Master curve generation and modeling of ac conductivity for $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$ spinel ferrite system

N. H. Vasoya*, Prafulla K. Jha*, K. G. Saija[†], J. A. Bhalodia[‡]
and K. B. Modi^{‡,§}

*Department of Physics, Faculty of Science, M. S. University of Baroda
Vadodara 390002, India

[†]Smt. R. P. Bhalodia Mahila College, Upleta 360490, India

[‡]Department of Physics, Saurashtra University, Rajkot 360005, India

[§]kunalbmodi2003@yahoo.com

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The compositional dependence of ac conductivity (σ_{ac}), real (σ') and imaginary (σ'') parts of complex electric conductivity (σ^*) was investigated as a function of temperature (T) and frequency (f) for $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$, $x = 0.0, 0.1, 0.2$ and 0.3 spinel ferrite system. The compositional dependence of lattice constant values suggested that the most of the substituted Si^{4+} -ions reside at grain boundaries and only a few Si-ions are inside grains. The variation of $\sigma_{ac}(x, f, T)$ is explained on the basis of segregation and diffusion of Si^{4+} ions at grain boundaries and grains, respectively, and the electrode effect. Thermal variation of ac conductivity at fixed frequency suggested two different mechanisms which could be responsible for conduction in the system. It is found that σ^* is not the preferred presentation for dielectric data and the scaling process of real part of conductivity by normalized frequency and the scaled frequency were found unsuccessful. The fitting results of ac conductivity data with path percolation approximation were found suitable in low-frequency regime while in high-frequency regime, effective medium approximation (EMA) was found successful.

Keywords: Ferrites; ac conductivity; scaling; modeling.

1. Introduction

The compositional, frequency and temperature dependence of electrical properties of ferrite materials are important from applied as well as fundamental research points of view. Conductivity measured as a function of temperature and frequency enabled us to understand the dynamics of charge carriers under an ac field in disordered solids like ferrites. Interestingly, the electric properties of everyday materials like ionic conducting glass, polycrystalline semiconductors, transition metal oxides, polymers, plastic etc. are remarkably similar in nature (called ac universality). The only common feature of the numerous different solids exhibiting such ac universality is their disorder,¹ though these important and fascinating aspects are not generally considered (e.g., with few exceptions the dc resistivity is Arrhenius temperature dependent). On the other hand, a large class of materials possesses strikingly universal ac properties, thus, it is always possible to scale measurements of the frequency-dependent conductivity at different temperatures into a single ‘master’ curve (i.e., scaling). In data evolution program, scaling is an important feature because systems that show scale invariant behavior lend themselves to simplified and often universal explanation. For the physical process, constructing ‘master’ curve is important because it contains much information than

any single temperature run, it also increases the reliability of the information as the density of data points is significantly higher than on the single temperature runs.

An extensive work was carried out to develop theories of ac conduction based on either tunneling or hopping models.^{1,2} Dyre *et al.*¹ applied both hopping and macroscopic models (the effective medium approximation (EMA) and the percolation path approximation (PPA)) in order to interpret ac universality. Hopping models usually assume noninteracting charge carriers, thus the self-exclusion effect is ignored as well as the coulomb interactions between the charge carriers. Recently, proposed models which include this effect being very complex have been studied by means of computer simulation. A macroscopic model includes Coulomb interaction via Gauss law without becoming extremely complex.³ The results were broadly similar with those found on the basis of hopping models, which are considered to be microscopic.⁴

Among the various soft ferrite systems, $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ (Ni-Zn ferrites) and $\text{Zn}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ (Mn-Zn ferrites) are the most promising candidates for high-frequency applications. When various parameters such as high initial magnetic permeability, saturation magnetization, electric resistivity and low power losses essential for high-frequency

applications are compared, Mn–Zn ferrite system, in general, and $\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ ferrite composition, in particular, were found to possess superior properties.⁵ To improve material's properties, the additionally small amount of cationic substitution is made. The incorporation of tetravalent cations like Si^{4+} and Ti^{4+} results in the high grain boundary resistivity due to complex compositions of the grain boundary layer on ferrite grains and it also forms strong chemical bonds with ferrous ion (Fe^{2+}), thereby reduces the mobility of charge carriers that leads to low power loss.²

