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Dielectric properties and conductivity of zinc ferrite and zinc ferrite doped with yttrium

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ABSTRACT

The electrical properties of spinel ferrites are determined by the different factors, of which synthesis method, chemical composition and grain size have the most important role. In this paper we investigate dielectric behavior and conductivity of the nanosized $ZnFe_2O_4$ and $Y_{0.15}Zn_{0.85}Fe_2O_4$ powders obtained by the coprecipitation method. The frequency dependence of the dielectric permittivity, the loss factor, and the conductivity of the samples are determined in the frequency range from 1 Hz to 100 kHz, at temperatures from 300 to 350 K. The dielectric behavior of ferrites is explained by the interface polarization, arising from the heterogeneous nature of its structure. Increasing trend of electrical conductivity (σ) and decreasing trend of the dielectric permittivity (ε) with increasing frequency are explained by the Koops model. The maximum values of $\tan\delta$ are noticed in the frequency range from 1 to 10 kHz.

1. Introduction

Spinel ferrites in nanosize form possess, as a rule, unique physical properties which are predominantly controlled by the method of preparation, the cation distribution between A and B sites of the spinel $(A_{1-\delta}{}^{2+}B_{\delta}{}^{3+})[A_{\delta}{}^{2+}B_{2-\delta}{}^{3+}]O_4{}^{2-}$ structure, the grain size and the grain boundaries. It is well known that ferrites have high-electrical resistivities, low-eddy currents and dielectric losses. Due to this fact, and because of their specific magnetic properties, they have a wide range of applications from microwave to radio frequencies as a core in magnetic seals, recording media, sensors, ferrofluids [1,2].

It has also been shown that their magnetic properties change with rare earth substitution. For example, the Curie temperature decreases and coercivity field increases with rare earth substitution in Ni, Zn ferrites [3]. Considering the fact that rare earth substituted magnetite has improved magnetic performance (i.e. high-saturation magnetization and coercivity) we expected that rare earth substitution in zinc ferrite may produce a material with low-electrical conductivity which is also necessary for its potential application. Hence, the aim of this work was to examine how the substitution of yttrium influences electrical parameters: the dielectric permittivity, the loss factor and the conductivity of the nanosized $ZnFe_2O_4$.

The investigation of the electrical properties of ferrites can give useful information concerning the behavior of localized charge carriers, leading to a better understanding of the mechanism of dielectric polarization of the ferrites. The interface polarization is dominant type of polarization below 30 kHz [4]. Behavior of these materials in the frequency region from 10^4 to 10^9 Hz is analogous with Debye type of relaxation process. The interface polarization at low frequencies and Debye type of the polarization at high frequencies behave in a similar way, since both types of polarization depend on the availability of the conduction electrons, which is equal to the concentration of the Fe^{2+} ions. The essential difference is that at low frequencies a large amount of electrons in the interface region effectively hop between the heterogeneities, while at high frequencies the hopping is between the Fe^{2+} and Fe^{3+} ions at the octahedral B sites.

A strong correlation has been noticed between the dielectric properties and the conduction mechanism in these materials [5]. According to the small polaron hopping model, it has been suggested that the conduction in the spinels is due to the transfer of electrons between cations of different charge at B sites (i.e. between the Fe^{2+} and Fe^{3+} ions at octahedral sites). The overlap between the wave function of ions at the adjacent sites is due (at least in part) to the fact that the electrons in ferrites are localized. It seems that the charge carriers are not free to move through the lattice. However, the presence of the lattice vibrations make possible the ions to come close enough and the transfer of charge carriers from one ion to another is happening with a high probability. The distance between the cations and the degree of covalence at the A sites are higher than the corresponding ones of the cations at the B sites, and, as a consequence, the mobility of the carriers at the A sites is expected to be smaller [6].

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2. Experimental

Nanosized powders were synthesized by previously described procedure [7]. Spinel type structure of samples was confirmed by X-ray diffraction analysis [8]. Frequency dependences of dielectric permittivity, tangent of losses and conductivity of $ZnFe_2O_4$ and $Y_{0.15}Zn_{0.85}Fe_2O_4$ samples were measured in the frequency range from 1 Hz to 100 kHz and temperature range from 300 to 350 K using a Dielectric Analyzer 2970 (DEA 2970). Samples (tablets with diameter $d = 10$ mm) were prepared by pressing to 500 MPa.

