Processing and Application of Ceramics 2 [1] (2008) 53–56

Dielectric Properties of Nanosized $ZnFe_2O_4$

Željka Cvejić*, Srđan Rakić, Stevan Jankov, Sonja Skuban, Agneš Kapor

Department of Physics, Faculty of Sciences, University of Novi Sad, Trg D. Obradovića 6
21000 Novi Sad, Serbia

Received 6 January 2008; received in revised form 19 May 2008; accepted 30 May 2008

Abstract

In this paper we present the results concerning the dielectric properties of the nanosized $ZnFe_2O_4$. Dielectric permittivity, the loss factor, as well as the conductivity, were measured in the temperature range 300-630 K and at 1 Hz, 10 Hz, 100 Hz, 1 kHz and 10 kHz frequencies. Significant improvements in permittivity, loss factor and ionic conductivity comparing to bulk samples have been observed.

Keywords: zinc-ferrites, dielectric properties

I. Introduction

Dielectric properties of nanosized ferrites are influenced mainly by the method of preparation, grain size, grain boundaries and cation distribution [1]. As a consequence of complex structure, dielectric behaviour of ferrites is explained by interface polarization. This type of polarization is dominant at frequencies below 30 kHz [2]. Dielectric constant does not decrease continuously with frequency increases as expected from interface polarization. Behaviour of these materials, in this frequency region is analogous with Debye type of relaxation process. Debye type of polarization is connected with polar materials which manifest the orientation polarization at 10^4–10^9 Hz. Ionic and electronic polarization have negligible influence to the value of dielectric constant due to the fact that the corresponding frequencies are located in the microwave region.

The presence of Fe^{2+} and Fe^{3+} ions at octahedral positions defines ferrites as polar materials. Fe^{2+} ions could be formed by partial reduction of Fe^{3+} during the sintering process. Rotational displacements of the dipoles result in the orientational polarization. The rotation or turning of dipoles can be explained as the interchange of the electrons between the ions, thus the dipoles align themselves with field. The potential barrier between two type of ions will impose an inertia to charge movement, resulting in a relaxation to the polarization process. Another possible source of the orientation polarization in ferrites is the existence of cation vacancies. In general, the occupied cations display a tendency to associate positive ion vacancies, and thus, the associated pairs have dipole moments.

The cations and the vacancies in the vicinity can exchange position when electric field is applied [3]. The behaviour of interface polarization at low frequencies and Debye type of the polarization at high frequencies is similar, 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 in interface region a large amount of electrons effectively hop between the heterogeneities, while at high frequencies the hopping is between the Fe^{2+} and Fe^{3+} ions.

There is a strong correlation between the dielectric properties and the conduction mechanism in ferrites. Iwauchi first noticed that fact [4]. The conduction mechanism is explained by hopping mechanism between the Fe^{2+} and Fe^{3+} ions at octahedral sites.

II. Experimental

Nanosized $ZnFe_2O_4$ powder was synthesized with previously described procedure [5]. Spinel type structure of as-prepared (S_1) and calcined (S_2) sample at 500°C was confirmed by X-ray diffraction analysis. The average crystallite sizes: 21.54 (4.34) Å and 81.21 (5.59) Å for (S_1) and (S_2) sample, respectively, were determined in [6]. Dielectric permittivity, loss factor, as well as conductivity were measured in 300–630 K tem-

---

[*] Corresponding author: tel: +381 21 485 2821
fax: +381 21 455 662, e-mail: *zeljkac@uns.ns.ac.yu*

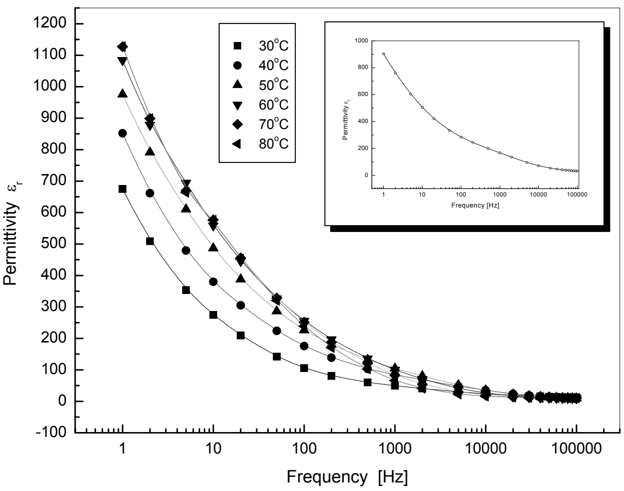

Figure 1. The frequency dependence of the dielectric permittivity at the different temperatures