Recently, the effect of SiO_2 , CaO , TiO_2 and Nb_2O_5 additives on loss characteristics of Mn–Zn ferrites was studied by Chen *et al.*^{3,6} These additives appeared to preferentially segregate at the grain boundaries and form a high-resistivity layer to lower the eddy current losses. The suitability of tetravalent cations, Ti^{4+} and Ge^{4+} , substitution in cobalt ferrite for magnetoelastic sensor applications was investigated by Nlebedim and Jiles⁷ while the effect of other tetravalent metallic cations such as Sn^{4+} and Zr^{4+} on magnetic and mechanical properties of NiCuZn ferrites was studied by Hsieh *et al.*⁸ On the other hand, influence of Bi^{3+} and Si^{4+} on physical, optical, electrical and thermal properties of Li–Zn glasses was studied by Rani *et al.*⁹ while the effect of nano Si^{4+} -substitution on magnetic and dielectric properties of $\text{Li}_{0.3}\text{Zn}_{0.4}\text{Fe}_{2.3}\text{O}_4$ ferrite was studied by Mahmoudi and Kavanlouei.¹⁰ Very recently, we have demonstrated advantages of electric modulus (M^*) presentation over the dielectric permittivity (ϵ^*) presentation to understand the dielectric properties of the system, $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$.¹¹

There is a lack of such comprehensive work on composition, frequency, and temperature dependent ac conductivity study on spinel ferrite system, $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$ ($x = 0.0, 0.1, 0.2$ and 0.3) in general, and a scaling behavior and fitting of experimental data by macroscopic models in particular. The main focus of the present communication is to explore (i) the role of Si^{4+} -substitution, as SiO_2 is known to segregate and diffuse at grain boundaries and grains, which affects ac conductivity to large extent, (ii) the mechanisms responsible for conduction, and (iii) the appropriateness of scaling parameters to generate a single 'master' curve and causes for success and failure of 'master' curve generation and macroscopic models.

2. Experimental Method

Polycrystalline samples of the spinel ferrite system, $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$, $x = 0.0, 0.1, 0.2$ and 0.3 , were prepared using the solid state reaction method. The highly pure ($> 99.3\%$) powders of manganese oxide (MnO), zinc oxide (ZnO), ferric oxide (Fe_2O_3) and silicon dioxide (SiO_2) (Sigma-Aldrich, India) were taken in stoichiometric proportions, mixed thoroughly, wet-ground by blending with acetone in an agate mortar and pestle for 3 h and then the

mixture was dried and pressed into pellets at a pressure of $2 \times 10^7 \text{ kg/m}^2$ using hydraulic press (BIMPEX machines international, Mumbai, India). The pellets were pre-sintered at 1100°C for 24 h. After regrinding and re-pelletizing, the samples were finally sintered at 1100°C for 24 h and slowly furnace cooled to room temperature with a cooling rate of 2°C/min . The sintering processes were carried out in air.

All powdered specimens so prepared were characterized by phase formation and structural parameters' determination by X-ray diffractometry with Philips, Holland, Xpert MPD automated X-ray powder diffractometer using CuK_α radiation ($\lambda = 1.5405 \text{ \AA}$), graphite monochromator and Xe-filled proportional counter. Data were collected in the 2θ range $5\text{--}95^\circ$ at a scan speed of 2° min^{-1} at 300 K. The disc-shaped spinel ferrite samples were polished using zero grade emery paper, washed with dilute HCl and acetone to obtain clean, flat and parallel faces. The dielectric measurement was done on samples properly rubbed with graphite and covered with aluminum foil for good Ohmic contacts. The measurement was carried out using Agilent (model 4284 A) impedance analyzer in the frequency range $f = 20 \text{ Hz}$ to 1 MHz at different temperatures from 300 to 673 K. The thermal variation was obtained by placing the sample holder containing pellet in a horizontal electric furnace and the temperature of the pellet was measured using Cr–Al thermocouple. The data were recorded during the cooling cycle at the interval of 20°C . The real (ϵ') and imaginary (ϵ'') parts of complex dielectric permittivity (ϵ^*) were calculated using the measured value of capacitance, C_p , and dissipation factor, D ($= \tan \delta$), with the help of standard relations: $\epsilon' = C_p/C_0$ and $\epsilon'' = \epsilon' \cdot D$, where $C_0 = \epsilon_0 A_p/t$. Here, ϵ_0 is the permittivity of free space ($8.85 \times 10^{-14} \text{ F/cm}$), ' A_p ' is a cross-sectional area in cm^2 and ' t ' is the thickness of the pelletized samples in centimeter. The ac conductivity (σ_{ac}) was calculated from dielectric data using the empirical relationship: $\sigma_{ac} = 2\pi f \epsilon' \epsilon_0 \tan \delta$.¹²