3. Results and discussion

The collected XRPD data for both samples were used to refine some structural parameters relevant for their electrical properties. The refinement was performed with the program Fullprof (Fig. 1(a) and (b)).

Both samples were refined in space group $Fd\bar{3}m$ assuming spinel type structure with Fe and Me (Me–Zn, Y) atoms in the special Wyckoff positions 8a (A) and 16d (B) and O in 32e. Cation distribution in tetrahedral 8a (A) and octahedral 16d (B) positions was determined by the parameter N refinement. Values of lattice parameters, temperature factors, occupation parameters of ions in A and B positions and average grain sizes are shown in Table 1. The obtained values for lattice parameters a are characteristic for spinel type structure. It can be noticed that the temperature factors increased for 16d and 32e position with yttrium substitution in zinc ferrite, while the variation of this parameter is negligible for the 8c position. The oxygen position for both samples is approximately the same ($x = y = z = 0.253(2)$ for $ZnFe_2O_4$ and $x = y = z = 0.246(5)$ for $Y_{0.15}Zn_{0.85}Fe_2O_4$).

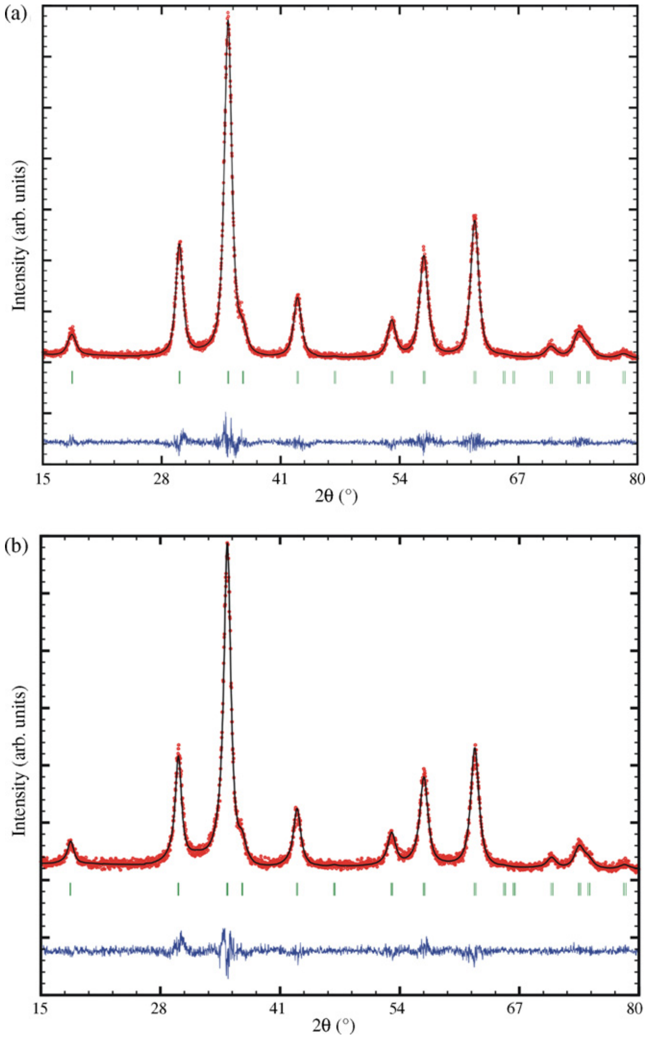

Fig. 1. Comparison of observed (circles) and calculated (solid line) intensities for (a) $ZnFe_2O_4$ and (b) $Y_{0.15}Zn_{0.85}Fe_2O_4$. The difference pattern appears below. The vertical bars, at the bottom, indicate reflection positions.

Table 1
Some crystal data and corresponding agreement factors for investigated specimens (crystal system: face centered cubic; space group: $Fd\bar{3}m$).

