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Dependence of dielectric behaviour of Mn-Zn ferrite on sintering temperature

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The dielectric constant of Mn-Zn ferrite was measured at different temperature and frequencies as a function of sintering temperature ranging from 1200°C to 1400°C at heating rate of 6°C/min. The resistivities as well as Seebeck coefficient were measured in the same range of temperature. More than one type of polarization is expected to vary the dielectric constant. Hoping mechanism was the predominant one in conduction processes. The grain size was calculated from X-rays and SE micrographs and it was found to decrease with increasing sintering temperature.

1. Introduction

Manganese-zinc ferrite belongs to a group of "soft" [1] materials characterized by high magnetic permeability, low losses and numerous electronic applications such as transformers, chock coils and noise filters. . .etc. In view of this wide range of applications mixed Mn-Zn ferrites have attracted a great deal of interest and are chosen for the present work to deal with the dielectric properties as a function of sintering temperature and frequency.

Many researchers [2–4] have been carried out much more experiments on the magnetic behavior of Mn-Zn ferrite as a function of concentration and frequency in the neighborhood of their Curie temperature. No studies are available on various non-magnetic properties of Mn-Zn ferrite, such as the elastic and electrical properties. Diamagnetic Zn^{2+} ions substituted in Mn ferrite is known to effect the above-mentioned properties where the addition of Zn is also promotes densification [5] and grain growth.

In stoichiometric spinel, 8 of the 64 possible tetrahedral A-sites and 16 of the 32 possible octahedral B-sites are occupied in the unit cell [6]. In Mn-Zn ferrite, the manganese cations are found on both A- and B-sites [7], which makes it a partially inverse spinel. The movement of the cations and anions is of great importance and affect directly on the distortion inside the system.

2. Experimental

The ferrite sample of the chemical formula $Mn_{0.28}Zn_{0.72}Fe_2O_4$ was prepared by the standard ceramic technique [8] using analar grade oxides. The mixture was grounded to a very fine powder using an agate mortar, then transferred to an electric shaker for about two hours. After that they were compressed under a pressure of 1.5×10^7 Nm^{-2} into pellets of diameter 10 mm and thickness ≅1.8 mm. The sample was sintered at heating rate 6°C/min and different sintering temperatures (1200°C→1400°C) using a Lenton UAF 16/5 furnace (UK).

X-ray diffraction was carried out using MZ VI Scintag to assure the formation of the samples. Scanning electron (SE) micrographs were done using JEOL JSMT 330A to calculate the grain size and comparing it with that obtained from X-rays.

The ac. resistivity and the dielectric constant were measured using self-calibrated Hioki Bridge (3530 Japan). The temperature of the sample was measured using a K-type thermocouple connected to a Digi-sense thermometer with the junction in contact with the sample. The accuracy of measuring temperature was better than ±1°C.

Seebeck coefficient for the investigated specimens were measured by using the special designed instrument with small temperature difference dT between the two sample surfaces.

3. Results and discussion

The representation of the real part of the dielectric constant ε_r' versus absolute temperature for $Mn_{0.28}Zn_{0.72}Fe_2O_4$ sintered at various temperatures is shown in Fig. 1. From the figure it is clear that the value of ε_r' is increased with increasing sintering temperature. At low sintering temperature (1200°C and 1250°C) ε_r' is slightly increased with temperature, while at 1300°C and 1400°C a strong increase in ε_r' is observed. A maximum in ε_r' is appeared around 500 K, shifted to higher value with increasing sintering temperature. Below 500 K the increase in ε_r' may be due to polarizability increasing and the thermal energy is quite sufficient to liberate some charge carriers. The field accompanied with the applied frequency (1 MHz) aligned them in

