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IMPEDANCE SPECTROSCOPY METHOD FOR INVESTIGATION THE POLYCRYSTALLINE INHOMOGENEOUS CERAMICS

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Abstract. The present paper introduces the principles of the Impedance Spectroscopy technique, as an important method in the characterization of the discrete materials working in real conditions in circuits. The method was firstly verified by using a RC series-parallel circuit and than was exemplified in studying two types of (Ni,Zn) ferrite ceramics.

Key words: Impedance Spectroscopy, RC series-parallel circuit, ferrite, complex impedance.

1. INTRODUCTION

The large majority of multifunctional materials with applications in microelectronics (dielectrics, ferroelectrics, ferromagnetics, ionic and protonic conductors) prepared as polycrystalline ceramics, films, heterostructures, multilayers, etc. are discrete systems containing multiple solid-solid, solid-liquid, solid-gases interfaces. The contribution of such interfaces to the functional properties become more important and even predominant over the volume effects, when geometric dimensions of the systems decrease down to nanoscale. At these interface, the physical properties

(mechanical, crystallographic, compositional, electrical, transport properties) show strong spatial variations.

From the electrical point of view, at the interfaces separating regions with different dielectric properties (and different polarizations), uncompensated polarization charges are located and their surface density is: $\sigma_{pol} = (\vec{P}_1 - \vec{P}_2) \cdot \vec{n}$, where $\vec{P}_{1,2}$ are the polarizations in the two regions and $\vec{n}$ the normal vector unit. If the polarization exhibits spatial variations, charges with volume density $\rho_{pol} = -\text{div } \vec{P}$ are also present. These polarization charges contribute to the dielectric and transport properties of the inhomogeneous system [1-2]. The interface contribution become more important in ceramics used for solid oxide fuel cells (SOFC) [3], that in the last years have a great development as alternative to the classical energy sources. In SOFCs the electrode-electrolyte junction is more complex than for the liquid cells and the electrolyte is a polycrystalline material with a large number of solid-solid interfaces. By applying an alternative electric field, each interface will have different polarizations and the variation rate of polarization in a given region is a characteristic for each interface: the process is slow for chemical reaction at tri-phase point (atmosphere, electrode, electrolyte) and relative fast long ways grain boundaries in polycrystalline electrodes.

Polycrystalline oxide ceramics as dielectrics, ferroelectrics, ferrites, etc. are generally employed in microelectronics applications and they are subjected to alternative fields. Their electrical response is strongly dependent on interfaces (grain boundary, material-electrode interface) and thus, their properties are determined by the ratio between the interface and volume contributions. The electrical response can be characterized by different rates if it is reported to bulk or boundary ceramic contribution. In consequence, these heterogeneous systems are characterized by different relaxation times τ_i from the electric point of view and they will respond in a different way at various frequency ranges. Double electric layers formed by electrolytes and their associate capacitive reactance are also characterized by different relaxation times or by distributions of relaxation times. Dielectric responses of such heterogeneous systems can strongly depend on the charge type (doped, charge defects), microstructure (grain shape and size for ceramic, open or closed porosity), texture, nature of the electrode and the

contact surface of the active material. The classical methods for electrical investigations (i.e. I-V characteristics, impedance measurements) for these systems do not give enough information, taking into account for their complexity.

One of the most used method of characterization the dielectric properties of bulk polycrystalline materials is the impedance spectroscopy, which was widely used to study the dielectric behavior of the crystalline and polycrystalline ceramics [3-5].

In the present work, the principles of the impedance spectroscopy for investigating polycrystalline ceramics are firstly reviewed. Then, a series-parallel (R,C) circuit for testing the method was designed, the complex impedance was determined and the obtained data were used to recover the constitutive circuit elements (R,C) on the basis of the Argand plot. Further, the method of impedance spectroscopy was employed to study two types of ferrite ceramics with the same composition $\text{Ni}_{0.50}\text{Zn}_{0.50}\text{Fe}_2\text{O}_4$ (NZF) and with different microstructural characteristics.