	Composition	
	$ZnFe_2O_4$	$Y_{0.15}Zn_{0.85}Fe_2O_4$
Lattice parameters a (Å)	8.4866(7)	8.4615(5)
Temperatures factors U_{eq} (Å^2)		
U_{8a}	0.0068(8)	0.003(8)
U_{16d}	0.0078(5)	0.015(5)
U_{32e}	0.0076(9)	0.017(9)
Occupation parameters N		
$N(Fe)_{8a}$	0.178(6)	0.204(6)
$N(Zn)_{8a}$	0.072(6)	0.046(6)
$N(Fe)_{16d}$	0.322(8)	0.296(7)
$N(Zn)_{16d}$	0.178(8)	0.166(7)
$N(Y)_{16d}$	–	0.038(7)
$N(O)_{32e}$	1.0000(1)	1.0000(1)
Average apparent size (Å)	21(4)	65(5)

There is a number of examples of metastable cation distribution. For instance, Zn^{2+} cations, which prefer tetrahedral positions, in nanozincferrites could be positioned in both A and B positions [9], which to a great extent affects, among the others, magnetic properties. Occupation parameter N refinement confirmed that fact in the cases of examined samples. Also, it can be noticed that the value of the occupation parameter of the iron ion in the octahedral position is higher for $ZnFe_2O_4$ sample than for the $Y_{0.15}Zn_{0.85}Fe_2O_4$ sample (Table 1).

Analysis of frequency dependence of electrical properties showed that the dielectric permittivity ε_r decreases, and conductivity increases with increasing frequency (Figs. 2 and 3). It cans also be noticed that both values slightly increase with increasing temperature. Small changes of the dielectric constant with increase in temperature and at the frequencies higher than 10 Hz are characteristic of the materials with ion chemical bonds [10]. This fact is a consequence of the interface polarization caused by impurities and interstitials, and they are temperature independent. In the narrow semiconducting zone the charge carriers are not free, but trapped, causing polarization. In the case of ferrites, conductivity growth with increasing temperature could be explained by increasing drift of temperature-activated electrons according to hopping mechanism. Namely, with increasing temperature electron exchange between Fe^{2+} and Fe^{3+} ions in the octahedral position is intensified. This confirms Iwauchi's [5] assumption that the process of dielectric polarization in ferrites develops by a mechanism similar to the conducting mechanism.

In lower frequency range, the decrease of ε_r value is more pronounced than at higher frequencies (around 10 kHz) where it reaches a constant value. The electrons involved in hopping between $Fe^{2+} \leftrightarrow Fe^{3+}$ ions are locally aligned with the electric field direction and define polarization process. Polarization decreases with increasing frequency and reaches a constant value when the frequency of electron hopping between $Fe^{2+} \leftrightarrow Fe^{3+}$ ions cannot follow any more the fast-changing of alternating field.

Table 2
Values of parameter log(A) and universal exponent n for frequencies below 10^4 Hz.

Sample	log(A)	n
$ZnFe_2O_4$ (330 K)	-8.47 ± 0.03	0.76 ± 0.01
$ZnFe_2O_4$ (350 K)	-8.03 ± 0.05	0.64 ± 0.01
$Y_{0.15}Zn_{0.85}Fe_2O_4$ (330 K)	-8.29 ± 0.03	0.71 ± 0.01
$Y_{0.15}Zn_{0.85}Fe_2O_4$ (350 K)	-7.92 ± 0.06	0.60 ± 0.01