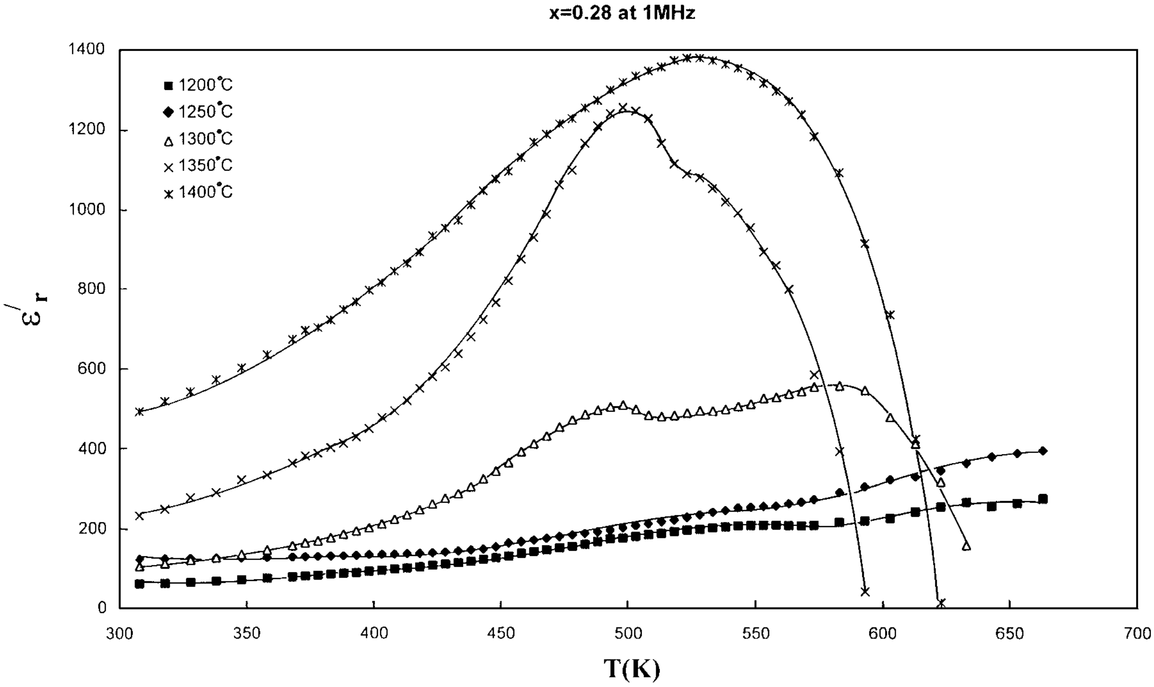
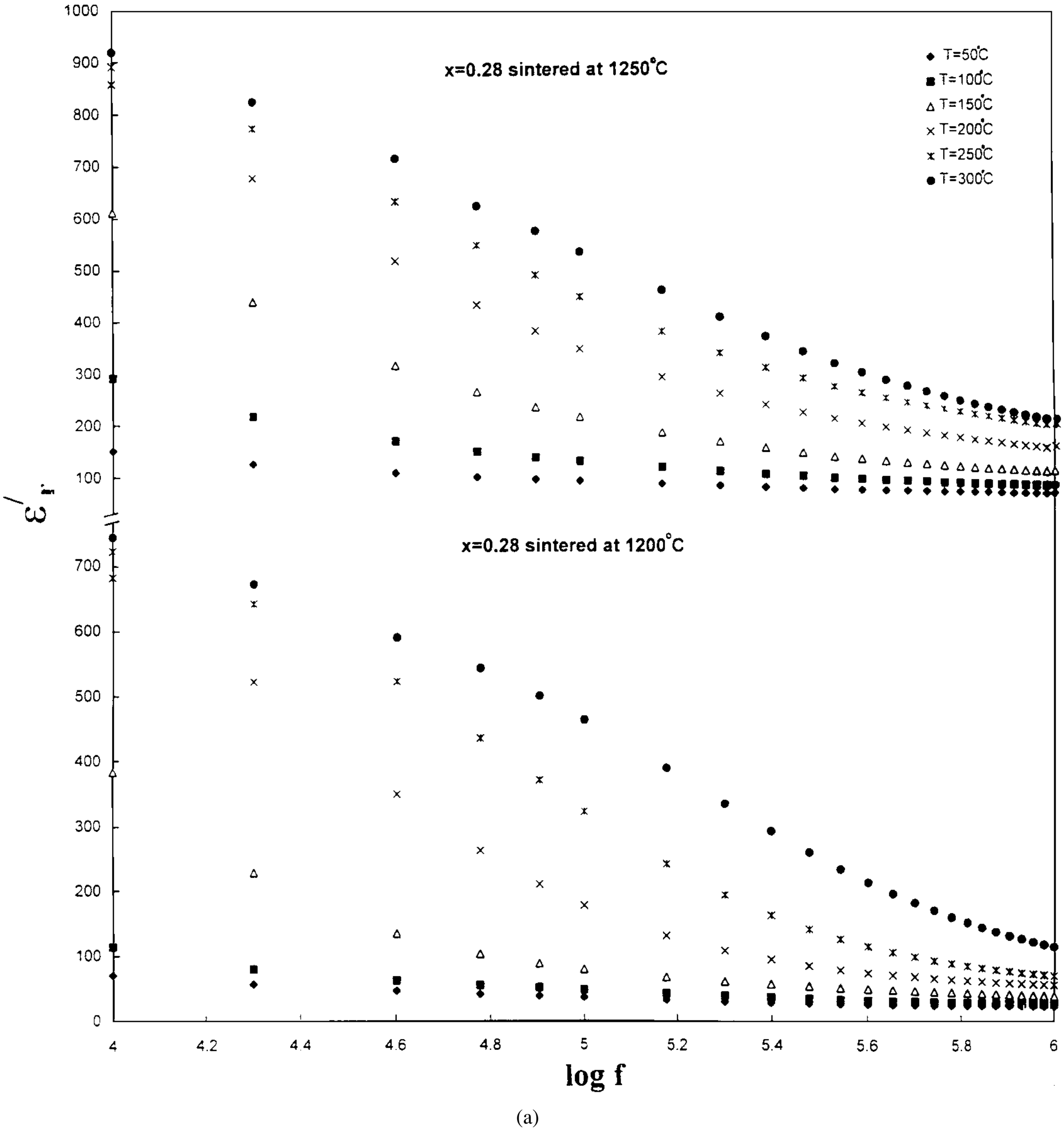