3. Results and Discussion

The X-ray diffraction (XRD) patterns of the system $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$ with $x = 0.0, 0.1, 0.2$ and 0.3 were obtained by powder X-ray diffractometry at 300 K. Indexing and Rietveld refinement using general scattering analysis software (GSAS) of XRD patterns revealed the single phase nature of the compounds which crystallized in face-centered cubic (fcc) structure (space group $O_h^7\text{Fd } \bar{3}m$).¹³ The unsubstituted composition ($x = 0.0$) possesses major spinel phase and minor $\alpha\text{-Fe}_2\text{O}_3$, hematite phase. Although a difference profile plot is probably the best way of following and guiding a Rietveld refinement, the fit of the calculated pattern to the observed data can also be given numerically. The fitting quality of experimental data was checked by using the various Rietveld discrepancy values, i.e., the weighted profile

Table 1. Rietveld refinement parameters, lattice constant (a) and Neel temperature (T_N) for $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$ system.

Mn-Si content (x)	R_{wp}	R_{exp}	χ^2	$a(\text{\AA}) \pm 0.002 \text{\AA}$	$T_N(\text{K}) \pm 2\text{K}$ [Ref. 20]
0.0	5.11	4.50	1.29	8.465	465
0.1	6.32	5.23	1.46	8.488	410
0.2	4.48	3.81	1.38	8.497	385
0.3	4.04	3.50	1.33	8.505	370

R -factor (R_{wp}), the expected R factor (R_{exp}), and the goodness-of-fit ($\chi^2 = (R_{\text{wp}}/R_{\text{exp}})^2$) parameter.¹⁴ It is found that χ^2 values for different compositions lie in the range 1.2–1.4, which suggest a good refinement of the data. The Rietveld agreement factors are summarized in Table 1. Figure 1 displays Rietveld-fitted XRD patterns for the typical samples with $x = 0.0$ and 0.2 .

The values of lattice parameter (a) thus determined are shown in Table 1. It is seen that the lattice constant increases with increasing Mn–Si content (x) in the system. Usually, in a solid solution of ferrite materials within the miscibility range, a linear change in lattice parameter with a concentration of the components is observed.¹⁵ In the present system, $2x$ amount of Fe^{3+} with ionic radius of $0.645 \text{\AA}$ is replaced by simultaneous substitution of x amount of Mn^{2+} ($0.83 \text{\AA}$) and x amount of Si^{4+} ($0.40 \text{\AA}$) ions according to

As the difference in average ionic radius is relatively small ($0.006 \text{\AA}$), one can expect almost no change or gradual decrease in lattice constant value with increase in Mn–Si content (x). In the present case, we have observed a slow linear

increase in lattice constant with x (Table 1). Earlier, it has been reported that the concentration of Si-ions at the grain boundaries is about 5–10 times greater as compared to that of inside grains for silica added M-type Sr-hexa ferrite ($\text{SrFe}_{12}\text{O}_{19}$). When the sintering temperature is sufficiently high ($> 1250^\circ\text{C}$), some of the Si-ions can diffuse into grains.¹⁶ In the present case, if it is assumed that the substituted Si^{4+} -ions deposited at grain boundaries and did not contribute to the lattice constant value, then lattice constant should increase rapidly due to the substitution of larger Mn^{2+} ions for smaller Fe^{3+} ions in the system but this is not the case. Based on the above facts, now it is possible to explain the observed variation in lattice constant ($a(\text{\AA})$) values with Mn–Si concentration (x) in the system. Initially, for $x = 0.0$ to $x = 0.1$ compositions, $a(\text{\AA})$ increases rapidly while for $x = 0.1$ to $x = 0.3$ compositions, it increases slowly (Table 1). This suggests that for $x = 0.1$ composition, large percentage of Si^{4+} ions reside at grain boundaries and only a small percentage of Si^{4+} ions along with cent percentage of Mn^{2+} ion are substituted inside grains. On increasing Mn–Si concentration (x) ($x = 0.2$ and $x = 0.3$), more and more amounts of smaller Si^{4+} ions ($0.40 \text{\AA}$) enter into the grains that compensate the enhancement in lattice constant value caused by replacement of smaller Fe^{3+} ions ($0.645 \text{\AA}$) by larger Mn^{2+} ions ($0.83 \text{\AA}$) in the system. The overall effect is a slow linear increase in lattice constant value with Mn–Si content (x) as observed (Table 1).