NZF are important soft magnetic materials that have many applications in both low- and high-frequency devices. They play an useful role in many technological applications, because of their high resistivity, low-dielectric loss, mechanical hardness, high Curie temperature, and chemical stability [6]. They were intensely studied due to their remarkable magnetic properties (high saturation magnetization and low coercive field) and low production cost. The microstructure, magnetic, and dielectric properties of NZF depend on the method of preparation, sintering conditions, and doping concentrations. More recently, functional properties related to the nanosized structures in NZF were reported [7,8]. NZFs have the general formula $\text{Fe}_{1-x}\text{Zn}_x(\text{Ni}_{1-x}\text{Fe}_{1+x})\text{O}_4$. The substitution of Ni^{2+} by the diamagnetic ion Zn^{2+} ions produces a mixed effect on the magnetic properties. In NiFe_2O_4 , the divalent metal ions occupying the octahedral sites (B) and the trivalent Fe ions are distributed among tetrahedral (A) and the octahedral sites (B). ZnFe_2O_4 has a spinel structure with Zn^{2+} ions occupying A sites and Fe^{3+} occupying B sites. Because Zn^{2+} (d10) has a site preference for the A sites, with more and more Zn^{2+} replacing Ni^{2+} , the spin-spin interaction between nonmagnetic Zn^{2+} and Fe^{3+} ions becomes increasingly uncoupled [6]. In $(\text{Ni}_{1-x}\text{Zn}_x)\text{Fe}_2\text{O}_4$ ferrite the tetrahedral (sub-lattice A) and octahedral (sub-lattice B) site Fe moments have collinear arrangement for $x \leq 0.5$ and a non-collinear one for $x \geq 0.50$, and the crossover composition $y=0.50$ presents the

highest value of the magnetization [9]. Besides the composition, the magnetic properties might be affected by microstructural characteristics in a given sample.

The reported dielectric properties of sintered ferrites are giving often controversial results [6-10]. This can be explained as due to slightly different compositions, impurities as induced by various preparation routes. Important changes on the dielectric properties can also be driven by various types of microstructures in samples with the same composition, as it will be demonstrated in the present paper.

2. EXPERIMENTAL DETAILS

$\text{Ni}_{0.50}\text{Zn}_{0.50}\text{Fe}_2\text{O}_4$ powders were prepared by coprecipitation at room temperature of the stoichiometry amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution with a stoichiometry amount NaOH solution (molar ratio OH / NZF = 8) [11]. The resulting gel was washed several times with water, freeze-dried and calcined at $400^\circ\text{C}/1\text{h}$ to promote formation of the ferrite phase. After checking the phase purity of the calcined powders by X-ray diffraction analysis (XRD), they were manually milled in an agate mortar, then isostatically pressed at $2 \cdot 10^8$ Pa and sintered to obtain two types of ceramic microstructures at $1050^\circ\text{C}/2\text{h}$ and at $1150^\circ\text{C}/2\text{h}$, respectively. The phase and crystallographic microstructure of the ceramics were examined by Scanning Electronic Microscopy (SEM, Philips, Model 515) analysis. The impedance spectroscopy system composed by an impedance analyzer (Solartron, SI 1260, 0.5V excitation voltage) and an oven with digital temperature controller (temperature sensor Pt100) assisted by PC-based custom applications within the LabView program allowed the measurement of the complex impedance between the frequencies (10^{-3} - 10^6) Hz.

3. REVIEW OF IMPEDANCE SPECTROSCOPY METHOD

3.1 Principles of the Impedance Spectroscopy

Impedance Spectroscopy (IS) is an electric method used for investigating solid materials, as well as in applied electrochemistry, engineering and biophysics [3-5], for describing the electric properties of complex systems, polycrystalline materials, inhomogeneous systems and interfaces with electrodes. It may be used to investigate the dynamics of bounded and mobile charges in bulk and interfacial regions of any kind of solid or liquid materials with ionic, semiconductive, mixed electronic-ionic, dielectric, piezoelectric and ferroelectric character.