perature range, on 1 Hz, 10 Hz, 100 Hz, 1 kHz and 10 kHz frequencies, using Dielectric Analyzer 2970 (DEA 2970). Sample (tablet with diameter *d* = 10 mm) was prepared by uniaxial pressing at 500 MPa.

III. Results and Discussion

It can be seen from Figs. 1 and 2 that dielectric permittivity of investigated samples decreases, while conductivity increases with increasing frequency. The main diagrams in Figs. 1–5 show dependence for the sample S_2, compared to the results for the sample S_1 which are shown in inset figures. At lower frequencies decreasing trend of dielectric permittivity is more pronounced, than at higher frequencies (approximately 10 kHz) where this parameter reaches constant value. Similar results are obtained in [7–9]. Electrons which take part in hopping process between $Fe^{2+} \leftrightarrow Fe^{3+}$ ions, arrange themselves locally with a field and define the polarization process. The polarization decreases with increasing frequency and reaches constant value when the hopping frequencies of electrons between $Fe^{2+} \leftrightarrow Fe^{3+}$ ions cannot follow any more the fast changing of alternating field.

Increasing trend of electrical conductivity σ and decreasing trend of dielectric permittivity ε with increasing frequency can be explained by phenomenological Koops theory [10], in which dielectric materials are treated as two layer structure of Maxwell-Wagner type [11]. In this model the grains represent a conducting layer, while grain boundaries represent a poorly conducting layer. The grain possesses small value of dielectric constant and have dominant role at high frequencies. The grain boundaries possess high value of dielectric constant, and mainly influence the dielectric properties at low frequencies.

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

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

where *A(T)* presents characteristic parameter for given material, and *n(T)* is the universal exponent (values of this parameter lies in 0<*n*<1 range). From the linear dependence ($\sigma_{ac} = f(\log \omega)$) at 350 K, and frequencies higher than 10 kHz, the values of the parameters *A* ($A = 2.29.10^{-8}$) and *n* ($n = 0.61\pm0.01$) for as-prepared sample were calculated. 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-neighbour interacting dipoles) [7]. The calculated value of exponent *n* corresponds to the interface polarization.

The loss factor at lower frequencies decreases, then increases, while maxima are noticed in 1 kHz – 10 kHz frequency range (Fig. 3). The position of maximum is shifted towards lower frequency when the samples are heated during the measurements. At higher temperatures, thermal movement is much more emphasized, therefore the maximum of loss factor is expected at lower frequencies. The frequencies corresponding to maxima of *tan*δ are the result of interface polarization.

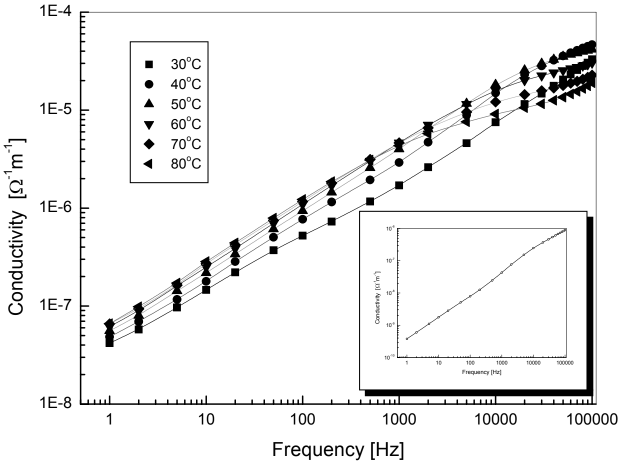

Figure 2. The frequency dependence of the conductivity at the different temperatures

