Grain size effect on the permittivity of La$_{1.5}$Sr$_{0.5}$NiO$_4$ nanoparticles

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Abstract. Using the annealing at different temperatures the La$_{1.5}$Sr$_{0.5}$NiO$_4$ ceramic samples with different mean grain size were manufactured. Mean grain size ($<D>$) of the samples was evaluated by Warren-Averbach method and their SEM images. The obtained results of both methods are almost the same, changing from 16.2 to 95 nm in dependence on the annealing temperature. The frequency dependence of dielectric constant in the frequency range of (1-13 MHz) was recorded for all samples. The real ($\varepsilon'$) and the imaginary parts ($\varepsilon''$) of the permittivity of La$_{1.5}$Sr$_{0.5}$NiO$_4$ samples abnormally depend on the frequency, exhibiting a dielectric resonance around 500 kHz. R-L-C in series equivalent-circuit fitted well for the obtained result. It was supposed that there exists magnetic contribution in material that suggests the material is a multiferroic one. Dependence of the ($\varepsilon'$) on the mean grain size supposed that the colossal dielectric property is an intrinsic behaviour of La$_{1.5}$Sr$_{0.5}$NiO$_4$ material.

Keywords: Colossal permittivity, multiferroics, dielectric resonance.

1. Introduction
The high permittivity material always is a current interest, because of its potential applications. Various materials of high permittivity have been reported such as the BaTiO$_3$ doped with La that has dielectric constant of $10^4$ [1], CaCu$_3$Ti$_4$O$_{12}$ with the permittivity of about $8\times10^4$ at temperature of 250 K and frequency up to 1 MHz [2]. Kim and co-workers have improved dielectric constant to $10^5$ for Pb$_{1-3x}La_x$TiO$_3$, Pb$_{1-x}La_x$Ti$_{1-x/4}$O$_3$ [3]. There was an interested recent result of Biskup et al. [4] that reported results of study on Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ perovskite, which informed a high dielectric constant of about $10^5$- $10^6$. In the last years, La$_2$NiO$_4$ compound has attracted much attention not only because of its potential applications in the solid oxide fuel cell cathodes [5], but also due to its very interesting structural, unusual magnetic, conducting properties, especially its permittivity. This material system is of the low dimension structure type which exhibits Charge-Density-Wave (CDW) property. Its permittivity is higher than $10^5$ at room temperature in a wide frequency range from 1 KHz up to 1 MHz [6]. So it has been called the colossal dielectric material. The interesting dielectric properties of this material have attracted researchers in both fundamental scientific and technological studies. Colossal dielectric constant behaviour is one of the most technically decisive factors for many applications of the high dielectric constant materials, such as random access memories based on capacitive elements (DRAM). The dependence of dielectric constant on frequency and temperature of La$_{1.5}$Sr$_{0.5}$NiO$_4$ material is very similar to that observed in the canonical CDW [7-9], as well as in the
left handed material (LHD) made by a composite of both ferromagnetic and ferroelectric constituents [10]. In this paper we present an observation of the negative permittivity of the material at the frequency range around the resonance frequency. The obtained experimental results are fitted well by an R-L-C circuit, R, L and C are equivalent conductance, inductance and capacitance.

2. Experiment
La$_2$O$_3$, SrO and NiO with purity of 99.9% were used as starting materials. The starting materials were thoroughly mixed and milled for 6 hours by using the reactive mechanical milling technique on D8000-Spex [11]. The milled powder was pressed into 7 pellets with diameter of 13 mm and height of 1.5 mm, heated in air for 1 hour at 7 different temperatures changing from 700 to 1000°C with the temperature step of 50°C, noted as S1, S2, S3, S4, S5, S6, and S7. Phase structure of all the samples was checked by powder X-ray diffraction by means of a SIEMENS D5000 diffractometer equipped with Cu-K$_\alpha$ radiation ($\lambda$ = 1.5406 Å) at room temperature. By using Warren-Averbach method combined with Win-Crysize program the crystalline grain size was estimated for all samples. Grain size of all the samples was estimated also from their FESEM images done by using the S-4800 FESEM microscopy. Dielectric constant at room temperature of all the samples was estimated via the capacitance and conductance of the disk capacitor in configuration of Ag/La$_{1.5}$Sr$_{0.5}$NiO$_4$/Ag that were measured in a frequency range of (1 KHz-13 MHz) by using a HP 4192A impedance analyzer.