A few different types of electric stimuli are currently used in IS measurements:

- (i) Transient measurements, where a step function of voltage [$V(t)=V_0$ for $t>t_0$, $V(t)=0$ for $t<t_0$] may be applied to the system and the resulting time-varying current $i(t)$ measured.
- (ii) The second method is to apply a signal $n(t)$ composed of white noise (random signal) to the system and measure the resulting current. This approach offers the advantage of fast data collection because only one signal is applied to the interface for a short time. The disadvantage is the requiring of a true white noise and then the need to carry out a Fourier analysis.
- (iii) The third approach is to measure the impedance by applying a frequency-dependent signal (voltage or current) to the system and measure the phase shift and amplitude (or the real and imaginary parts of the impedance), of the resulting current at the given frequency using either analog circuits or fast Fourier transform (FFT). The advantage of this technique are the use of automatic instruments (commercial instruments interfaced to laboratory microcomputers able to measure automatically the impedance as a function of frequency in the range $10^{-3} - 10^6$ Hz) as well as the

fact that in this range it can be achieved a better signal-to-noise ratio than by the other methods.

In material science investigations, the method (iii) is mostly used. It determines the complex impedance in a wide frequency range and it is analyzed with models of equivalent circuits. The electrical heterogeneity regions of a polycrystalline systems (characterized by different permittivities and conductivities) generates multiple components in the impedance diagram, while electrically homogeneous regions characterized by a single relaxation time gives a single characteristic semicircle in the Cole-Cole diagram [4]. Every intrinsic property that can contribute to the material-electrode system impedance can be studied by IS techniques. The parameters that derived from these measurements are divided in two categories:

- (a) intrinsic properties of the investigated material (conductivity, permittivity, charge mobility, equilibrium concentration of charges, rate of generation-recombination in volume), and
- (b) properties determined by the interface material-electrode (rate adsorption-reaction, interface material-electrode capacitance, diffusion coefficient of the neutral species in the electrode). IS technique is used for solids as ionic and protonic conductors, electrolytes, ceramic materials with semiconductor or dielectric character, and also for studying emulsions, electroplating, thin-film technology, materials fabrication, corrosion phenomena, etc.

3.2 Elementary analysis of the impedance spectra

Impedance spectroscopy is particularity characterized by the measurements and analysis of the impedance-related functions $\bar{Z}$ (complex impedance), $\bar{Y} = \bar{Z}^{-1}$ (complex admittance), $\bar{M} = \bar{\epsilon}^{-1}$ (complex dielectric modulus) and $\bar{\epsilon}$ (complex permittivity) in the complex plane. The complex impedance $\bar{Z}$ is real only when we have purely resistive behaviour. The other derived quantities related to the impedance are generally called *immittances*. The determination of these parameters by means of IS allows to obtain important information about the physical system.

A detailed model of all the processes that might occur in an electrode-material system is rather complicated. One idea was to show that the experimental impedance data characteristic to the system $\bar{Z}_{sys}(\omega)$ may be approximated by the impedance $\bar{Z}_{eq}(\omega)$ of an equivalent circuit formed by ideal resistors, capacitors and inductances. In such a circuit the resistance describes the conductive path and a given resistor in the circuit might account for the bulk conductivity of the material and capacitance and inductance are associated with space charge polarization regions [12,13]. It should be pointed out that ordinary circuit elements are always considered as lumped-constant quantities which involve ideal properties.

The physical interpretation of the distributed elements in an equivalent system is related to the finite spatial extension of any real system. One is associated with non-local processes which can occur even in a completely homogeneous material, such as diffusion of charge mobility. The other comes from microscopic material properties that are distributed. The macroscopic impedance which depends, for example, on the reaction rate distribution across such an interface is measured as an average over the entire electrode. It is assumed that material properties are continuously distributed over a given range from minimum to maximum values.

The characterization of a given material by IS involves the following steps:

- (i) determination of the complex impedance in a large frequency range;
- (ii) use a realistic model of equivalent circuits,
- (iii) fitting the experimental data in order to determinate material constant (permittivity, conductivity).

It is important to know that the equivalent circuits are not unique and more possible circuits can be designed in order to describe by the same complex diagram.

Fig. 1 (a) SEM image of a polycrystalline ceramic of BaSrTiO₃, (b) model for microstructure, (c) „brick layer” model.