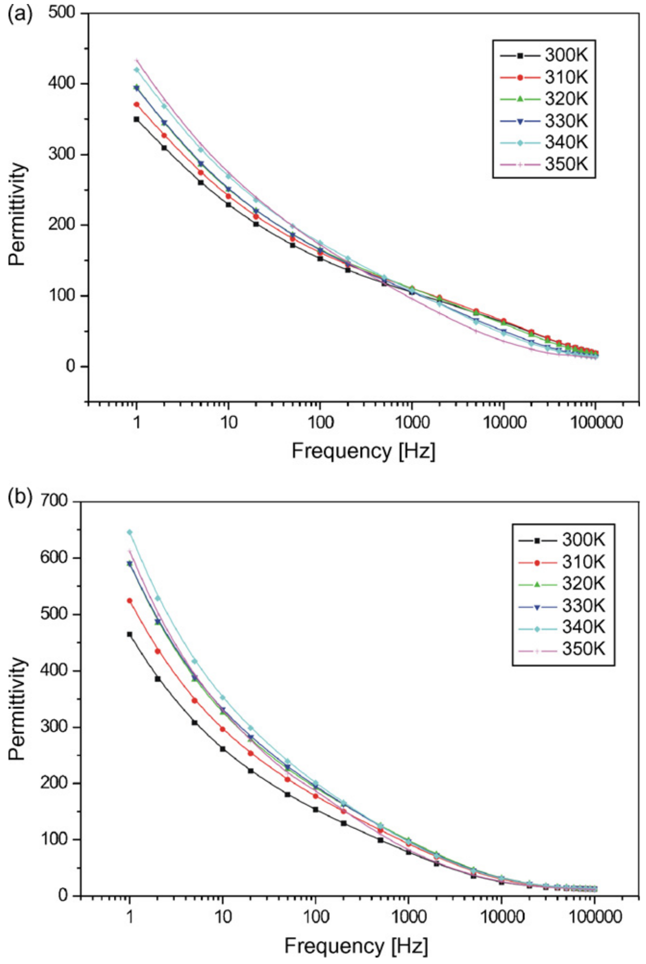

Fig. 2. Variation of dielectric permittivity with frequency of (a) $ZnFe_2O_4$ and (b) $Y_{0.15}Zn_{0.85}Fe_2O_4$.

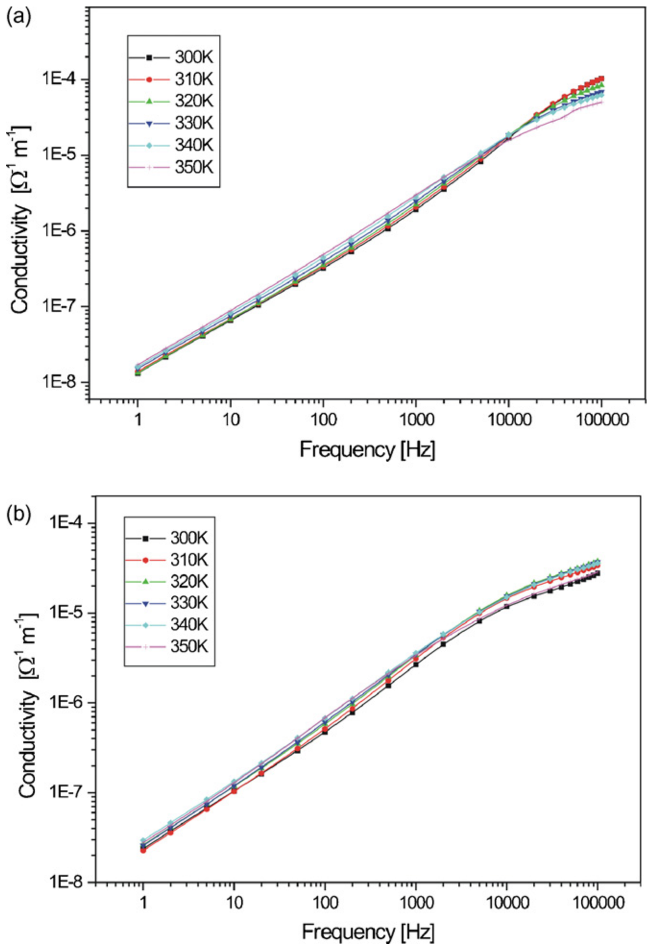

Fig. 3. Variation of conductivity with frequency of (a) $ZnFe_2O_4$ and (b) $Y_{0.15}Zn_{0.85}Fe_2O_4$.

Increasing trend of the electrical conductivity σ, and decreasing trend of dielectric permittivity ε with increasing frequency can be explained by the phenomenological Koops theory [11], in which dielectric materials are treated as a two-layer structure of Maxwell–Wagner type [12].