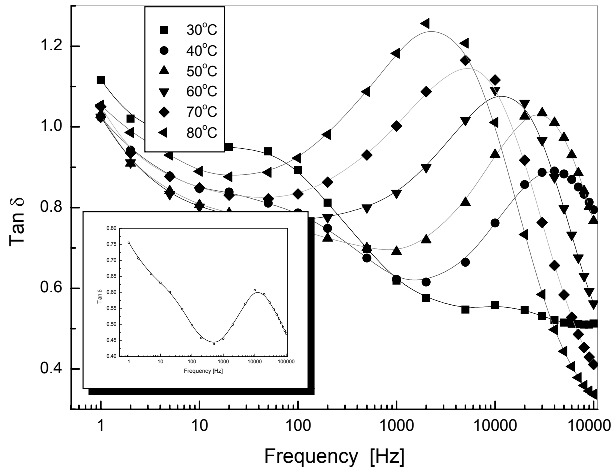

Figure 3. The frequency dependence of the loss factor at different temperatures

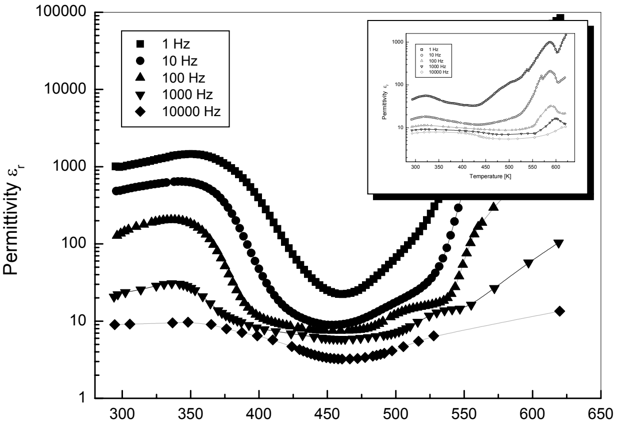

Figure 4. The temperature dependence of the dielectric permittivity at different frequencies

The behaviour of *tan*δ in Koops theory [10] is explained with the fact that at lower frequencies, when the resistivity is high and the grain boundaries effect is dominant. Thus, more energy is required for electron interchange between Fe^{2+} and Fe^{3+} ions, located at grain boundaries, and *tan*δ manifested a high value. At higher frequencies, when the resistivity is low and the grain influence is dominant, low energy is needed for hopping process between iron ions located in the grains, and as a result *tan*δ possesses small values. The maximal value of *tan*δ is observed when the hopping frequency is equal to the frequency of applied field.

The temperature dependencies of the dielectric permittivity and the conductivity of the investigated sample are obtained in 300–650 K temperature range, and at 1 Hz, 10 Hz; 100 Hz; 1 kHz and 10 kHz (Figs. 4 and 5).

The negligible varying of dielectric permittivity - ε on temperatures, at frequencies higher than 10 Hz, is characteristic for materials with ionic chemical bonds [12]. High values of ε at low frequencies and high temperatures are due to the presence of permanent dipole moment, i.e. the effective charge decoupling is small [7,8]. In the majority of cases, atoms or molecules can not be oriented in low temperature region. The orientation of dipoles at high temperatures is much more relieved, and the polarization increases. The thermal oscillations are intensified at high temperatures, thus dielectric permittivity overcomes its maximum value. It can be seen from Fig. 1 at high frequencies, the variation of dielectric permittivity ε is negligible. This phenomenon can be explained by the fact that at higher frequencies dipoles are no longer free to rotate and change their orientation, and the polarization decreases.

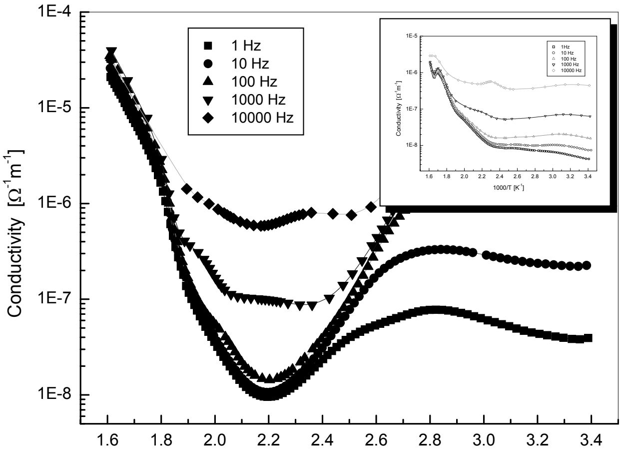

Figure 5. The temperature dependence of the conductivity at different frequencies