Each material-electrode system can be characterized by a geometrical capacitance C and a parallel volume resistance R that determines the time constant of the system: $\tau = RC$ and is represented by a unique semicircle in the complex impedance plane. In a polycrystalline ceramic material, the material-electrode interfaces are characterized by different circuit elements. If their time constants have distinct values, more deconvoluted semicircles appear in the complex plane. Such representation is common to polycrystalline ceramics, where the permittivity and conductivity are different in bulk and grain boundaries. Such systems are theoretically described by “brick layer models”, in which the microstructure is treated like an array of cubic grains, separated by flat grain boundaries (Fig. 1) and the electrical behaviour of the sample is described by effective field theories [14].

The analysis of the experimental data that yield a full semicircular arc, such as that in Fig.2, can provide the values for the R and C circuit parameters. However, experimental data are rarely found to follow a full semicircle with its center on the real axis of the complex plane. A few typical perturbations from the ideal behaviour are:

- The arc does not pass through the origin because the circuit contains also a series resistance $R_\infty > 0$;
- The center of circle is displaced below the real axis because of the distributed elements in the material-electrode system that gives different relaxation times.

Fig.2 Impedance plane plot for a depressed circular arc showing definitions of quantities used in its analysis.

The $-Z''$ value reaches its maximum y_0 when $\omega = \omega_m = \tau_R^{-1}$ and $\omega\tau_R = 1$. At this point the half-width of the arc on the real axis is: $Z' - R_\infty = x_0 \equiv R_R/2$. From the experimental data, the complex plane plot and the estimate values of x_0 , y_0 and ω_m , one can estimate R_∞ , R_0 , R_R , τ_R . In order to obtain the phase angle θ , the position of the center is firstly determined. The easiest graphical method is to draw on the complex plane $\bar{Z}$ several lines perpendicular to the semicircle. If there is an overlapping of several semicircle arcs at low frequency, then the method can be used only for $\omega < \omega_m$. In this case all the parameters must be estimated from the left part of the semicircle, for $\omega > \omega_m$. We find that the phase angle is: $\theta = \pi/2 - x$ and no depression of the arc and a single time constant Debye response with $A_0 = C_R$ is characteristic for the investigated system. If the system has more than one component in the complex diagram, then C_R is distributed on the circuit elements.

In the case of an electroded polycrystalline ceramic, a more complex diagram is appropriate, as proposed in the Fig. 3, in which different groups of RC-circuits describe: (i) the ceramic grain (R_G , C_G), (ii) the ceramic grain boundaries (R_{CG} , C_{CG}), (iii) the electrode-ceramic

interfaces (R_I , C_I). Dependent on their local electrical properties, these contributions are often convoluted and in such a case their separation is very difficult.

Fig. 3 Model adopted for a real electroded ceramic containing three distinct contributions: ceramic grain (R_G , C_G), ceramic grain boundaries (R_{GB} , C_{GB}) and electrode-ceramic interfaces (R_I , C_I).

4. RESULTS AND DISCUSSIONS

4. 1. Testing the IS method for a known (RC) circuit

In order to test the method, it was firstly realized a series-parallel (RC) circuit, known from the literature as *the circuit of Randels* [15]. This circuit was proposed to simulate the complex impedance response of a semiconductive or a solid ionic ceramic system and it has the following elements: $R_\infty=2298 \, \Omega$, $C_1=10.6 \, \text{nF}$, $C_2=102.32 \, \text{nF}$, $R_1=2421 \, \Omega$, and $R_2=2056 \, \Omega$ (Fig. 4 a). Using this model circuit, an RC series-parallel circuit was realized, as shown in the Fig. 4 b. The impedance characteristics were measured in a large

frequency range from 20 Hz to 2 MHz and the resulted data give an Argand plot composed of two arcs in the complex plane (Fig. 5).

Fig. 4 The circuit proposed by Randels to test the IS method [15]: (a) scheme, (b) the circuit.

