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Dielectric Properties of Hydrothermal Nickel-Zinc Ferrites

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Abstract. — NiZn ferrites were hydrothermally prepared and sintered at different experimental conditions, leading to materials of composition Ni$_{0.34}$Zn$_{0.60}$Fe$_{2.06}$O$_4$. An investigation of the dielectric properties over a wide frequency range showed the semiconductor character of the ferrites and the presence of a masked relaxation, revealed after a mathematical treatment. The relaxation was modeled using a Cole-Cole model and the parameters correlated with the microstructural evolution of the ferrites during the sintering. The contributions of hopping electrons and space charges to the total conductivity have been discussed.

Résumé. — La méthode hydrothermale a été utilisée pour préparer des poudres de NiZn. Ces matériaux ont été synthétisés sous différentes conditions expérimentales. Après frittage, la composition est Ni$_{0.34}$Zn$_{0.60}$Fe$_{2.06}$O$_4$. L'investigation des propriétés diélectriques, sur un large intervalle de fréquence, a démontré le caractère semi-conducteur des ferrites et l'existence d'une relaxation masquée, mise en évidence après un traitement mathématique. Cette relaxation a été traitée par un modèle de type Cole-Cole et les paramètres corrélés à l'évolution microstructurale des ferrites, pendant le processus de frittage. Les contributions à la conductivité complexe dues aux électrons ("hopping") et aux charges d'espace ont été discutées.

1. Introduction

Ferrites are ferrimagnetic materials with good dielectric properties and a large number of technological applications: antenna rods, inductors, magnetic cores, filter components, etc. Among these materials, some soft ferrites of the type NiZn, MnZn, CoZn, CuZn with very high dielectric constants (10$^5$) at low frequencies are particularly useful in designing electronic devices [1,2]. Several investigators have studied the frequency dependence of the dielectric response of these ferrites, and the results showed different behaviors varying with composition and processing parameters, suggesting several mechanisms and theoretical interpretations [1,3,4]. In spite of this, a few papers presented a thorough investigation of the dielectric relaxation [3,5] and, at our knowledge, no study of the dielectric behavior of ferrites obtained by hydrothermal process has been reported in the literature. This non-conventional method produces mono-sized powders in the nanometric range, which leads to ceramic bodies after sintering with

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suitable characteristics for applications in the electronic industry. The production of nanomaterials with appropriate compositions, microstructures and, consequently, desirable dielectric properties (high dielectric constants) after sintering is the goal in magnetic ceramics research today.

The dielectric response of the soft ferrites depends on many factors, such as the preparation method and the sintering conditions [6, 7]. An understanding of the mechanisms involved in the changes caused by the hydrothermal synthesis in the starting powders and the different sintering conditions on the resulting ceramic bodies provides information which permits a reliable formulation for specific applications. In the present work we have prepared ultrafine NiZn ferrite particles by hydrothermal process and sintered these powders without any sintering aids. A detailed investigation of the frequency dependence of the dielectric properties of hydrothermal NiZn ferrites sintered at various temperatures and times was carried out, in view to contribute to the understanding of the polarization mechanisms, electrical losses and grain structures in these materials. The variations in dielectric properties were analyzed by complex impedance technique and correlated to powder characteristics and ceramic density, porosity, and microstructure after sintering.

2. Experimental Procedure

A detailed description of the hydrothermal synthesis of NiZn ferrites has been given in a previous paper [8]. In the sintering process, polyvinylalcohol (2.5% weight) has been dissolved and mixed with deionized water in the ferrite powder and the samples have been compacted at 196 MPa. The sintering was carried out in air, in a Lindberg furnace (±1 °C), with heating and cooling constant rates of 100 °C/min, at temperatures between 1100 and 1400 °C and times varying from 5 to 240 minutes. The ceramic bodies were characterized by chemical analysis (wet-route), X-ray diffraction (Philips), helium picometry (Micromeritics), and scanning electron microscopy (Jeol SP733 and ISM35c). The samples with dimensions of 9 mm of diameter and 1.8 mm of thickness were submitted to the dielectric investigations. The electrodes were applied by gold evaporation on the circular faces of the samples. The impedance measurements were performed in the frequency range 5 Hz–13 MHz, at room temperature, using a Hewlett-Packard Model 4192A equipment.