The number of charge carriers exponentially increases at $T \geq 500$ K, and causes interface polarization at large scale. Increasing trend of the conductivity at higher temperatures and higher frequencies can be expected due to the increase in the number of charge carriers or increasing trend of mobility of charge carriers [13,14]. In the case of the ferrite materials, the fast increase in the conductivity can be explained by the increase of the drift mobility of thermally activated charge carriers. Namely, the interchange of electrons between Fe^{2+} and Fe^{3+} ions at octahedral sites is intensified with temperature growth. It is in agreement with Iwauchi′s assumption that the polarization process occurs according to the mechanism similar to the conduction process.

According to the results [15,16], the increasing conductivity at lower temperatures is explained by the impurity presence at the grain boundaries. The energy levels of these impurities lay below the conduction zone, and the small activation energy is required for the electron transition from its level to the levels in the conducting zone. Therefore, at temperatures below 350 K, the main contribution to conduction mechanism is derived from grain boundaries, while the grains have leading contribution at higher temperatures.

This conclusion is in agreement with Koops theory, in which the grain boundaries manifest low conductivity while the grains manifest high conductivity. Using the equation:

$$\sigma = \sigma_0 e^{-\frac{E_a}{kT}}$$

where σ_0 denotes temperature independent coefficient, E_a represents the activation energy and k is the Boltzmann constant, i.e. from the slope of the functional dependence:

$$\ln\sigma = \ln\sigma_0 - \frac{E_a}{kT}$$

(Fig. 6), the values of activation energy for conducting process at kHz range are calculated for the temperature range: $T \leq 500$ K and $T \geq 500$ K. The obtained values $E_a = 1.12 \pm 0.02$ eV for $T \leq 500$ K and $E_a = 1.76 \pm 0.03$ eV for $T \geq 500$ K, are in agreement with results in [3,17].

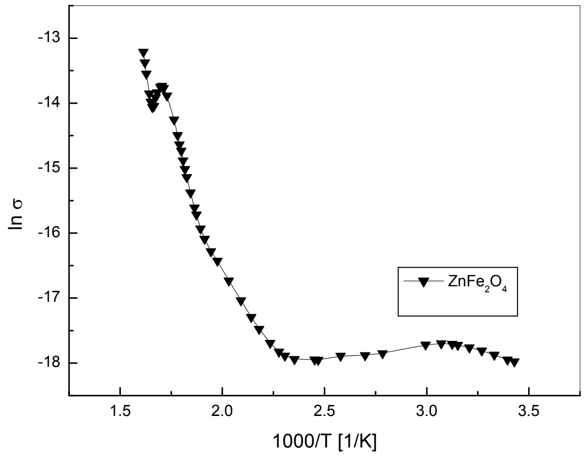

Figure 6. The functional dependence of lnσ vs. 1000/T

The change of the slope of the conductivity curve for the as-prepared (S_1) and the calcined (S_2) sample can be connected with Curie temperature. It is supposed that during the sintering in the inert gas atmosphere, the oxygen content is increased, which is influenced by vacancy origination. As a result, the created vacancies present the trapping centers. During the sample heating, the charge carriers become free and take part in conduction process along with the hopping electrons arisen from interchanging between Fe^{2+} and Fe^{3+} ions.

IV. Conclusions

Dielectric permittivity (ε) of nanosized $ZnFe_2O_4$ decreases while specific conductivity (σ) increases with increasing frequency of alternating field. The behaviour of electrical conductivity is explained by hopping mechanism between Fe^{2+} and Fe^{3+} ions at octahedral sites, and can be described by the exponential law. The calculated value of the exponent *n* from this law corresponds to the interface polarization.

The maximum of the loss factor (*tan* δ) is noticed in 1 kHz – 10 kHz frequency range. This maximal value is observed when the hopping frequency is equal to the frequency of the applied field.

The temperature dependence behaviour of dielectric permittivity (ε) at frequencies higher than 10 Hz is characteristic for materials with ionic chemical bonds.

At temperatures below 350 K, the increasing conductivity is explained by the impurity presence at the grain boundaries. At temperatures higher than 350 K, the grains mainly influence the conducting behaviour of investigated samples.