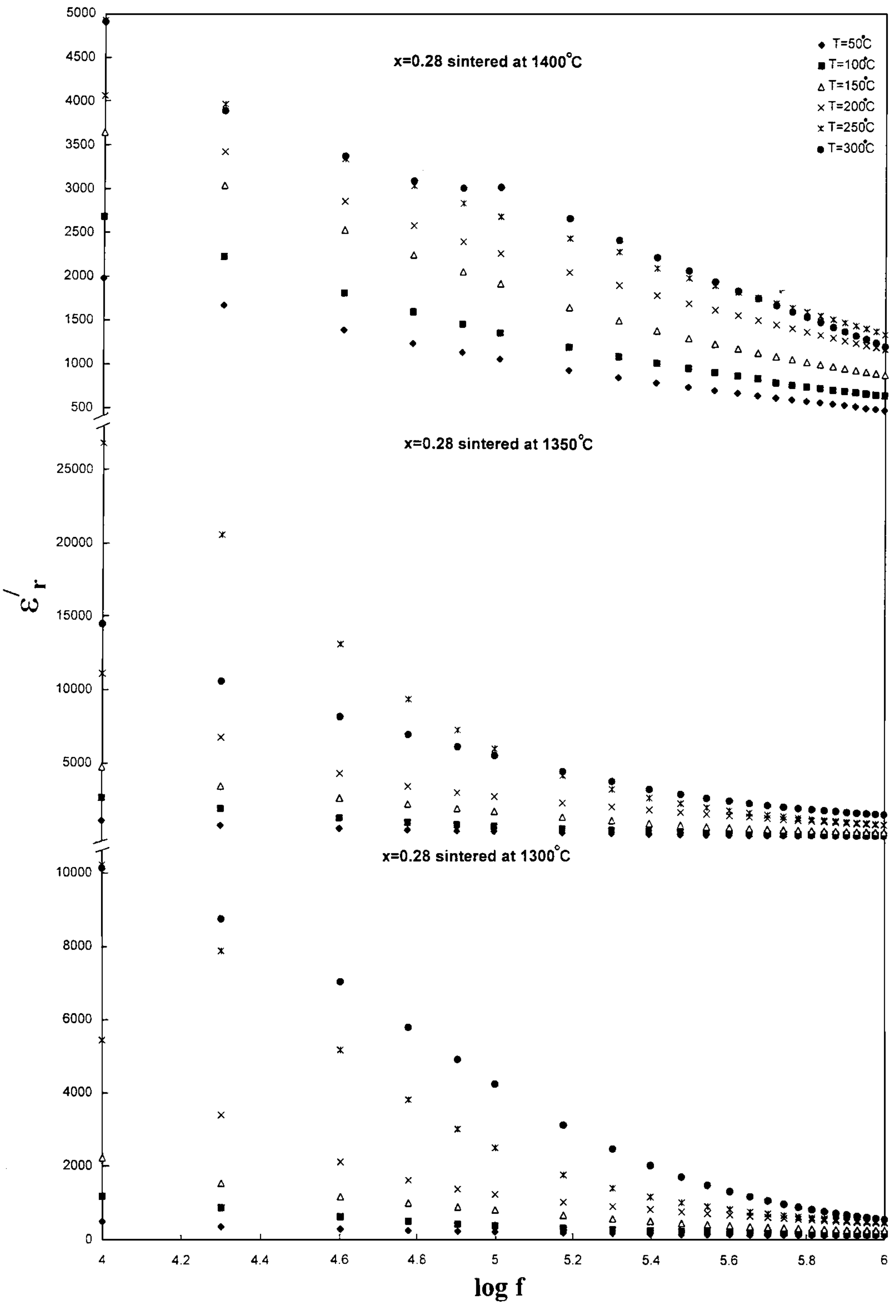