Conductivity of zinc-ferrite is lower than that of zinc-ferrite doped with yttrium at the frequencies below 10^4 Hz. Above this frequency, the conductivity of $Y_{0.15}Zn_{0.85}Fe_2O_4$ is lower than that of $ZnFe_2O_4$. Such result can be explained in the following manner. Conductivity of these samples at the frequencies below 10^4 Hz is caused, above all, by the grain boundaries, i.e. by electron hopping between heterogeneities, while above this frequency the conductivity is determined by the grain itself, i.e. by the electrons hopping between Fe^{2+} and Fe^{3+} ions in the octahedral positions. Since the obtained value of occupation parameter of iron ion in the octahedral B position is higher for zinc ferrite than for zinc ferrite doped with yttrium, the number of available Fe^{2+}/Fe^{3+} ions involved in the polarization process is larger and, consequently, the conductivity values are higher.

The behavior of the electrical conductivity, caused by hopping mechanism, can be described by the following law:

$$\sigma_{ac} = A(T) \cdot \omega^{n(T)}$$

where $A(T)$ represents a parameter characteristic for the given material, and $n(T)$ is the universal exponent (value of this parameter lies in the $0 < n < 1$ range). From the linear dependence (Fig. 4; $\log \sigma_{ac} = f(\log \omega)$) at 330 and 350 K, the values of the parameters A and n below 10^4 Hz, for $ZnFe_2O_4$ and $Y_{0.15}Zn_{0.85}Fe_2O_4$, respectively, were calculated (Table 2). The exponent n is the measure of departure from ideal Debye type of relaxation process ($n = 0$). It has been shown that when $n \leq 0.3$ the polarization process is of Debye-type (the case of nearest-neighbor interacting dipoles) [13]. The calculated value of the exponent n in the frequency range below 10^4 Hz corresponds to the interface polarization.

The loss factor, i.e. the tangent of losses with zinc ferrite and zinc ferrite doped by yttrium, decreases in the frequency range up

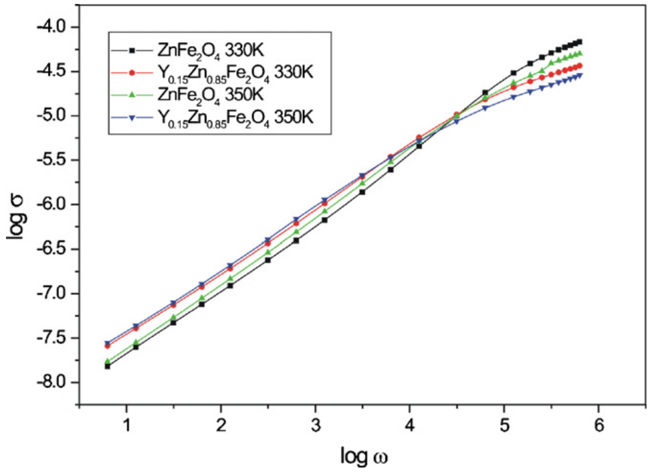

Fig. 4. Functional dependence $\log \sigma_{ac}$ vs. $\log \omega$ at 330 and 350 K for both samples.