3. Results and Discussion
Figure 1 shows X-ray powder diffraction patterns of the samples recorded at room temperature. Comparing the PDF (Powder Diffraction File) card with number 32-1241 [12] identified that the prepared samples are of La$_{1.5}$Sr$_{0.5}$NiO$_4$ single phase, belong to the F$_4$K$_2$Ni-type, tetragonal structure with space group of I4/mmm (no. 139). La$_{1.5}$Sr$_{0.5}$NiO$_4$ displays a quasi two-dimension structure in which the perovskite blocks are separated by the presence of rock-salt type (La-Sr/O) layers along the c axis. The full width at half maximum of the X-ray diffraction lines decreases with the samples annealed at higher temperature. Probably this is an evidence of growing up crystalline grain. The average crystalline size (<D>) of La$_{1.5}$Sr$_{0.5}$NiO$_4$ grain, determined by Warren-Averbach method for all the samples, was presented in table 1.

![Figure 1. The X-ray powder diffraction patterns of 7 samples.](image-url)
Table 1. Average grain size ($<D>$) and the results of fitting the equations (5) and (6) for $\varepsilon'(f)$ and ($\varepsilon''(f)$) to the experimental data for the 7 samples.

| Sample (notation) | 700°C (S1) | 750°C (S2) | 800°C (S3) | 850°C (S4) | 900°C (S5) | 950°C (S6) | 1000°C (S7) |
|-------------------|------------|------------|------------|------------|------------|------------|-------------|
| $<D>$ nm          | 16.2       | 17.0       | 23.5       | 35.0       | 41.6       | 61.3       | 95.0        |
| $f_0$ (Hz) x $10^5$ | 5.607      | 4.886      | 5.131      | 5.411      | 6.807      | 7.645      | 7.608       |
| $\alpha \times 10^6$ | 3.327      | 3.208      | 2.758      | 2.005      | 1.659      | 1.235      | 1.027       |
| $R$ (Ω)           | 3.741      | 3.638      | 3.086      | 2.251      | 1.342      | 0.992      | 0.852       |
| $L$ (μH)          | 0.562      | 0.567      | 0.559      | 0.561      | 0.405      | 0.402      | 0.415       |
| $\tau$ (ns)       | 284        | 326        | 310        | 294        | 234        | 208        | 209         |

Figure 2. FESEM image of two samples S1 and S7.

It is clear that the grain size increases significantly with increasing annealing temperature. The mean grain size of the samples was also estimated by means of FE-SEM image (figure 2). It was shown that the obtained result is comparable to that obtained by Warren-Averbach method.

It was known that the frequency dependence of capacitance and dissipation factor of the flat disk capacitor can be expressed as follows:

$$C(\omega) = \frac{\varepsilon'(\omega)\varepsilon_0 S}{d},$$  \hspace{1cm} (1)

$$tg \delta(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)},$$ \hspace{1cm} (2)

where $S$ and $d$ are the area and thickness of capacitor, respectively, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the dielectric constant of vacuum, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real and imaginary part of the dielectric constant, respectively.

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega),$$ \hspace{1cm} (3)

In this work, the capacitor with $S = 78.5 \text{ mm}^2$ and $d = 1.5 \text{ mm}$ was used.

Figure 3 presents the frequency dependence of the real part $\varepsilon'(\omega)$ and imaginary part $\varepsilon''(\omega)$ of the permittivity at room temperature of three samples S1 (a), S4 (b), and S7 (c). A dielectric resonance at a frequency range $4 \times 10^5 \div 8 \times 10^5$ Hz was observed and its resonance frequency shifts to higher frequency when increasing grain size.

The dielectric constant at low frequency range is positive and higher than $10^5$ for all the samples. But it exhibits a negative dielectric constant at frequency over the resonance frequency $f_0$ and looks like that of a composite Left Handed Material (LHM) consisting of both ferromagnetic and ferroelectric compounds [10].
Figure 3. The dependence on frequency of the real part $\varepsilon'(\omega)$ and imaginary part $\varepsilon''(\omega)$ of the permittivity at 300 K for three examples samples S1 (a), S4 (b), and S7 (c).

As known the collective oscillator system with damping is determined by equation [13]

$$\frac{d^2 P}{dt^2} + 2\alpha \frac{dP}{dt} + (\omega_0^2 - \frac{N\varepsilon^2}{3m\varepsilon_0})P = \frac{N\varepsilon^2}{m}E,$$

where $P$ is the polarization of material, $\alpha$ is the damping factor, $\omega_0$ is the resonance frequency ($\omega_0 = 2\pi f_0$), $N$ and $m$ are the number and the induced mass of oscillators, respectively. The equation (4) is similar to the equation for the RLC series circuit, where $R$, $C$ and $L$ are the resistance, capacitance and inductance of the equivalent circuit, respectively. Therefore the solution of equation (4) could be accepted as a solution of the equation describing the RLC series circuit with the damping factor:

$$\alpha = \frac{\Delta \omega_0}{2} = \frac{R}{2L}.$$

By solving equation (4) we have the frequency-dependence expressions for real part ($\varepsilon'(\omega)$) and imaginary part ($\varepsilon''(\omega)$) of the permittivity:

$$\varepsilon'(\omega) = \frac{\left(\omega_0^2 - \omega^2\right)}{L\left(\omega_0^2 - \omega^2\right)^2 + (2\alpha\omega)^2} \times \frac{d}{\varepsilon_0 S},$$

$$\varepsilon''(\omega) = \frac{2\alpha\omega}{L\left(\omega_0^2 - \omega^2\right)^2 + (2\alpha\omega)^2} \times \frac{d}{\varepsilon_0 S}.$$