3. Results and Discussion

3.1. HYDROTHERMAL SYNTHESIS AND SINTERING OF NiZn FERRITES. — After hydrothermal synthesis, the presence of NiZn ferrite, crystalline, single-phase and impurity free particles, with sizes smaller than 50 nm, was confirmed. The precipitation of NiZn ferrite occurred according to the reaction:

\[
2.09\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + 0.53\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + 0.38\text{NiSO}_4 \cdot 9\text{H}_2\text{O} + 6\text{NaOH} + 0.5\text{O}_2 \Rightarrow \\
\Rightarrow \text{Ni}_{0.38}\text{Zn}_{0.62}\text{Fe}_{2.09}\text{O}_4 + 3\text{Na}_2\text{SO}_4 + 21.72\text{H}_2\text{O}
\]

The X-ray diffraction of the sintered bodies showed only the presence of a spinel type phase. The results of chemical analysis indicated a considerable reduction in the ferrous content: 0.94%FeO compared with 11.07%FeO in the hydrothermally prepared powder. The stoichiometry after sintering was Ni_{0.34}Zn_{0.66}Fe_{2.06}O_4. This result is already expected, since during sintering and subsequent cooling the ferrous ion is oxidized, mainly at grain boundaries [9].

Let us now consider the Figure 1, which shows the relative density and the porosity obtained from the Bruch’s relation [10], as a function of the sintering conditions. An increase in the final density with time and temperature is observed; the converse holding for the porosity. These
The results are confirmed by scanning electron microscopy, as it can be seen in Figure 2, where micrographs are presented for different samples sintered at temperatures ranging from 1100 (top) to 1400 °C (bottom), during 5 (left) and 240 (right) minutes. The temperature and time effects on microstructures of NiZn ferrites are rather simple. It is important to stand out the little effect of temperature on grain growth of sintered ferrites for 5 minutes; however, it is meaningful the attained densification for 1400 °C. On the other hand, a considerable increase in the grain size with temperature for 240 minutes of sintering was detected. The time effect is clear when we compare the two sequences (Fig. 2): the increasing of the sintering time only influences significantly the grain growth rate for temperatures higher than 1200 °C. We observe also a porosity transition from intergranular to intragranular above 1300 °C, characterizing the crossing from an intermediate stage to a final stage of the sintering process.

3.2. Dielectric Investigations. — According to Largeteau et al. [11], many studies of NiZn ferrites show that the electrical resistivity ($\rho$) varies abruptly with composition. Cation-deficient ferrites have resistivities of c.a. $10^4 \Omega \text{ cm}$, while cation-rich ones show resistivities of c.a. $10^2 \Omega \text{ cm}$. The latest group of materials has received increasingly scientific and technological attentions, due to their higher grain conductivity and, consequently, higher permittivity values ($\varepsilon'$) in the frequency range $10^2 - 10^6$ Hz.

The $\varepsilon'$, $\varepsilon''$ and $\rho'$ variations presented by our samples, as a function of the frequency, are exemplified in Figures 3 and 4, which show the behavior of two samples sintered at the limit temperatures and times (1100 °C for 5 min and 1400 °C for 240 min). We observe permittivity values ($\varepsilon'$) between $10^5$ and $10^6$ in the frequency range $10^2 - 10^4$ Hz, and a decrease tendency with frequency for all samples of sintered NiZn ferrites. The imaginary part of the dielectric constant ($\varepsilon''$) and the real resistivity ($\rho'$) decrease also with frequency; however, $\rho'$ remains constant in the frequency range $10^2 - 10^4$ Hz for the most part of the studied samples. This result can be explained and correlated to the presence of ferrous ions, which lead to the appearance of a high d.c. conductivity, responsible for the observed behavior.

According to Irvine et al. [3], ferrites with $x > 2$ exhibit high conductivity due to the presence of the ferrous ions themselves, and the conduction mechanism would be electron hopping between Fe$^{+2}$ and Fe$^{+3}$ cations. Non-stoichiometric and cation-rich NiZn ferrites are
Fig. 2. — NiZn ferrite microstructural evolution with temperature (from the top to the bottom: 1100, 1200, 1300 and 1400 °C), for sintering times of 5 minutes (left) and 240 minutes (right).
Fig. 3. — Frequency dependence of $\varepsilon'$ and $\varepsilon''$ of the ferrites sintered at 1100 °C for 5 minutes and 1400 °C for 240 minutes. Insert: $\varepsilon''$ as a function of $\varepsilon'$ for the same samples.

