Nanopowder grain size effect on the ac electric properties of Eu doped BaTiO$_3$ nanoceramic

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Abstract. The impedance spectra of BaTiO$_3$ nanoceramics doped with Eu were measured. The samples originated from nanopowder which differed in grain size. The impedance spectra showed strong dependence on the measurement temperature. An electric equivalent circuit was elaborated and fitted to the measured spectra. Its analysis allowed to identify both conduction mechanisms and dielectric properties. The conductance analysis pointed to the diffusion as the main conductivity process which was independent on the grain size. The analysis of the dielectric properties suggested a coexistence of two phases: amorphous and crystalline. Contribution of the amorphous phase to the total electric permittivity was greater than the crystalline phase contribution at measurement frequencies below 1 MHz. Dielectric properties of the crystalline phase could be determined by the high frequency measurements or equivalent circuit modelling. The ferroelectric-paraelectric transition was observed in the crystalline phase. Contribution of the crystalline phase to the total permittivity increased with the grain size.

1. Introduction

The properties of BaTiO$_3$ ceramics are commonly known. They are ferroelectric materials with the potential use as piezoelectrics or high-k dielectrics[1-4]. Interesting phenomena in ceramic materials occur when the grain size is decreased to the nanometer scale[5-8].

This paper describes the ac electric properties of nanoceramic BaTiO$_3$ doped with Eu, which were measured with the use of impedance spectroscopy and analyzed by equivalent circuit modeling.

2. Samples preparation

Samples preparation has been already described elsewhere [9]. The BaTiO$_3$ nanopowder was fabricated in sol-gel method [10] and sintered in the low temperature high pressure (LTHP) process at the pressure of 4 GPa [9][11].

The XRD measurements were performed using the Kuma Diffractometer MK4 CCD with Mb radiation ($\lambda=0.7093\text{Å}$) in order to measure an average grain size in the prepared powder and the crystalline core size of the grains after sintering.

Table 1. Sample grain sizes

| Sample | Grain size [nm] | Crystalline core size after sintering [nm] |
|--------|----------------|------------------------------------------|
| #1     | 20             | 17                                       |
| #2     | 28             | 19                                       |
| #3     | 43             | 17                                       |
| #4     | 54             | 18                                       |
the sintering process which was lower due to the grain deformation during sintering. The deformed part of nanoparticles was non-crystalline.

3. Measurement setup
Electric properties of the BaTiO$_3$ nanoceramics were measured in capacitor configuration. A capacitor was created by coating the disc-shaped sample with silver conductive paint. The investigated material acted as dielectric in the parallel-plate capacitor. All measurements were performed with the use of Agilent 4294A impedance analyzer and a resistively heated stage with controlled temperature.

4. Results and discussion
4.1. Impedance spectra
The impedance spectra were measured. To obtain information about the temperature dependence of the material properties the measurements were performed during a slow temperature change.

The frequency range was 100 Hz to 5 MHz and the temperature of heated stage changed from 210°C to 50°C at a 1°C per minute rate. The possibility of silver diffusion from electrodes was the reason for the upper temperature limit of 210°C.

A strong temperature dependence was observed for the measured spectra. The spectra analysis showed the existence of low frequency dispersion (LFD) and low frequency conductance related to the diffusion [12].

4.2. The electric equivalent circuit
In order to analyze the measured spectra an equivalent electric circuit was created (Figure 2). The parallel equivalent circuit was chosen as it was suitable for the investigated materials [13, 14]. The circuit consisted of parallelly connected DC resistance, $R_{DC}$, two constant phase elements [15], CPE$_1$ and CPE$_2$, and a number of series RC circuits. In addition, series resistance, $R_s$, was also included. This common model could be fitted to all measured spectra.

The CPE admittance depends on the frequency and two parameters $Q$ and $n$:

$$Y_{CPE} = Q \cdot (j \omega)^n$$  (1)

where

$$\omega = 2 \cdot \pi \cdot f$$  (2)

The effect of equivalent circuit elements on the total impedance spectrum was shown in Figure 3. The main frequency response shape of sample was determined by $R_{DC}$, CPE$_1$ and CPE$_2$ and it was modified by the existence of one or more series RC circuits.
It was not always possible to fit the $R_S$ and $R_{DC}$ values to the spectra as they exceeded the analyzer’s precision and/or measurement range. The actual number of series RC circuits varied between samples and changed depending on the measurement temperature. The values of the elements of the series RC subcircuit could be fitted only if the subcircuit conductance was big enough to be distinguishable in the total spectrum, which was not always the case. Otherwise the RC subcircuit was omitted in the fitting procedure.

![Figure 3: Spectra of the equivalent circuit components](image)

Figure 3: Spectra of the equivalent circuit components

![Figure 4: Temperature dependence of the equivalent circuit elements](image)

Figure 4: Temperature dependence of the equivalent circuit elements: a) $R_{DC}$, b) CPE $Q$ coefficient, c) CPE $n$ coefficient

Temperature dependences of the main equivalent circuit components are shown in Figure 4. The $R_{DC}$ changed according to the Arrhenius law with activation energies similar to the expected Eu donor level depth [16]. $R_{DC}$ was not measurable at any temperature for the sample #4.

CPE$_1$ and CPE$_2$ temperature dependences were similar in each sample analyzed. For clarity, only results for the samples #2 and #4 are shown in Figures 4b and 4c. The $Q_{CPE1}$ values remained constant in the wide temperature range with a slight drop above the BaTiO$_3$ Curie point (389K [1]) while the $n$ coefficient was also constant and close to 1. The $Q_{CPE2}$ values rose according to the Arrhenius law (discussed below) while the $n$ coefficient was close to 0.5.