From the experimental impedance plot, the values of the constitutive RC elements were recovered: from the intersection of the plot with real axis, the resistances were determined with 0.05% accuracy: $R_{\infty}=2300 \Omega$, $R_1=2421 \Omega$, $R_2=2056 \Omega$. From the maximum of the imaginary parts of impedance and relaxation times the capacitances were also determined: $C_1=10 \text{ nF}$, $C_2=102.5 \text{ nF}$, matching very well with the employed circuit elements. It results that the IS instrument and method is able to detect multiple components in the impedance plot and might be further applied for investigating complex solid materials.

Fig. 5 Argand diagram for the Randels [15] series-parallel circuit.

4.2. IS investigation of the (Ni, Zn) ferrite

After validation the IS technique with a given circuit, we applied the method for analyzing the room temperature impedance characteristics of two samples of NZF with the same compositions, but processed from the same starting powders in two different conditions in order to develop different microstructural characteristics. The ceramic ferrites sintered at the two temperatures show some important microstructural differences, as visible in the Fig. 6 (a, b). By increasing the sintering temperature, a higher density and a bimodal grain distribution, with big blocks of above 50 μm surrounded by smaller ones (Fig. 6 b) resulted. It is clear that the two samples have completely different microstructures with various types of grain boundaries and boundary conditions and these might result in visible effects on their impedance responses, in spite of their similar compositions.

Fig. 6 SEM micrographs of the $\text{Ni}_{0.50}\text{Zn}_{0.50}\text{Fe}_2\text{O}_4$ ceramic sintered in air at: (a) 1050°C/1h, (b) 1150°C/1h (bar: 10 μm).

Fig. 7 a, b show the room temperature complex impedance characteristics for the NZF ceramics sintered in air at the two temperatures: $T_s=1050^\circ\text{C}$ and $T_s=1150^\circ\text{C}$, respectively. A single-relaxation Debye process for the ferrite sintered at lower temperature (Fig. 7, a) and two well-resolved Debye semicircles of the impedance plot

for the ferrite ceramic sintered at higher temperature (Fig. 7, b) are obtained. The dielectric properties of the ferrite ceramics are mainly attributed at low frequencies to the interfacial polarization and to low-frequency dispersion and at high frequencies to the orientational polarization [16,17]. These properties result in the dielectric loss which composed of a Debye-like loss peak at high frequency and strong low-frequency dispersion below 1 Hz.

Fig. 7 Complex impedance plot at room temperature for NZF ceramic sintered at:
(a) $T_s=1050^\circ\text{C}$, (b) $T_s=1150^\circ\text{C}$.

In the present case, the bi-modal distribution observed on the SEM photos in the Fig. 6, b seems to be responsible for the two-components on the impedance plot reported in the Fig. 7, b. These results are interpreted on the basis of a distribution of the time-constant of the impedance response, associated with the grain size distribution. A decrease in resistivity was also observed as the grain size increased, which can be explained by an increase in the mean free path of electrons.

The frequency-dependence of the imaginary part of the impedance (Fig. 8) allows the determination of the characteristic time constants: $\tau \sim 50$ ms, typical for both ceramics

and a faster process with relaxation time of $\tau \sim 0.45 \mu\text{s}$, only typical to the ceramic sintered at $T_s = 1150^\circ\text{C}$, besides the slow one. This result is related to the distribution of time-constant of the impedance response, associated with the grain size distribution of the ferrite sample.

Fig. 8 Frequency-dependence of the imaginary part of the impedance for NZF ceramics sintered at two different temperatures.