The compositional variation of ac conductivity (σ_{ac}) values at selected temperatures and applied signal frequencies is shown in Table 2. In the present system, magnetic Fe^{3+} -ions ($5 \mu_B$) are replaced by magnetic Mn^{2+} -ions ($5 \mu_B$) and nonmagnetic Si^{4+} -ions ($0 \mu_B$) simultaneously. The incorporation of Si^{4+} -ions which do not participate in the conduction process limits the degree of $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + e^-$

Fig. 1. Observed (Solid Circles) and calculated (Solid line) X-ray powder diffraction patterns for (a) $x = 0.0$ and (b) $x = 0.2$ compositions of $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$ system at 300 K. The difference between the observed and calculated spectra is plotted at the bottom. The ticks indicate allowed Bragg peaks positions.

Table 2. AC conductivity (σ_{ac}) at fixed temperature and frequency for $Mn_{0.7+x}Zn_{0.3}Si_xFe_{2-2x}O_4$ system.

Mn-Si content (x)	$\sigma_{ac}(\Omega^{-1}.cm^{-1})$			
	T = 473 K		T = 673 K	
	10 kHz $\times 10^{-6}$	500 kHz $\times 10^{-6}$	10 kHz $\times 10^{-5}$	500 kHz $\times 10^{-5}$
0.0	5.99	18.10	3.60	6.69
0.1	4.21	17.80	6.40	25.0
0.2	1.90	5.50	1.18	3.69
0.3	1.63	8.79	2.04	4.89

conduction.¹⁷ Thus, the conductivity is expected to decrease with increase in Si^{4+} -content (x) in the system, $Mn_{0.7+x}Zn_{0.3}Si_xFe_{2-2x}O_4$. We have observed this expected trend at $T = 473$ K, while at $T = 673$ K random variation of σ_{ac} with composition have been observed. It is possible to explain the compositional variation of ac conductivity for the substituted ferrites ($x = 0.1, 0.2, 0.3$) in the light of Si^{4+} -substitution in the system. Initially, for $x = 0.1$ and 0.2 compositions majority of Si^{4+} -ions reside at grain boundaries and hence increase the grain boundary resistivity as a result resistivity of the sample increases. The segregation of Si^{4+} ions at grain boundaries increases with increasing x for $x = 0.1$ to 0.2 and as a result, ac conductivity decreases with increase in Si^{4+} concentration (x). This can be explained as follows: polycrystalline or multi-crystalline materials consist of tiny crystals or grains. Adjacent grains possess different crystallographic orientations and are separated by a grain boundary. According to Maxwell–Wegner two-layer model and Koops phenomenological theory of dielectrics,¹² it is well established that the ferrite samples consist of well-conducting grains separated by poorly conducting grain boundaries. There exists some atomic mismatch within the grain boundary region (which is probably just several atomic distances wide) in a transition from the crystalline orientation

of one grain to that of an adjacent one. Between adjacent grains, various degrees of crystallographic misalignment are possible. Along a grain boundary, the atoms are bonded less regularly as bond angles are longer and consequently there is an interfacial or grain boundary energy which is a function of the degree of misorientation, being larger for high angle boundaries.¹² These grain boundaries prevent long distance interactions. Si^{4+} ion goes along grain boundary and raises the resistance between the adjacent grains¹² that are likely to impede electron hopping between Fe^{2+} and Fe^{3+} ions at the octahedral (B-) sites on the expense of cations vacancies in the lattice. On the other hand, for $x = 0.3$ compositions, Si^{4+} concentration is beyond a particular limit as discussed earlier and hence enhances the sintering rate. Thus, a large fraction of Si^{4+} -ions enters into grains and thereby decreases the grain boundary resistivity. This, in turn, results in higher value of conductivity for $x = 0.3$ composition as compared to $x = 0.2$ composition of $Mn_{0.7+x}Zn_{0.3}Si_xFe_{2-2x}O_4$ system.

AC conductivity (σ_{ac}) of the ferrite compositions has been recorded as a function of frequency at different temperatures and is shown in Fig. 2. From the plots, we have observed the following characteristics in dynamical conductivity: (i) the ac conductivity is almost independent of frequency at sufficient low temperatures, that suggests the presence of dc leakage current throughout the sample (marked as region I, inset of Figs. 2(a) and 2(b)); (ii) in the mid and high frequency regions frequency-dependent plateau has been observed; (iii) for compositions, $x = 0.0$ and 0.1 , the variation of σ_{ac} is sensitively dependent on frequency and temperature (iv) while for $x = 0.2$ and 0.3 compositions, σ_{ac} is temperature-dependent but having less effect of frequency at high temperatures (v) there is an overall increase in σ_{ac} with increase in frequency and temperature.