Figure 1 Correlation of the real part of the dielectric constant ε'_r and absolute temperature for $Mn_{0.28}Zn_{0.72}Fe_2O_4$ as a function of sintering temperature and heating rate of 6°C/min.



(a)

Figure 2 Effect of frequency on ε'_r for $Mn_{0.28}Zn_{0.72}Fe_2O_4$ as a function of sintering temperature and heating rate of 6°C/min *(Continued)*.



(b)

Figure 2 (Continued).

its direction leading to an increase in ε'_r as a result of cooperation between orientational and rotational polarization. The electron hopping between Fe^{2+} and Fe^{3+} is expected to be increased, helping in increasing ε'_r until reaching the Curie temperature. Above 500 K the thermal energy due to heating is high enough to overcome the field effect as well as disturbing the ordered dipoles thus decreasing ε'_r. Another transition in a form of a shoulder at $\cong$580 K and sintering temperature of 1300°C is appeared and becomes small at 1350°C and disappeared at 1400°C. This confirms the existence of another types of polarization such as migrational and Maxwell-Wagner that take place in the regions separating the grains. Above 580 K the recovering effect produced from dipoles disordering is greater than that from aligned them in the field direction and a drastic decrease in ε' is observed.

The effect of frequency on ε'_r for $Mn_{0.28}Zn_{0.72}Fe_2O_4$ as a function of sintering temperature at heating rate of 6°C/min is shown in Fig. 2 as a typical curve. The figure shows that, as the frequency increases ε'_r decreases due to decrease in the polarizability at all sintering temperatures and this obviously appeared in the reported data Table I. This may be due to the effect of the field

