots in general are not exactly semicircular and vary with different degrees of distortions. The centers of these semicircles are depressed below the real axis by an angle. In an ideal case with Debye behavior a perfect semicircle with its center lying on the real impedance axis indicates the single relaxation process. In polycrystalline materials, in addition to the arc for dielectric relaxation within the grains (bulk relaxation), another arc due to the partial or complete blocking of charge carriers at the grain boundary may also be formed. Generally the electrode processes relax at low frequencies, grain boundaries relax at intermediate frequencies and the relaxation due to the grains of the samples occurs at higher frequencies [16].

The observed behavior clearly indicates that the present Mn-substituted lithium ferrites have semiconductor-like behavior. The increase of electrical conductivity with increasing temperature and frequency may be related to the increase of the drift mobility of electron and hole by hopping conduction [18]. It is noticed from the figure that the conductivity is increasing with increasing temperature and with substitution of Mn ion at Fe site.

4. Conclusions

In conclusion, X-ray diffraction data confirms that all the compositions in $LiFe_{5-x}Mn_xO_8$ ferrites are single phase with no detectable impurity and crystallize in spinel structure. The impedance analysis reveals that the low conductivity and the high impedance values are observed at low temperatures. A broad peak observed in Z'' versus frequency plots at a particular temperature is sensitive to the concentration of manganese and the peak shifts towards higher frequencies side with the increasing temperatures, which represents the multiple relaxations process in the materials. The relaxation time of dipoles is found to decrease with increasing temperature. It has been established that as the temperature increases, the area under the semicircles of the Nyquist plots are decreasing, which represents the tendency of better conductivity of the samples.

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