The mechanism responsible for the conduction in ferrite materials can be explained based on the hopping of charge carriers i.e., electrons, between Fe^{3+} and Fe^{2+} ions at the octahedral (B-) sites of the spinel lattice. The increase in applied frequency enhances the hopping of charge carriers,

Fig. 2. Frequency dependent ac conductivity (σ_{ac}) for (a) $x = 0.1$, (b) $x = 0.2$ and (c) $x = 0.3$ compositions at different temperatures.

leads to the increase in conduction process thereby, increasing the conductivity. The third observation suggests that grain boundary effects are not sufficiently minimized for highly pressed pellet even at high temperatures. On the other hand, the fourth observation indicates that for $x = 0.2$ and 0.3 compositions, grain boundary contributions are negligible at least at high temperatures. It is seen that after the dc plateau (region I) two different kinds of relaxations are encountered: at low and intermediate frequency dispersion (region II) associated with electrode and grain boundaries contributions, while at high frequency, region III associated with contribution from grains. In some cases, only two regions, I and II are observed. In region II, contributions from grains and grain boundaries as well as an electrode are merged.

A conventional formalism to analyze the frequency-dependent conductivity behavior at constant temperature used for a wide variety of materials is based on the power law proposed by Jonscher:¹⁸

$$\sigma(\omega) = \sigma(0) + A(2\pi f)^s, \quad (1)$$

where A is temperature-dependent pre-exponential factor and s is frequency exponent ($0 < s < 1$). The term $\sigma(0)$ corresponds to the translation hopping gives the long-range electrical transport (i.e., dc conductivity) in the long time limit (i.e., as the frequency approaches zero). The second term, $A(2\pi f)^s$, characterizes the low-frequency region and corresponds to the translational hopping motion (short range hopping). The term $\sigma(\omega)$ is the total conductivity. The exponent, s , represents the degree of interaction between mobile ions and environments surrounding them.

Equation (1) was used to fit ac conductivity data and fitted plots for the typical composition with $x = 0.3$ at $T = 300$ – 773 K are shown in Fig. 3. In the fitting procedure, A and s values have been varied simultaneously to get the best fit. The values of s are found to vary within the expected range of 0.3 – 0.55 while the values of A are of the order of 10^{-7} for the

different compositions at different temperatures. It is found that at low temperatures ($T \leq 473$ K), only high-frequency region while at high temperatures ($T > 473$ K), for an entire range of frequencies, the σ_{ac} versus frequency curves were fitted well by a power law.

A new graphical representation for dielectric data was suggested by Wei *et al.*¹⁹ In this representation, imaginary part (σ'') ($= 2\pi f \cdot \epsilon_0 \cdot \epsilon''$) of the complex conductivity ($\sigma^* = \sigma' - i\sigma''$) is plotted against real part (σ') ($= 2\pi f \cdot \epsilon_0 \epsilon''$) of σ^* . For Debye relaxation with dc conductivity, this representation yields a semicircle. The $\sigma''(f)$ versus $\sigma'(f)$ plots recorded at different temperatures for $x = 0.0, 0.1, 0.2$ and 0.3 compositions of the spinel ferrite system, $Mn_{0.7+x}Zn_{0.3}Si_xFe_{2-2x}O_4$ are depicted in Fig. 4. It is clearly seen that σ'' versus σ' presentation fails to form a semicircular arc, this is probably due to the lack of high-frequency data (up to GHz) for which it is particularly suited. This leads us to conclude that σ^* presentation was not found suitable to represent dielectric data of ferrite materials under investigation.

Figure 5 represents ac conductivity (σ_{ac}) of the ferrite materials observed as a function of temperature (T) at different frequencies. AC conductivity, σ_{ac} , patterns for the different compositions indicate a progressive rise in σ_{ac} with rise in temperature having maximum enhancement in σ_{ac} at higher frequencies. We have observed higher magnitude of σ_{ac} for all the samples in the low-temperature region at higher frequencies. This is an expected result in view of strong frequency dependence under these conditions. On increasing temperature, σ_{ac} recorded at different frequencies approaches each other in the higher temperature region. These features indicate that electrical conduction in the materials is a thermally activated process governed by the release of space charge.

The thermal activation energy of charge carriers contributing to ac conductivity has been calculated using the Arrhenius equation given by

$$\sigma_{ac} = \sigma_0 \exp\left(\frac{-E_a}{kT}\right), \quad (2)$$

where σ_0 , E_a , k and T are pre-exponential factor of conductivity, activation energy, Boltzmann constant and absolute temperature, respectively.