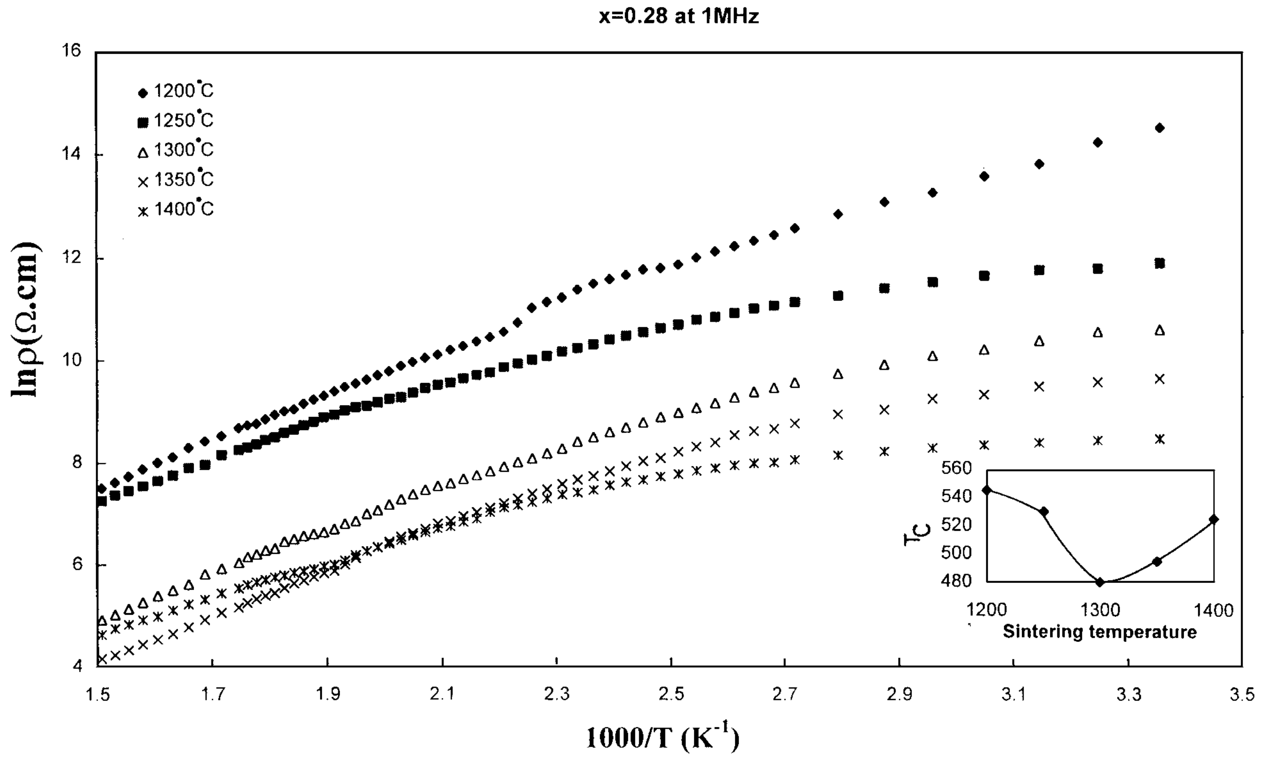


Figure 3 The relation of $\ln \rho$ versus the reciprocal of absolute temperature for Mn-Zn ferrite sample at 1 MHz as a function of sintering temperature. The inset: Variation of the Curie temperature with the sintering one.

TABLE I Values of ε_r' at different logarithmic frequencies and heating temperature 200°C as a function of sintering temperature

Log f	1200°C	1250°C	1300°C	1350°C	1400°C
4.3	525	675	3400	7000	3350
4.6	350	510	2100	4000	2800
5.0	175	350	1600	3200	2250
5.4	80	230	700	2000	1790
5.8	55	150	550	1500	1500

TABLE II Values of the activation energy in the low and high Temperature regions at 1 MHz) and the grain size of all Sintering temperatures

Sintering temperature	E_{I}(eV)	E_{II}(eV)	Grain size $\times 10^{-7}$ mm
1200	0.18	0.43	0.809
1250	0.14	0.32	0.637
1300	0.17	0.43	0.636
1350	0.12	0.32	0.659
1400	0.06	0.38	0.425

on hopping process that takes place between Fe^{2+} and Fe^{3+} as a result of its fast variation [8].

Fig. 3 correlates $\ln \rho$ versus the reciprocal of absolute temperature for the investigated sample at 1 MHz as a function of sintering temperature. The change in the slope was orginally anticipated to be due to Curie temperature that varies from one line to another depending on sintering temperature. It was believed that the sintering of the sample in no inert gas may helps in increasing very slightly the oxygen content and produces the cation vacancies. This parallels the case of oxygen excess magnetite for which cation vacancy ordering has been conclusively proved [9]. As a result the vacancies are formed at different depths and act as charge trapping centers. During heating, the charge carriers are liberated and participate in conduction process simultaneously with those produced the valence exchange between $Fe^{2+} \Leftrightarrow Fe^{3+}$ and $Mn^{+3} \Leftrightarrow Mn^{2+}$.

