Structural, microstructural and impedance spectroscopy study of functional ferroelectric ceramic materials based on barium titanate

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Abstract. The differences between the physical properties of barium titanate BaTiO₃ and newly obtained BaHfₓTi₁₋ₓO₃ were identified. These ceramics were prepared by solid-phase reaction from simple oxides and carbonates using the conventional method. The structure and morphology of investigated samples were characterised by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The application of impedance spectroscopy made possible to characterize of these materials in the terms of electrical properties.

1. Introduction

Ceramic ferroelectric materials due to the availability of advanced materials are now the increasingly important elements of active intelligent systems. The systems, in which there is a feedback loop between a sensor and a actuator and the response of the system is varied and flexible. Among these materials, ferroelectrics with perovskite ABO₃ structure type have a special place, barium titanate in particular. BaTiO₃ (BT) is the piezoelectric material of the greatest importance (module piezoelectric d₃₃ is of the order 10⁻¹² C/N and electromechanical coupling coefficient kₚ = 0.38) [1-3]. Therefore it is used as mechanical-electrical sensors measuring and recording e.g. vibration, speed, acoustic emission signals, etc. The ceramics based on BaTiO₃ has a great range of physicochemical properties. In many recent works [4-9] the effects of isovalent substitutions such as Zr⁴⁺, Sn⁴⁺ for Ti⁴⁺ and Ca²⁺, Sr²⁺ for Ba²⁺ on the microstructure, dielectric properties and phase transition of BT ceramics have been extensively studied. The purpose of the work was the investigation of the role of Hf⁴⁺ substitution on the structural, microstructural and dielectric properties of the system BaTiO₃ - BaHfO₃ over a wide temperature and frequency range.

2. Experimental methods

The investigated samples BaTiO₃, BaTi₀.₉₂₅Hf₀.₀₇₅O₃, BaTi₀.₈₅Hf₀.₁₅O₃ (abbreviated to BT, BTH7.5, BTH15) were prepared by a solid state synthesis reported earlier [10]. The X-ray studies were performed by means of an X’Pert PRO (PANalytical) diffractometer with the Cu-Kα radiation (λ=1,5406 Å) and a graphite monochromator [9, 11]. A profile-fitting program FULLPROF [12] based on the Rietveld method was used to analyse and fit the spectra. In order to study the surface structure and morphology of the samples the high performance Hitachi S4700 electron scanning microscope with field emission and the Noran Vantage EDS (Energy-Dispersive X-Ray Spectroscopy) system was applied [9, 11]. The investigations of microstructure were performed on fractures and polished sections. Before the measurements the samples were sputtered with carbon. Dielectric measurements were carried out using an Alpha-AN modular measurement system together with cryogenic temperature control system - Quatro Cryosystem and WinDETA Novocontrol software, at frequency varying from 0.1 Hz to 10 MHz and temperature range from 130 K to 600 K.
3. Results and discussion
A powder X-ray diffraction pattern shows (figure 1) that the BaHf,Ti$\text{1-x}$O$_3$ polycrystalline samples at room temperature are of single-phase perovskite structure. In figure 1, shifting the diffraction peaks towards lower angles with comparison to the pure barium titanate BaTiO$_3$ with increasing Hf content are visible. This behavior indicates, that the values of the lattice parameters in BTH7.5 and BTH15 increased. The merging of the splitting of some peaks indicates a transformation from tetragonal symmetry phase (P4mm) to a higher symmetry –rhombohedral (R3m). The values of the lattice constants at room temperature were calculated. The determined cells parameters are: for BaTiO$_3$ $a=3.9943\text{Å}$, BaTi$_{0.925}$Hf$_{0.075}$O$_3$ $a=4.0215\text{Å}$ and for BaTi$_{0.85}$Hf$_{0.15}$O$_3$ $a=4.0348\text{Å}$.

![Figure 1](image1.png)

**Figure 1.** Room temperature X-ray diffraction profiles for BT, BTH7.5 and BTH15 samples.

The atomic composition of the ceramics BT, BTH7.5 and BTH15 was carried out by using the EDS. In an EDS survey spectrum (not shown here) nothing more than the expected elements are seen. They confirm the high purity and the expected qualitative composition. The images of fractures of investigated samples are shown in figure 2. The surface of the fracture goes along grains as well as along the boundaries between the grains. The fracture has a fragile character and a tendency to formation of crystalline structures can be observed in the grains. A good homogeneity of the microstructures and a small degree of porosity were observed. Pores have an irregular shape without curvings and narrowings. The growth terraces of grains are clearly seen. They indicate that the growth of grains took place according to a layer mechanism with a screw dislocation. Using the linear intercept method the grain size was determined from SEM photographs. The average grain size of BTH ceramics is included in the range from 8µm to 11µm.