The real part of dielectric constant ε*'*, loss factor *tan*δ and resistivity for the investigated nanocrystalline ferrites are higher than those of the bulk Fe_3O_4 by two orders of magnitude.

The anomalous frequency dependence of ε*'* has been explained on the basis of charge carriers hopping mechanism. Obtained values of dielectric loss classify these materials as promising for microwave applications.

Acknowledgements: The Serbian Ministry of Science has financially supported this work: Project No. 142059.

References

1. G. Mathew, S.N. Swapna, M.J. Asha, P.A. Joy, M.R. Anantharaman, “Structural, magnetic and electrical properties of the sol-gel prepared $Li_{0.5}Fe_{2.5}O_4$ fine particles”, *J. Phys. D, App. Phys.*, **39** (2006) 900–910.
2. S.D. Shenoy, P.A. Joy, M.R. Anantharaman, “Effect of mechanical milling on the structural, magnetic and dielectric properties of coprecipitated ultrafine zinc ferrite”*, J. Magn. Magn. Mater.*, **269** (2004) 217–226.
3. M.H. Abdulah, A.N. Yusoff, “Frequency dependence of the complex impedances and dielectric behaviour of some Mg-Zn ferrites”, *J. Mater. Sci.*, **32** (1997) 5817–5832.
4. K. Iwauchi, “Dielectric properties of fine particles of Fe_3O_4 and some ferrites”, *Jpn. J. App. Phys.*, **10,** (1971) 1520–1523.
5. M. Maletin, Ž. Cvejić, S. Rakić, V.V. Srdić, “Low-temperature synthesis of nanocrystalline $ZnFe_2O_4$ powders”*, Mater. Sci. Forum,* **518** (2006) 91–94.
6. Ž. Cvejić, S. Rakić, S. Jankov, S. Skuban, A. Kapor, V. Srdić, “Grain size influence on dielectric permittivity of nanocrystalline zinc ferrite”, *XIV Conference of the Serbian Crystallographic Society*, Vršac (2007) p.48.
7. M.A. Ahamed, J Elhiti, “Electrical and dielectric properties of $Zn_{0.8}Co_{0.2}Fe_2O_4$”, *Physique III,* **5** (1995) 775.
8. A.M. Snaikh, S.S. Bellard, B.K. Chougule, “Temperature and frequency-dependent dielectric properties of Zn substituted Li-Mg ferrites”, *J. Magn. Magn. Mater.,* **195** (1999) 384–390.
9. M.A. Ahamed, J Elhiti, E.I. Nimar, A.M. Amar, “The ac electrical conductivity for Co-substituted SbNi ferrites”, *J. Magn. Magn. Mater.,* **152** (1996) 391–395.
10. C.G. Koops, “On the Dispersion of Resistivity and Dielectric Constant of Some Semiconductors at Audiofrequencies” *Phys. Rev.*, **83** (1951) 121.
11. K.W. Wagner, *Am. J. Phys*., **40** (1973) 317.
12. A.A. Sattar, A.R. Samy, “Dielectric properties of rare earth substituted Cu-Zn ferrites” *Phys. Stat. Solidi (a)*, **200** (2003) 415–422.
13. P.V. Reddy, R Sathyanarayana., T.S. Rao, “Electrical conduction in nickel ferrite”, *Phys. Stat. Solidi (a)*, **78** (1983) 109.
14. A. Verma, T.C. Goyal, R.G. Mundiretta, R.G. Gupta, “High-resistivity nickel-zinc ferrites by the citric precursor method”, *J. Magn. Magn. Mater.,* **192** (1999) 271–276.
15. O.S. Joyulu, J. Sobhandri, “DC conductivity and dielectric behaviour of cobalt-zinc ferrites”, *Phys. Stat. Solidi (a)*, **59** (1980) 323–329.
16. A.A. Sattar, “Temperature dependance of the electrical resistivity and thermoelectric power for rare-earthsunstituted Cu-Cd ferrite”, *Egyp. J. Solidi*, **26** [2] (2003)
17. M.A. Ahmed, E.H. El- Khawes, F.A. Radwan, “Dependence of dielectric behaviour of Mn-Zn ferrite on sintering temperature”, *J. Mater. Sci. Lett.*, **36** (2001) 5031–5035.