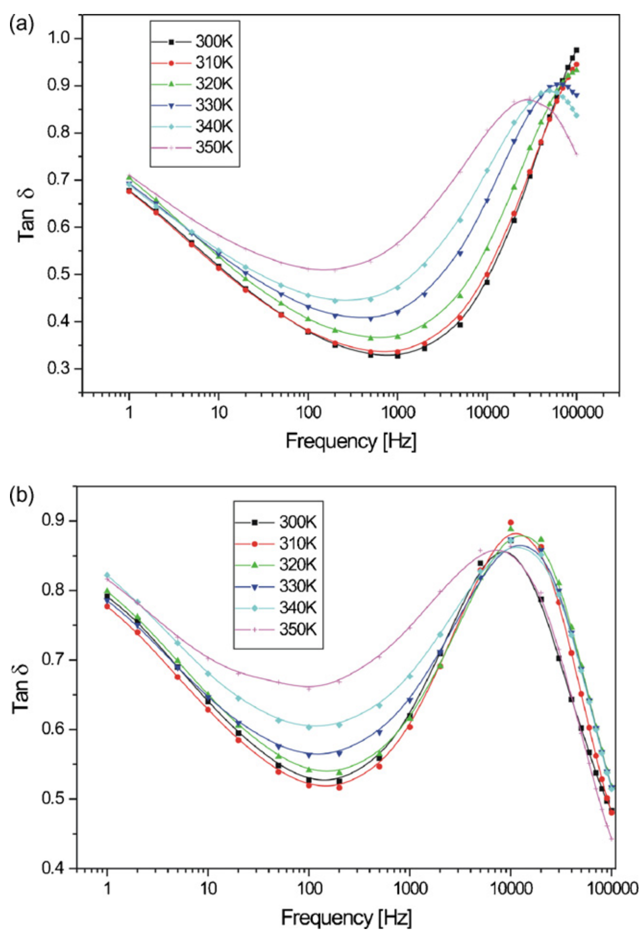

Fig. 5. Variation of tan δ with frequency for (a) $ZnFe_2O_4$ and (b) $Y_{0.15}Zn_{0.85}Fe_2O_4$.

to 100 Hz (Fig. 5). At the frequencies above 100 Hz it increases, and maximal values are observed above 10 kHz. The maximum position shifts towards lower frequencies as heating increases during the course of measuring. At higher heating temperatures, thermal movements are more intensive, and therefore the maxima occur at lower frequencies. Maximum frequencies tan δ correspond to the frequencies for interface polarization.

According to Koops' model [11], the decrease of the tangent of losses, tan δ, is explained by the fact that at lower frequencies, where the resistivity is high and the grain boundary effect is dominant, more energy is needed for the exchange of electrons between Fe^{2+} and Fe^{3+} ions located at grain boundaries, i.e. energy loss (tan δ) is high. At high frequencies, when the resistivity is low and grains themselves have a dominant role, little energy is needed for hopping of electrons between the Fe^{2+} and Fe^{3+} ions located in a grain, and therefore tan δ is also small. The maximum value of the tangent of losses is observed when hopping frequency corresponds to the frequency of the external field.

As was already mentioned, the values of dielectric permittivity and conductivity are related to the materials pressed to 500 MPa. Previous studies indicated that ferrite ceramics are undeformable, i.e. grains do not change either shape or size. Increased pressure changes only the grain surroundings, lowering ceramic's porousness [14,15]. Due to the decreased porousness, higher pressure decreases the value of both dielectric permittivity and conductivity. Our current studies indicate such behavior.

Table 3
Dielectric parameters of samples on $T_1 = 330$ K and $T_2 = 350$ K.

Sample	ε'_{st}	ε'_{op}	ω_{max} (kHz)	τ ($\times 10^{-5}$ s)	U (eV)
$ZnFe_2O_4$ (T_1)	106	7.4	4.7	2.12	0.29
$ZnFe_2O_4$ (T_2)	111.7	7.4	2.2	4.42	0.29
$Y_{0.15}Zn_{0.85}Fe_2O_4$ (T_1)	140.4	10.8	1.6	6.12	0.24
$Y_{0.15}Zn_{0.85}Fe_2O_4$ (T_2)	146	10.8	1.0	9.95	0.24

Cole and Cole have established that the real and the imaginary part of dielectric permittivity in the Cartesian coordinate system with axes ε' and ε'', for different frequencies, in the dispersion area lie over the semicircle with the center at ε' [16]. From the Cole–Cole diagram, the values of ε'_{st} and ε'_{op}, as well as ω_{max} (the frequency at which the period of external electric field matches with time of relaxation of τ dipole) are determined.