![Figure 2](image2.png)

**Figure 2.** The photograph of microstructure of BT, BTH7.5 and BTH15 samples (mag. 10000x).

An impedance spectroscopy is useful for attempting to separate intra-granular (bulk), inter-granular and sample electrode interface effects [13]. These effects usually are related to the sites of traps for
oxygen vacancies and other defects. The impedance analysis is also helpful in establishing a space charge polarization (i.e. an accumulation of charges at the interface between the sample and electrodes) and its relaxational mechanism. In figures 3-6 the impedance data of the investigated samples are presented in the form of Nyquist diagrams ($Z''$ vs. $Z'$) for several representative temperatures (>570K).

![Figure 3](image1) ![Figure 4](image2)

**Figure 3.** The imaginary versus the real part of impedance for BT sample. **Figure 4.** The imaginary versus the real part of impedance for BTH7.5 sample.

The impedance plots $Z''(Z')$ are composed of two semicircle arcs which cannot be presented (and observed) simultaneously within the same scale in the one graph. The first process takes place within impedance regions from about 0 to $\sim10^5\Omega$ and second one (stronger) reaches the maximum values of impedance even one order of magnitude higher ($\sim10^6\Omega$). Thus the weaker process is presented as expanded insets with visible closer details. The weaker process can be prescribed to the grain (bulk) of impedance response. We postulate that the second one (stronger) originates from the free charge and the induced polarization occurring on grain boundaries. For BTH15 ceramics in the low frequency range, there is an additional short inclined straight line which may be attributed to the interface between the sample and the electrode relaxation (space charge polarization). The two semicircular arcs of the impedance plot can be expressed as an equivalent circuit consisting of two parallel R (resistance) and C (capacitance) elements connected in series; one RC element for the bulk and the other for the grain boundary response [14]. The relaxation time for the grain and grain boundary can be calculated from the relation $\omega \tau = 2\pi \nu \text{max} \times \text{RC} = 1$, where the $\nu \text{max}$ is the frequency of the maximum of the semicircle, $\omega = 2\pi \nu \text{max}$ and $\tau = \text{RC}$ is a relaxation time. Both processes are represented by not perfect but flattened semicircles. This flattening of the electrical response of the grain and grain boundary might be due to a nonexponential process, such as a diffusion or nonuniformities in the microstructure of material, leading to the distribution of relaxation times, characteristic for this ceramics type. It is frequently described as the semicircles with centres shifted below the real axis $Z'$. In the case of BTH7.5 sample the smallest “diffuse” of semicircle arcs for bulk (grain) are observed. The temperature increase causes the decrease of the experimentally observed semicircle radiiuses for all investigated samples. This is attributed to a cationic disorder due to the random distribution of B-site cations (Hf$^{4+}$, Ti$^{4+}$) having a different ionic radius. It can have an influence on a diffusion of Hf ions during the synthesis. In these materials the partial substitution of Ti by Hf takes place, and therefore the formation of new crystalline structures depending on the level of substitution occurs. Due to the fact that the ionic radii of Ti$^{4+}$ and Hf$^{4+}$ and the covalence degree of the bonds are different, it should be expected that the competition between Ti-O and Hf-O bonds exists. The variation of the relaxation times as a function of reciprocal temperature shows the Arrhenius behavior in the paraelectric phase (figure 6). The activation energy was determined from the equation $\tau = \tau_0 \exp(-E_a/kT)$, where $\tau_0$ is a pre-exponential factor, and $k$ and $T$ have their usual significance. The grain (bulk) and grain boundary relaxation activation energy were evaluated and were given in figure 6. The similar values of
activation energies obtained from the impedance and electrical plots modulus (not shown here) indicate the localized conduction (dielectric relaxation) of charge species in the boundary of sample.

4. Conclusions
The polycrystalline samples of BaHf$_{1-x}$Ti$_x$O$_3$ were obtained by means of a conventional ceramic technology. The synthesized material was determined by the X-ray diffraction and scanning electron microscopy. The analysis of the X-ray diffraction pattern revealed the formation of the single perovskite phase at room temperature. From the obtained results it was stated that the values of the lattice parameters in BTH7.5 and BTH15 increase in comparison with the values for pure barium titanate. The performed SEM and EDS studies revealed that the samples were of good quality and chemically homogeneous. The investigated material was dense and possessed a compact structure. It is found that hafnium concentration has significant influence on dielectric properties of BT. The grain and grain boundary relaxation activation energies were evaluated. The obtained results showed, that the conduction process occurs both in the grains and grain boundaries.

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