It is clearly seen that each plot is divided into different regions of activation energy. The activation energies, E_a , calculated from the slope of $\log \sigma_{ac}$ versus $1000/T$ plots are shown in Fig. 5 for the typical composition with $x = 0.3$ at selected frequencies, 1 kHz, 100 kHz and 1 MHz. The values of activation energy were found to vary between 0.05 eV and 0.01 eV for the low-temperature region while for high-temperature region E_a was found to vary between 0.35 eV and 0.20 eV for the different compositions at different frequencies.

The temperature at which change in the slope was observed closely related to the corresponding Neel

Fig. 3. Frequency dependent ac conductivity and its continuous fitting curves using power law for $x = 0.3$ composition at different temperatures.

Fig. 4. $\sigma''(f)$ versus $\sigma'(f)$ plots for $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{SiFe}_{2-2x}\text{O}_4$ system at different temperatures for (a) $x = 0.0$ (b) $x = 0.1$ (c) $x = 0.2$ and (d) $x = 0.3$ compositions.

temperature (T_N) determined from the thermal variation of low field ac susceptibility measurements (Table 1).¹⁸ This suggests the effect of magnetic ordering on conduction mechanism. Thus, activation energy in the low-temperature region may be referred to as activation energy (E_f) of ordered ferrimagnetic region ($T < T_N$). On the other hand, activation energy corresponding to the high-temperature region may be related to activation energy (E_p) of the paramagnetic region ($T > T_N$). Here, it is important to note that from the thermal variation of dc resistivity measurements, no such change in the vicinity to corresponding T_N value was observed.^{20,21}

One can draw two significant findings: (i) the activation energy values increase with an increase in temperature ($E_p > E_f$) at a constant frequency. This can be attributed to more energy required to overcome the thermal fluctuations by the charge carriers i.e., electrons, at the high-temperature region. (ii) The activation energy decreases with increasing frequency. This may be due to the fact that at low-frequency regime the overall conductivity is due to the hopping-mobility transportation of charge carriers over a large distance. In the high-frequency regime, hopping-transportation is

restricted to only nearest neighboring defect sites due to smaller response time available to respond to the external field.²²

We have applied different scaling approaches to conductivity spectra recorded at different temperatures. The real part of conductivity (σ') scaled as a function of normalized frequency (f/f_{max}) and scaled frequency (f/σ_{dc}) at different temperatures are illustrated in Fig. 6. The characteristic frequency (f_{max}) is the peak frequency observed in the frequency dependence of imaginary component (M'') of complex electric modulus ($M^* = M' + jM''$) recorded at different temperatures.¹¹ It can be seen that the scaling process shows very limited success in the low-frequency range. The unsuccessful mastering process of σ' at low frequency as in the present case was also observed earlier by Saafan *et al.*²³ for Al-substituted Mn-Zn ferrites. They attributed it to the existence of positive charge carriers whose thermal dependence cannot be eliminated by scaling x-axis by either σ_{dc} or f_{max} . This is expected based on the fact that σ_{dc} and f_{max} are characteristic values concerned with the electrons' motion and do not involve any information about motion of positive charge carriers.²³ For the system under study,

Fig. 5. Variation of ac conductivity as a function of temperature at different frequencies for (a) $x = 0.1$ (b) $x = 0.2$ and (c) $x = 0.3$ compositions.

Fig. 6. σ' master curves for $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$ system recorded at different temperatures for (a) $x = 0.0$ (b) $x = 0.1$ (c) $x = 0.2$ and (d) $x = 0.3$ compositions. Inset figure shows scaling behavior by $(f/\sigma_{dc}T)$.

$\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$, from thermoelectric power measurements, it is established that the conduction is due to electron exchange between ferrous Fe^{2+} and ferric (Fe^{3+}) ions at the octahedral sites of the spinel lattice.²⁰ Thus, we expect that the motion of holes (positive charge carriers) as minority charge carriers or polaron hopping is not revealed in σ_{dc} values which are responsible factors for the unsuccessful master curve generation. Rolling *et al.*²⁴ suggested that σ_{dc} and $\sigma_{dc}T$ can be used as the scaling parameters for the conductivity and frequency axes, respectively. Based on the above fact, we have made an attempt to scale frequency axis by $\sigma_{dc}T$ (i.e., $f/\sigma_{dc}T$) in σ'/σ_{dc} curves. Such curves for the typical composition with $x = 0.3$ are shown in the inset of Fig. 6. It is observed that the scaling of frequency axis by $\sigma_{dc}T$, i.e., $(f/\sigma_{dc}T)$ does not improve mastering process when compared with curves scaled by σ_{dc} , i.e., (f/σ_{dc}) only (Fig. 6).