Fig. 4. — Frequency dependence of the real resistivity of the ferrites sintered at 1100 °C for 5 minutes and 1400 °C for 240 minutes.

n-type semiconductors [1, 3, 5, 11-15]. The results obtained in the present work are consistent with the Irvine observations and with the theoretical assumptions by Ravinder [13], mainly for the high dielectric constant values found, certifying their elevated conductivity (the presence of ferrous ions was proved by chemical analysis, as indicated before).
The study of the dielectric properties of ferrites like Ni$_y$Zn$_{3-y-x}$Fe$_x$O$_4$ with $x > 2$, as in the present case, is not an obvious task [11]. The relatively high conductivity of the material makes the polarization weak, since the space charges have no difficulties in “flow” through the conducting grains. Thus the relaxation is “partially masked” (see the insert of Fig. 3). Largeteau et al. [11] discussed the models developed in the 80’s, which allow to reveal the relaxation through the elimination of the static or low frequency conductivity. This procedure is based on the additivity of different contributions to the total permittivity. The low frequency portion of the Argand diagram ($\varepsilon'' = f(\varepsilon')$) corresponds to the static conductivity contribution, whose locus in a log-log plot is a straight line [11]. According to the above model, this straight line must be subtracted from the measured permittivity at each frequency $\omega$. The resulting corrected values for $\varepsilon_{\text{relax}}'' = f(\varepsilon_{\text{relax}}')$ reveal the relaxation. The curves $\varepsilon_{\text{relax}}''$ versus $\varepsilon_{\text{relax}}'$ (henceforth $\varepsilon''$ and $\varepsilon'$) are displayed in Figures 5a and 5b, for a representative set of samples. The similarities of these results with those of Largeteau et al. [12], suggest that the observed relaxation would be due to space charge polarization.

A succession of models exists in the literature to study dielectric relaxation phenomena, outstanding the theoretical discussions by Cole-Cole [16], Cole-Davidson [17], Koops [18], Jankowski [19], Largeteau [12] and Jonscher [20]. For our results of Figure 5, the best fit between theoretical and experimental curves was found with the classical Cole-Cole model. In this case, the dielectric permittivity is given by $\varepsilon^*(\omega) - \varepsilon_\infty = (\varepsilon_s - \varepsilon_\infty) / [1 + (i\omega\tau_0)^{1-\alpha}]$, where $\varepsilon_\infty$ is the permittivity at very high frequency, $\varepsilon_s$ is the static permittivity, $\tau_0$ is the time constant and $\alpha$ is the distribution parameter of relaxation times. Thus, the real and imaginary parts ($\varepsilon'$ and $\varepsilon''$) of the dielectric constant are written as:

$$
\varepsilon' - \varepsilon_\infty = \frac{((\varepsilon_s - \varepsilon_\infty)|1 + (\omega\tau_0)^{1-\alpha}\sin\left(\frac{\alpha\pi}{2}\right)|}{1 + 2(\omega\tau_0)^{1-\alpha}\sin\left(\frac{\alpha\pi}{2}\right) + (\omega\tau_0)^2(1-\alpha)}
$$

and

$$
\varepsilon'' = \frac{((\varepsilon_s - \varepsilon_\infty)(\omega\tau_0)^{1-\alpha}\cos\left(\frac{\alpha\pi}{2}\right))}{1 + 2(\omega\tau_0)^{1-\alpha}\sin\left(\frac{\alpha\pi}{2}\right) + (\omega\tau_0)^2(1-\alpha)}.
$$

The Cole-Cole diagrams of the sintered NiZn ferrites are presented as full-lines in Figures 5a and 5b. The parameters $\varepsilon'_{\infty}$, $\varepsilon''_{\infty}$, $\alpha$ and $\tau_0$ characterizing the relaxation have been obtained for all samples.