The inset of Fig. 3 shows the variation of the Curie temperature with sintering one. This behavior shows that the Curie temperature is continuously decreased until reaching 1300°C and starts to increase again at 1350°C which is considered as a critical sintering temperature. The peculiar behavior of the data at 1300°C agree well with the results of ε' at such critical sintering temperature.

The activation energy are calculated at 100 kHz and different sintering temperature and reported in Table II, in the low and high temperature regions.

SE micrographs were carried out for the investigated samples. From the micrographs the grain size was calculated and compared with those calculated from X-ray diffractograms. The average values were reported in Table II.

In region I and II the activation energy ranged from 0.18 eV to 0.06 eV and 0.43 eV to 0.38 eV respectively. This shows a gradual decrease with increasing sintering temperature. The high activation energy in region II suggests that the conduction mechanism in this region can neither be due to electron nor to the hole hopping. Different mechanisms may be responsible for the conduction process. The decrease in activation energy in both region means that the sintering temperature affects directly Fe^{2+}/Fe^{3+} ratio, increasing the carriers hopping and in turns increase the conductivity of the system.

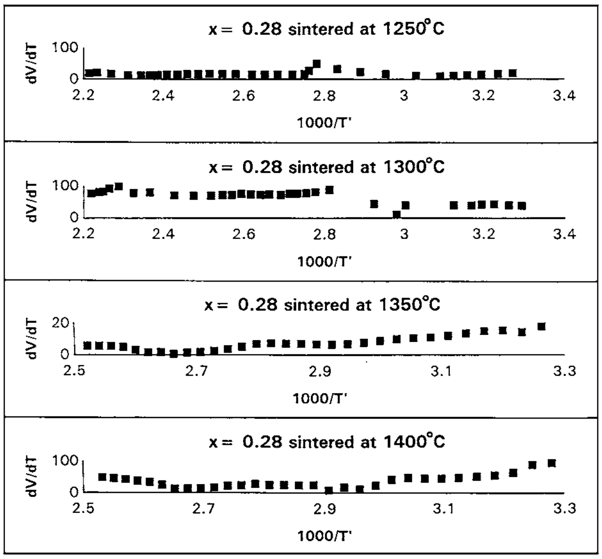


Figure 4 Correlates the Seebeck coefficient dV/dT and the reciprocal of absolute temperature for $Mn_{0.28}Zn_{0.72}Fe_2O_4$ at different sintering temperature ranging from 1250°C up to 1400°C.

The values of the reported average grain size Table II at different sintering temperature indicate that the grain size decreases with increasing sintering temperature and begins to increase slowly up to 1350°C. This behavior agrees well with the suggestion of the critical sintering temperature.

Fig. 4 correlates the Seebeck coefficient dV/dT and reciprocal of absolute temperature for $Mn_{0.28}Zn_{0.72}Fe_2O_4$ at different sintering temperature ranging from 1250°C up to 1400°C. The data is classified into two characters, one at 1250°C, 1300°C and the other at 1350°C, 1400°C. The first one shows nearly stable holes number while the second gives peculiarity. At 1400°C, the Seebeck Coefficient decreases from $\cong$300 K to 339 K and has nearly no variation from 339 K to 370 K after which it increases again. This means that, the number of holes varies with the temperature region as a result of the holes leaving behind the electrons that are escaped from the trapping centers. This was expected to occur in the range of 370 K up to 392 K. Generally, the variation of Seebeck coefficient with temperature suggests that the investigated ferrite is nondegenerate semiconductor.

4. Conclusion

In conclusion one can state that, the increase in ε_r' with applied frequency is due to the cooperation between orientational and rotational polarization as well as the electron hopping between Fe^{2+} and Fe^{3+}. The existence of shoulder at 580 K indicates the existence of migrational and Maxwell-Wagner polarization. The change in the slopes of resistivity curves is due to Curie temperature which vary depending on sintering temperature.

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