The experimental data of ac conductivity (σ_{ac}) was attempted to fit with Dyre's macroscopic model in its two approximations, PPA and effective medium approximation (EMA), based on the relationship equations established by Saafan *et al.*²³ for spinel ferrite system. These two approximations are well discussed in Ref. 1, 4 and 23. Figure 7 depicts the indirect fitting of conductivity data with the PPA and EMA for all the four compositions of the system $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$. It is seen that the experimental data at different temperatures are collected in a master curve for all the compositions when fitted with the PPA model, as compared to the EM approximation. The master lines show a significant change in slope at $f = f_{\max}$ (the frequency of conductivity relaxation) and indicate that the choice of $f_{\max}$ as the scaling parameter is more convenient for the presently investigated materials than any other scaling parameters (Fig. 6). For the low-frequency region ($f < f_{\max}$ and $f/f_{\max} < 0$), the slopes became closer to unity (ideally they can show unity if the model is completely correct) suggesting that the PPA works well at lower frequencies as expected.

Fig. 6. (Continued)

As discussed above according to the PPA, not only the dc currents but also the low-frequency ac currents mainly follow the percolation paths, in which the solid is regarded as having several independently conducting channels, each channel corresponding to a percolation path.⁴ This hypothesis had been experimentally viewed in a real solid by Topfer *et al.*²⁵ These results suggest that the PPA picture is realistic to a great extent and proves large success than the EMA. We have

to be careful since in the present study data are recorded at relatively low frequencies ($< 10^6$ Hz). According to the Dyre *et al.*,⁴ at high frequencies, the percolation picture starts to break down. On the other hand, EMA is satisfactory at frequencies higher than $f_{\max}$ ($f > f_{\max}$, $f/f_{\max} > 0$). Ideally, one straight line with a slope of unity should be obtained for all the compositions and temperatures (one master line) if the model is satisfied completely. Here, this is not the case

Fig. 7. Indirect fitting of conductivity data with PPA and EMA for (a)(e) $x = 0.0$ (b)(f) $x = 0.1$ (c)(g) $x = 0.2$ and (d)(h) $x = 0.3$ compositions of $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$ spinel ferrite system at different temperatures.

Fig. 7. (Continued)

because many approximations have been assumed in the derivation of used relationship (Fig. 7). It is seen that the fitting of experimental data with the PPA is found suitable as compared to the EM approximation. This suggests that the EMA failed to recognize that percolation effects become important at low frequencies. In this regime, most transport occurs as the infinite cluster from percolation theory and is better described by the PPA.²⁵ This suggests that the conductivity data is better described and understood by considering the concept of conducting ‘channels’ (percolation path) rather than by basing it on the concept of ‘effective medium’ in the ferrite compositions under investigation.

4. Conclusions

The compositional variation of σ_{ac} at fixed temperature and frequency can be explained in the light of substitution of nonmagnetic Si^{4+} -ions for magnetic Fe^{3+} -ions, segregation and diffusion of Si^{4+} -ions at grain boundaries and in grains, respectively, as revealed from the variation of lattice constant with Mn-Si concentration (x) in the system, $\text{Mn}_{0.7+x}\text{Zn}_{0.3}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$. The nature of σ_{ac} curves as a function of composition, frequency, and the temperature is mainly governed by grains, grain boundaries’ contributions and electrode effect

to the conduction mechanism. The frequency dependence of conductivity was found to obey well the power law, while the thermal variation of σ_{ac} follows the Arrhenius law with two set of activation energies suggestive of two different conduction mechanisms. The σ^* presentation is not the preferred presentation to represent dielectric data of ferrite ceramics under study. The collective contribution of two types of charge carriers to the conduction mechanism is responsible for unsuccessful scaling behavior of a real part of conductivity. Fitting of ac conductivity data with the path percolation approximation is found suitable as compared to the EMA.

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References

- J. C. Dyre and T. B. Schroder, Universality of ac conduction in disordered solids, *Rev. Mod. Phys.* **72**(3), 873 (2003).