The origin of the dielectric and transport properties in ferrites is still a matter of debate. As in other solid oxides containing ions with fluctuating oxidation states, e.g. iron, transitions $\text{Fe}^{2+} \Leftrightarrow \text{Fe}^{3+} + e^-$ take place in the crystallographically equivalent sites without causing changes in the energy state of the crystal [18-20]. As a consequence, the collective contribution of the hopping conductivity both of n-type (electron exchange) between Fe^{2+} and Fe^{3+} states and p-type hopping (hole exchange) between the Ni^{3+} and Ni^{2+} states are responsible for the dielectric and conductive properties of the $(\text{Ni}_{0.50}\text{Zn}_{0.50})\text{Fe}_2\text{O}_4$ ceramics [19,20]. Moreover, in a real sample, different values of the $\text{Fe}^{2+} / \text{Fe}^{3+}$ ratio and related variations of the local oxygen stoichiometry are expected (the presence of Fe^{3+} being associated to oxygen vacancies). The contribution of oxygen vacancy to the dielectric relaxation can be 3-fold: (a) It can hop in the lattice, leading to the associated dipolar moment reorientation; (b) It is creating conducting electrons through the ionizations: $V_o \Leftrightarrow V_o^\bullet + e'$, $V_o^\bullet \Leftrightarrow V_o^{\bullet\bullet} + e'$; the conducting electrons in their

turn can hop from one localized state to another one in the lattice, equivalent to the reorientation of effective electric dipoles [21]; (c) Different levels of oxygen deficiency in different spatial regions within the sample can lead to electric heterogeneity even in single phase materials, leading to interfacial polarization (Maxwell-Wagner or space charge relaxation mechanism) [22]. The grain boundary in polycrystalline ceramics and various defect structures (such as twin boundaries, dislocations) in single crystals and interphases in composites play an important role in this mechanism. All the mentioned mechanisms are thermally activated at temperatures above 200°C with activation energies $E_a < 0.3 \text{ eV}$ in pure $(\text{Ni}_{0.50}\text{Zn}_{0.50})\text{Fe}_2\text{O}_4$ ceramics [23].

Due to the complexity of the present polycrystalline ferrite system, the exact attribution of the observed components to a specific relaxation mechanism is a very difficult task at this stage. Further investigations of the ferrite ceramics by comparison with single crystal's characteristics at various temperatures will be performed in order to determine activation energies and the associated responsible mechanisms for the observed properties. Here it was only demonstrated the important role of the microstructural differences of the $(\text{Ni}_{0.50}\text{Zn}_{0.50})\text{Fe}_2\text{O}_4$ ceramics on their impedance response.

5. CONCLUSIONS

In this paper, the general principles of the Impedance Spectroscopy techniques were reviewed. The method was firstly tested for a known circuit and the complex impedance response was used to recover the RC circuit elements. Then the method was applied to characterize polycrystalline ferrite ceramics with composition $(\text{Ni}_{0.50}\text{Zn}_{0.50})\text{Fe}_2\text{O}_4$. The ceramics have been sintered at different temperatures in order to result different microstructural characteristics. At ambient temperature, the ceramic sintered at lower temperature shows a single component in the Argand diagram, while the sample sintered at higher temperature presents two distinct well-resolved components in the complex impedance diagram. The obtained electrical inhomogeneity has been interpreted as being

related to the higher degree of oxygen-deficiency and to the bi-modal grain size distribution for the samples sintered at higher temperature.

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References:

- [1] A. Jonscher, *Dielectric relaxation in solids*, Chelsea Dielectric Press, London (1983)
- [2] L. Mitoseriu, V. Tura, *Fizica dielectricilor*, Ed. Univ. “Al.I. Cuza” Iasi (1999)
- [3] J.T. Irvine, D.C. Sinclair, A.R. West, *Electroceramics: characterisation by impedance spectroscopy*, Adv. Mater. 2, 1990, pp. 132–138
- [4] E. Barsoukov et al., *Impedance Spectroscopy Theory, Experiment & Applications*, Wiley Interscience (2005)
- [5] A.D. Franklin, H.J. deBruin, *Fourier Analysis of Impedance Spectra of Electroded Solid Electrolytes*, Phys. Stat. Sol. (a) 75, 1983, pp. 647-656
- [6] P.I. Slick, in *Ferromagnetic Materials*, ed. by E.P. Wohlfarth (North-Holland, Amsterdam, The Netherlands, 1980), Vol. 2, pp. 189
- [7] Z. Yue, J. Zhou, L. Li, H. Zhang and Z. Gui, *Synthesis of nanocrystalline NiCuZn ferrite powders by sol–gel auto-combustion method*, J. Magn. Magn. Mater., 208, 2000, pp. 55-60
- [8] C. Caizer, M. Stefanescu, *Magnetic characterization of nanocrystalline Ni-Zn ferrite powder prepared by the glyoxylate precursor method*, J. Phys. D: Appl. Phys. 35, 2002, pp. 3035-3040
- [9] N. Ponpandian, A. Narayanasamy, C.N. Chinnasamy, N. Sivakumar, J.-M. Greneche, K. Chattopadhyay, K. Shinoda, B. Jeyadevan, and K. Tohji, *Néel temperature enhancement in nanostructured nickel zinc ferrite*, Appl. Phys. Lett. 86, 2005, 192510
- [10] R. Peelamedu, C. Grimes, D. Agrawal, R. Roy and P. Yadoji, *Ultralow dielectric constant Nickel Zinc ferrites using microwave sintering*, J. Mater. Res. 18, 2003, pp. 2292-2295