The relation between ω_{max} and relaxation time is $\omega_{max} \cdot \tau = 1$. Since the relaxation time is defined as a period during which a particle in a dielectric, in the case of a change of electric field, transcends from one equilibrium position into another, which are separated from each other by a potential barrier of the height U (this energy is also called activation energy of dipole transitions) from $\tau = (1/2\omega_0)\exp(-(U/kT))$ (where ω_0 is the frequency of particle oscillation in an equilibrium position), it is possible to calculate the activation energy of the polarization process. The obtained values are given in Table 3.

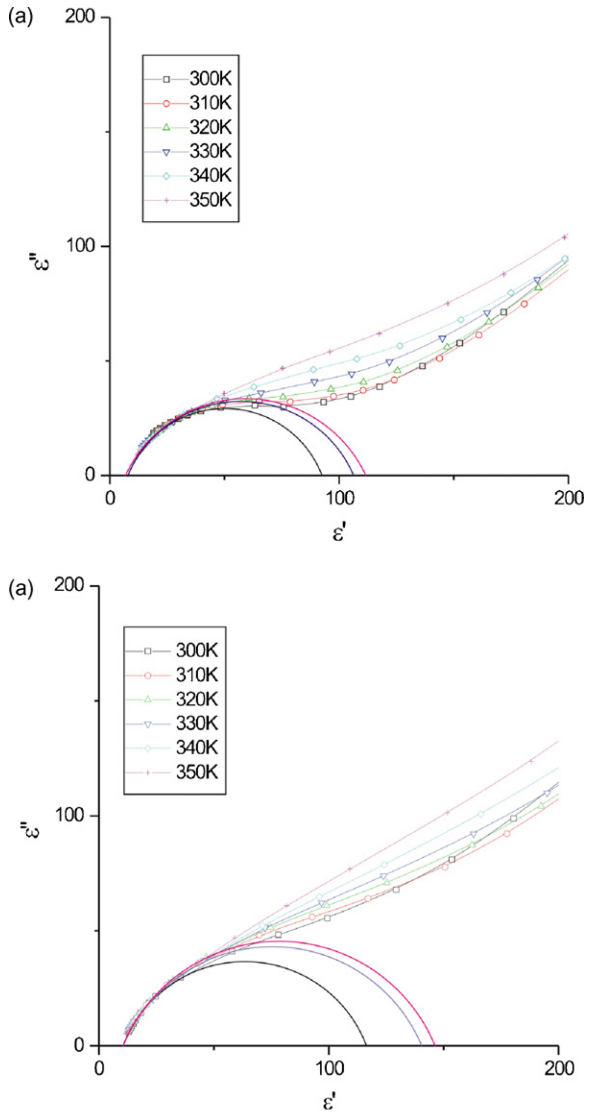

Fig. 6. Cole–Cole diagram for (a) $ZnFe_2O_4$ and (b) $Y_{0.15}Zn_{0.85}Fe_2O_4$.

It can be noticed that the center of semicircle is positioned significantly below the ε' coordinate axis (Fig. 6). Again, it can be concluded that this is a composite dielectric to which the Debye theory at higher frequencies (above 10 kHz) can be applied. Position of the center of the circle moves to higher values of the dielectric permittivity with increasing temperature, and the radius of the circle increases. Deviations at lower frequencies are caused by the superposition with the second dispersion region (conditioned by grain boundaries), which extends on even lower frequencies and whose presence is obvious at higher temperatures.

4. Conclusion

Dielectric properties and conductivity of nanosized $ZnFe_2O_4$ and $Y_{0.15}Zn_{0.85}Fe_2O_4$ powder obtained by coprecipation method are investigated. The dependence of both dielectric permittivity and conductivity on frequency can be explained by Koops' phenomenological theory of dielectric dispersion. Conductivity of these samples at frequencies below 10^4 Hz is primarily caused by the grain boundaries, while above this frequency the conductivity is determined by the grain itself. Also, above this frequency, the conductivity of zinc-ferrites doped with yttrium is lower than that of zinc-ferrites, which is explained by the value of the occupation parameters of iron ion at the octahedral B sites. The obtained Cole–Cole diagram (above 10^4 Hz) shows one semicircle corresponding to grain conductions. Deviations at lower frequencies are caused by supervention of the second dispersion region which is conditioned by the grain boundaries.

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