- ²T. B. Schroder and J. C. Dyre, Scaling and universality of ac conduction in disordered solids, *Phys. Rev. Lett.* **84**(2), 310 (2000).
- ³W. Sea-Fue, C. Ying-Jung, H. Yung-Fu and C. Chi-Huei, Effects of additives on the loss characteristics of Mn–Zn ferrite, *J. Magn. Magn. Mater.* **365**, 119 (2014).
- ⁴J. C. Dyre, Universal low-temperature ac conductivity of macroscopically disordered nonmetals, *Phys. Rev. B* **48**(17), 12511 (1993).
- ⁵A. Goldman, *Modern Ferrite Technology* (Springer, NY, 2006).
- ⁶W. Sea-Fue, H. Yung-Fu and C. Chi-Huei, Effects of Nb₂O₅, TiO₂, SiO₂, and CaO additions on the loss characteristics of Mn–Zn Ferrite, *J. Electroceram.* **33**, 172 (2014).
- ⁷I. C. Nlebedim and D. C. Jiles, Suitability of cation substituted cobalt ferrite materials for magnetoelastic sensor applications, *Smart Mater. Struct.* **24**, 0250061 (2015).
- ⁸W. Sea-Fue, Y. Hasio-Ching, H. Yung-Fu and H. Chung-Kai, Effects of SnO₂, WO₃, and ZrO₂ addition on the magnetic and mechanical properties of NiCuZn ferrites, *J. Magn. Magn. Mater.* **374**, 381 (2015).
- ⁹S. Rani, S. Sanghi, N. Ahlawat and A. Agarwal, Influence of Bi₂O₃ on physical, electrical and thermal properties of Li₂O · ZnO · Bi₂O₃ · SiO₂ glasses, *J. Alloys Compd.* **619**, 659 (2015).
- ¹⁰M. Mahmoudi and M. Kavanlouei, The effect of nano SiO₂ on magnetic and dielectric properties of Li–Zn ferrites, *Int. J. Mater. Res.* **105**(11), 1097 (2014).
- ¹¹N. H. Vasoya, P. K. Jha, K. G. Saija, S. N. Dolia, K. B. Zankat and K. B. Modi, Electric modulus, scaling and modeling of dielectric properties for Mn²⁺–Si⁴⁺ co-substituted Mn–Zn ferrites, *J. Elect. Mater.* **45**(2), 917 (2016).
- ¹²N. H. Vasoya, Ph.D. Thesis, Scaling and modeling of dielectric data for spinel ferrite systems, Saurashtra University, Rajkot, India (2012).
- ¹³H. M. Rietveld, A profile refinement method for nuclear and magnetic structures, *J. Appl. Cryst.* **2**, 65 (1969).
- ¹⁴B. H. Toby, R factors in Rietveld analysis: How good is good enough? *Powder Diff.* **21**, 67 (2006).
- ¹⁵C. G. Whinfrey, D. W. Eckart and A. Tauber, Preparation and X-ray diffraction data for some rare earth stannates, *J. Am. Chem. Soc.* **82**, 2695 (1960).
- ¹⁶F. Haberey and F. Kools, The effect of silica addition in M-type ferrites, *Proc. Third Int. Conf. Ferrites (ICF 3)*, Kyoto, (Reidel, Dordrecht-Boston-London, 1980), p. 356.
- ¹⁷V. K. Lakhani and K. B. Modi, Effect of Al³⁺ substitution on the transport properties of copper ferrite, *J. Phys. D* **44**, 245403 (2011).
- ¹⁸A. K. Jonscher, Dielectric relaxation in solids, *J. Phys. D* **32**, R57 (1999).
- ¹⁹Y. Z. Wei and S. Sridhar, A new graphical representation for dielectric data, *J. Chem. Phys.* **99**(4), 3119 (1993).
- ²⁰K. G. Saija, Synthesis and characterization of tetravalent cation substituted Mn–Zn ferrite suitable for high frequency applications, Ph.D. Thesis, Saurashtra University, Rajkot, India (2012).
- ²¹G. S. N. Rao, O. K. Caltun, K. H. Rao, B. P. Rao, H. L. Wamocha and H. H. Hamdeb, Influence of silicon and cobalt substitutions on magnetostriction coefficient of cobalt ferrite, *Hyper. Int.* **184**, 179 (2008).
- ²²S. Dussan, A. Kumar, J. F. Scott and R. S. Katiyar, Effect of electrode resistance on dielectric and transport properties of multiferroic superlattice: A Impedance spectroscopy study, *AIP Adv.* **2**, 0321361 (2012).
- ²³S. A. Saafan, A. S. Seoud and R. E. El Shater, Theoretical investigation of some experimental data of Al-substituted MnZn spinel ferrites, *Physica B* **365**, 27 (2005).
- ²⁴B. Rolling, A. Happe, K. Funke and M. D. Ingram, Carrier concentrations and relaxation spectroscopy: New information from scaling properties of conductivity spectra in ionically conducting glasses, *Phys. Rev. Lett.* **78**, 2160 (1997).
- ²⁵J. Topfer, H. Kahnt, P. Nauber, S. Senz and D. Hesse, Microstructural effects in low loss power ferrites, *J. Eur. Ceram. Soc.* **25**(12), 3045 (2005).