The dielectric relaxation time ($\tau$) is defined by formula

$$\tau = \frac{1}{\omega_0}.$$

Figure 4 presents the experimental data of the real $\varepsilon'(\omega)$ and the imaginary parts $\varepsilon''(\omega)$ (mark points) and fitted results by using equations (6) and (7) in a frequency range around the resonance value (lines). The obtained fitting parameters such as resonance frequency value $f_0$, damping factor $\alpha$, $R$, $L$, and relaxation time ($\tau$) are presented in table 1.

As seen in table 1 the obtained fitting values $L$ are almost not changed with increasing grain size, but the obtained values of $C$ increases. The relaxation time and dissipation parameter decrease with increasing grain size. It is supposed to be related with an effect of the grain boundary that decreases with increasing grain size. Bai et al. [10] observed the same phenomenon in a composite created by mixing a ferromagnetic with a ferroelectric composition. He observed resonance at different
frequencies in range of GHz, depending on the ratio of two components. We observed the resonance frequency much lower than that reported by Bai et al. It is supposed to be related with the high dielectric constant of the La$_{1.5}$Sr$_{0.5}$NiO$_4$ material.

The dissipation factor is the most important parameter of the insulator material, suggesting the possibilities of its application. Therefore in the aim of searching the application possibilities we plot curves of dissipation factor at low frequencies ($f < f_0$) at 300 K for all the La$_{1.5}$Sr$_{0.5}$NiO$_4$ samples (figure 5). It is clearly seen that all the La$_{1.5}$Sr$_{0.5}$NiO$_4$ samples have quite low dielectric loss ($\sim 10^{-4} - 10^{-5}$) in a wide frequency range, decreasing in dependence of the grain size of La$_{1.5}$Sr$_{0.5}$NiO$_4$. Finally we would like to confirm that the colossal dielectric constant that obtained for La$_{1.5}$Sr$_{0.5}$NiO$_4$ samples is an intrinsic behaviour of material as reported by Rivas et al. [6]. As shown in figure 6, the dielectric constant of samples is about $10^5$, increasing with grain size. This obtained result is opposite to report of Lunkenheimer et al. [14], who theoretically suggested that the grain effect is a main reason of the colossal dielectric constant that observed in the related oxides materials. By means of Lunkenheimer [14] the dielectric constant should increase with decreasing grain size, but in our case we have obtained an opposite result. It is supposed to conclude that the observed colossal permittivity is an intrinsic behaviour of La$_{1.5}$Sr$_{0.5}$NiO$_4$ material.

In aim of searching the influence of grain boundary effect we set up the dependence between $\epsilon''(\omega)$ and $\epsilon''''(\omega)$ that called Cole-Cole diagram for all the samples, presented in figure 7. It is clear that the Cole-Cole diagram of samples consisting of grains with size larger than 40 nm exhibits circles.
It means that the dielectric relaxation in these samples is a single relaxation process and the influence of the long time relaxation process concerning the surface states at grain boundary is reasonably neglected. The grain boundary effect is clearly observed at the Cole-Cole diagrams of the samples with grain size smaller than 40 nm. Cole-Cole diagrams of the samples deviated essentially at the low frequency region. It is evidence related with the effect induced by the grain boundary states, which normally characterize the low frequency process.

4. Conclusions
The La$_{1.5}$Sr$_{0.5}$NiO$_4$ ceramic samples with the average crystals size ($<$D$>$) changing from 16.2 to 95 nm were successfully manufactured by using the reactive mechanical milling technique combined with annealing at different temperatures in air. All the samples La$_{1.5}$Sr$_{0.5}$NiO$_4$ have perovskite layers structure of K$_2$NiF$_4$-type. They exhibit a colossal dielectric constant about $10^5$ and low dielectric loss ($\sim 10^{-1} – 10^0$) in a wide frequency range. The colossal dielectric constant is an intrinsic behaviour of the La$_{1.5}$Sr$_{0.5}$NiO$_4$ material. A low frequency resonance (about $10^5$ Hz) was observed. It behaves like the R-L-C circuit. L and C components probably are contributed by the FM and the FE composition existing in La$_{1.5}$Sr$_{0.5}$NiO$_4$, so called the multiferroics one.

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