- [11] A. Testino, L. Mitoseriu, V. Buscaglia, M.T. Buscaglia, I. Pallecchi, A.S. Albuquerque, V. Calzona, D. Marre, A.S. Siri, P. Nanni, Preparation of multiferroic composites of BaTiO₃–Ni_{0.5}Zn_{0.5}Fe₂O₄ ceramics, *J. Eur. Ceram. Soc.* 26, 2006, pp. 3031-3036
- [12] K.S. Cole, R.H. Cole, *Dispersion & Absorption in Dielectrics. I. Alternating - Current Characteristics*, *J.Chem. Phys.* 9, 341 (1941)
- [13] J. Maier, *On the Conductivity of Polycrystalline Materials*, *Ber. Bunsenges Phys. Chem.* 90, 26 (1986)
- [14] N.J. Kidner, N.H. Perry, T.O. Mason, E. Garboczi, *The Brick Layer Model Revisited: Introducing the Nano-Grain Composite Model*, *J. Am. Ceram. Soc.*, 91, 1733 (2008)
- [15] J.R. Macdonald, J. Schoonman, A. P. Lehen, *Three dimensional perspective plotting and fitting of immittance data*, *Solid State Ionics* 5, 1981, pp. 137–140
- [16] C.M. Fu, C.Y. Hsu, Y.C. Chao, D.S. Kim, N. Matsushita, M. Abe, *The electric and dielectric properties of the ZnNi-ferrite plated NiFe microspheres synthesized from aqueous solution*, *IEEE Trans. Magn.* 39, 2003, PP. 3136-3138
- [17] Q. Chen, P. Du, W. Huang, L. Jin, W. Weng and G. Han, *Ferrite with extraordinary electric and dielectric properties prepared from self-combustion technique*, *Appl. Phys. Lett.* 90, 2007, 132907
- [18] A. Molak, M. Paluch, S. Pawlus, J. Klimontko, Z. Ujma and I. Gruszka, *Electric modulus approach to the analysis of electric relaxation in highly conducting (Na_{0.75}Bi_{0.25})(Mn_{0.25}Nb_{0.75})O₃ ceramics*, *J. Phys. D: Appl. Phys.* 38, 2005, pp. 1450-1460
- [19] A.M. Abdeen, *Dielectric behaviour in Ni–Zn ferrites*, *J. Magn. Mater.* 192, 1999, pp. 121-129
- [20] B.P. Rao and K.H. Rao, *Direct current resistivity studies of various polycrystalline Ni–Zn–Sc ferrites*, *J. Appl. Phys.* 80, 1996, 6804
- [21] O. Bidault, M. Maglione, M. Actis, M. Kchikech, B. Salce, *Polaronic relaxation in perovskites*, *Phys. Rev. B* 52, 1995, pp. 4191-4197
- [22] J.V. Mantese, A.L. Micheli, D.F. Dungan, *Applicability of effective medium theory to ferroelectric/ferrimagnetic composites with composition and frequency-dependent complex permittivities and permeabilities*, *J. Appl. Phys.* 79, 1996, 1655

[23] B.P. Rao and K.H. Rao, *Direct current resistivity studies of various polycrystalline Ni-Zn-Sc ferrites*, J. Appl. Phys. 80, 1996, 6804.