4.3. AC conductance

The coefficients of CPE used in the equivalent circuit were analyzed not directly but by an analysis of the CPE’s conductance, $G_{CPE}$, susceptance, $B_{CPE}$, and capacitance, $C_{CPE}$. $G_{CPE}$ was calculated using the following equation:

$$G_{CPE} = \Re \{ Y_{CPE} \} = Q \cdot \omega^n \cdot \cos \left( \frac{\pi}{2} \cdot n \right)$$  (3)
The conductance of both CPE$_1$ and CPE$_2$ was shown in Figure 5. The temperature dependences of CPE conductance in all samples were similar: CPE$_1$ did not take significant role in the AC conductance while the CPE$_2$ conductance changed according to the Arrhenius law with an activation energy around 0.20 eV.

As mentioned before, the equivalent circuits included also a number of series RC circuits which were necessary to precisely fit a model impedance to the measured spectra. In the case of the sample #1 only one series RC circuit had to be used, in the samples #2 and #3 three RC circuits up to four RC circuits in the sample #4.

Apart from the sample #3, the activation energy of the RC circuit time constant (Figure 6) was similar to the activation energy of CPE$_2$ conductance which suggested that the RC circuit time constant was conductance-related.

4.4. AC dielectric properties
To calculate the effect of CPE1 and CPE2 on the total electric permittivity their susceptance and capacitance had to be calculated:

$$B_{CPE} = \Im\{Y_{CPE}\} = Q \cdot \omega^{n} \cdot \sin\left(\frac{\pi}{2} \cdot n\right)$$  \hspace{1cm} (4)$$

$$C_{CPE} = \frac{B_{CPE}}{\omega} = B_{CPE} \cdot \omega^{(n-1)} \cdot \sin\left(\frac{\pi}{2} \cdot n\right)$$  \hspace{1cm} (5)$$

Please note that the CPE capacitance varies with the frequency if the $n$ coefficient is less than 1. The CPE contribution to the total relative dielectric permittivity $\epsilon_{CPE}$ was calculated as follows:

$$\epsilon_{CPE} = \frac{C_{CPE}}{C_0}$$  \hspace{1cm} (6)$$
Calculations were performed for the frequencies: 1 kHz, 100 kHz and 10 MHz. The results are shown in Figures 7 and 8.

![Figure 7: Simulated CPE relative permittivity vs temperature in the sample #2 at 1 kHz, 100 kHz and 10 MHz: a) CPE1, b) CPE2 and c) CPE](image)

The $\varepsilon_{CPE1}$ temperature dependence showed the maximum at the Curie point. That led to the conclusion that the CPE$_1$ modeled the crystalline phase in which the ferroelectric – paraelectric transition occurred, however in the unlikely low Curie temperature of 280K as fitted by the regular Curie-Weiss law equation.

The $\varepsilon_{CPE2}$ temperature changes confirmed that the CPE$_2$ describes the diffusion mechanism which took place in the analyzed samples.

The strong frequency dependence of $\varepsilon_{CPE2}$ (Figure 8c) caused that at frequencies below 1 MHz the effective permittivity was mainly determined by the $\varepsilon_{CPE2}$. This made impossible to observe the ferroelectric – paraelectric transition in simple effective permittivity measurements performed at frequencies below 1 MHz.

The comparison of $\varepsilon_{CPE1}$ to $\varepsilon_{CPE2}$ for all samples at 1 kHz was shown in Figure 8.

![Figure 8: Comparison of relative permittivities at 1 kHz: a) CPE1, b) CPE2, c) relative permittivity at 410K](image)

All samples exhibited the $\varepsilon_{CPE1}$ maximum at the BaTiO$_3$ Curie point as well as the similar temperature dependence of $\varepsilon_{CPE2}$, however the $\varepsilon_{CPE1}/\varepsilon_{CPE2}$ ratio shows that the CPE$_1$ contribution in total relative permittivity increases with the nanopowder grain size. The difference between the CPE$_1$ and CPE$_2$ temperature dependences and the results of previously performed structural investigations confirmed the coexistence of crystalline nanopowder cores (modeled by CPE$_1$) as well as the amorphous phase (modeled by CPE$_2$) formed during nanopowder preparation and the high pressure sintering.

All investigated samples showed the similar ac conductance. It was modeled in equivalent circuit by $R_{\text{DC}}$ and CPE$_2$. The activation energies of both elements are shown in Table 2. The dielectric relaxation time constants, with the exception of sample #3, changed with the same activation energy as $G_{CPE1}$.
Table 2: The comparison of the equivalent circuit modelling results.

| Sample | Activation energies of equivalent circuit components [eV] | Relative permittivity at 1 kHz, 410K |
|--------|---------------------------------------------------------|-------------------------------------|
|        | R<sub>DC</sub> | G<sub>CPE1</sub> | R-C time constant | ε<sub>CPE1</sub> | ε<sub>CPE2</sub> |
| #1     | 0.65         | 0.23          | 0.27              | 335             | 304             |
| #2     | 0.81         | 0.25          | 0.25              | 436             | 730             |
| #3     | 0.61         | 0.18          | 0.075, 0.092      | 364             | 235             |
| #4     | 0.20         | 0.16, 0.21, 0.21, 0.30 | 826             | 359             |

The dielectric properties changed with the nanopowder grain size. The contribution of ferroelectric phase increased with the increase of grain size, however, ferroelectric-paraelectric transition was observed in all samples.

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