The complex impedance spectroscopy was employed in this work in order to clarify the grain and grain boundaries impedance contributions. The results presented above show that our goal has been successfully achieved. We verify that the grains exhibit high conductivity (since we observe only one arc in the Argand diagram) and that the grain boundaries are responsible for the observed relaxation. The $\varepsilon'_{\infty}$ values show no variations as a function of heating treatment; however, $\varepsilon''_{\infty}$ values have a tendency to decrease with sintering time and to increase with sintering temperature, as it can be seen in Figure 5. This behavior represents the different microstructures found, or best, the changes in porosity and grain sizes. In the samples sintered at 1100 °C, the grain growth process did not occurred, but the densification process is remarkable. This leads to conclude that the reduction of porosity level acts in the reduction of permittivity $\varepsilon''_{\infty}$. The principal effect of temperature on NiZn ferrite samples is the increasing of the grain size. Therefore, the static permittivity increase with temperature is related to the grain growth process rather than densification.
The relaxation frequency ($\tau_0^{-1}$) is another important variable to consider. This parameter, as a function of sintering temperature, shows a minimum for 1200 °C, for all sintering times studied (the highest values of $\tau_0^{-1}$ occurred in smallest sintering temperatures). These results are exemplified in Figure 6, for the limit times investigated. It is interesting to note the discrepancies between the behavior expected by the space charge model, discussed by Largeteau et al. [12], and that observed here. According to Largeteau et al. [12], the relaxation frequency decreases continuously with the densification and the grain growth processes, i.e. with reduction of porosity level. Really, these processes decrease the relaxation frequency, since the porosity acts like an “impregnant agent”, insulating the grains each other. In the micrographs presented in Figure 2, we can observe (in the left side) the process of densification without grain growth. Above 1300 °C, the transition of porosity (intergranular to intragranular) and the pore intragrain growth are clearly verified. Similar observations can be drawn for samples sintered for 240 minutes (right side of this figure), although the grain growth process was more
pronounced. The conclusion for the observed behavior is that the transition of porosity play a major role than the processes of densification and grain growth on the relaxation phenomenon. Initially, the densification and grain growth processes promote the decreasing of the relaxation frequency (Fig. 6). Subsequently, the intragranular pores and, finally, the pore coarsening act like an insulating material, creating new barriers for the space charge polarization and increasing the relaxation frequency.

In a previous work, Ahmed et al. [6] show interesting conclusions about NiAl ferrites. The dielectric constant rises with frequency until a maximum, then decreases continuously. This peak in $\varepsilon'$ was related to aluminum content, occurring at lower frequencies with increasing aluminum quantities. This behavior was explained on the basis of the similarities between the mechanism of the polarization and that of the conduction in ferrites. When the system presents electronic exchange $\text{Fe}^{+2} \leftrightarrow \text{Fe}^{+3}$, corresponding to a "normal dielectric behavior", the dielectric constant decreases with increasing frequency. However, it can occur the appearance of $p$-carriers in Ni-ferrites: $\text{Ni}^{+2} \leftrightarrow \text{Ni}^{+3}$. According to the Rezlescu model [21], local displacement of $p$-carriers takes part in the polarization in an opposite direction to that of the external field and can promote the so-called "abnormal dielectric behavior", resulting in a collective contribution of two types of carriers to the polarization. The contribution of $p$-carriers is lower and with an opposite sign to that of the electronic exchange $\text{Fe}^{+2} \leftrightarrow \text{Fe}^{+3}$. In addition, since the mobility of $p$-carriers is lower than that of n-type, their contribution to polarization will decrease more rapidly at lower frequencies. The samples of sintered NiZn ferrites analyzed by complex impedance technique in this work do not show any abnormal dielectric behavior, prove that there is no contribution of $p$-carriers to polarization (the ions Ni$^{+3}$ were not found in our samples).

### 4. Conclusions

The results present here show the ability to produce ferrites with good dielectric properties from adequate sintering of hydrothermally prepared NiZn ferrite powders. The sintering temperature and time effects on microstructure were make clear through micrographs, which shown the densification process with and without grain growth, as well as the porosity transition (inter-
intra-grains). The complex impedance results reveal a material with high conductivity, mainly due to the grains. The use of a Cole-Cole model, after rigorous mathematical treatment to reveal the relaxation, was applied and satisfactorily fitted to our results. The observed variations in the adjustment parameters were consequence of the microstructural changes after different sintering conditions. The static permittivity increase is related to the grain growth process rather than densification. The presence of ferrous ions in sintered samples and the observance of no peaks in dielectric constant in the low frequency region indicate that the conduction mechanism is the electron hopping, and that there is no contribution of p-carriers to this phenomenon. The transition of porosity from intergranular to intragranular play a major role than the processes of densification and grain growth on the relaxation frequency. The intragrain pores create additional barriers for the space charge polarization and increase the relaxation frequency.

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