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The influence of Nb_2O_5 on $BaTiO_3$ ceramics dielectric properties

V.V. Mitić[a,b,*], I. Mitrović[a]

[a]*Faculty of Electronic Engineering, University of Niš, Beogradska 14, 18000 Niš, Serbia, Yugoslavia*
[b]*Institute of Technical Sciences, Serbian Academy of Sciences and Arts, Knez Mihailova 35, 11000 Belgrade, Serbia, Yugoslavia*

Abstract

The purpose of the present investigation was to study the influence of Nb_2O_5 on dielectric properties of $BaTiO_3$ ceramics. Microstructure investigations of sintered samples were carried out by scanning electron microscopy (SEM) method. The qualitative and quantitative analysis of sintered samples have been done by energy dispersive spectroscopy (EDS) method. The measurements of capacitance, dielectric constant and dissipation factor are carried out as well as the frequency characteristics of $BaTiO_3$ ceramics samples are obtained in order to determine the influence of Nb_2O_5 on $BaTiO_3$ ceramics dielectric properties. The aim of the present investigation is to enable the prognosis of microstructural and dielectric properties of $BaTiO_3$ ceramics considering the materials' density, additive's concentration and consolidation parameters according to the triad synthesis (technology)–structure–property.

Keywords: $BaTiO_3$; Capacitors; Dielectric properties; Niobates; Sintering

1. Introduction

The optimisation of the dielectric behaviour of $BaTiO_3$ ceramics requires high density microstructures with homogeneous grains of sizes lower than 1 μm. It was determined that additives are an effective way to achieve the microstructure control—fine grained $BaTiO_3$ microstructure can be formed improving the properties for various electronic applications.[1] Numerous investigations have been carried out in order to characterize the structure of defects and the $BaTiO_3$ ceramics behaviour during sintering.[2] Temperature-stable $BaTiO_3$ based dielectrics with high dielectric constant are widely used as multilayer capacitors.[3] A small variation of the dielectric constant with the temperature can be achieved by inducing the small contact of niobium addition in the microstructure of $BaTiO_3$.[4] Furthermore, the existence of a core–shell or a diffuse phase transition (DPT) structure in doped $BaTiO_3$, improves the use of $BaTiO_3$ ceramics as boundary-layer capacitor (GBBL).[5]

It was shown that niobium addition at low concentrations can produce a charge compensation mechanism by electron mobility causing the important reduction of the titanium valence (Ti^{4+} to Ti^{3+}). Thus, the structures of $Ba^{+2}\left(Ti^{+4}_{1-2x}Nb^{+5}Ti^{+3}_{x}\right)O_3$ could appear.[4] Also, when the niobium concentrations increases, a charge compensation mechanism by ionic defects occurs.[6] In addition to these equilibria mechanisms, the segregation of titanium-rich phase with incorporated niobium can be expected in $BaTiO_3$-based ceramics.[7]

In this paper, the effect of the niobium addition (up to 1.5 wt.%) on the microstructure development and dielectric properties of $BaTiO_3$ ceramics was studied.

2. Experimental

$BaTiO_3$ ceramics samples are made of MURATA barium-titanate powders as well as powder of additive Nb_2O_5. In order to investigate the influence of additive's concentration on the dielectric properties of $BaTiO_3$ ceramics, the weight percentages range from 0.5 to 1.5% of Nb_2O_5 were used. The samples were sintered in the tunnel furnace type CT-10 MURATA at the temperature of 1300 °C for 3 h. Microstructural characterizations for various samples have been carried out by scanning electron microscope of the Jeol-JSM-T20 type, which enables the observation of samples surface by enlarging to 35 000 times, with the resolution of 4.5 nm. The application of EDS analysis has been done by energy dispersive spectrometer. EDS-system QX2000S

* Corresponding author. Tel.: +381-18-550881; fax: +381-18-46180.
E-mail address: vmitic@elfak.ni.ac.yu (V.V. Mitić).

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(Oxford Instruments, UK) connected with scanning electron microscope and multichannel analyzer (MCA) is used. The impedance measurements have been done by HP 8753C Network Analyzer in the frequency range from 1 to 100 MHz. The capacitance and dissipation factor were measured using HP 4276A LCZ meter in the frequency range from 1 to 20 KHz.

3. Results and discussion

3.1. Results obtained by SEM and EDS methods

In Fig. 1(a)–(d) SEM microphotographs of $BaTiO_3$ ceramics samples with 0.5, 1 and 1.5 wt.% of Nb_2O_5 are shown. The enlarged detail showing grains with increased concentration of Nb_2O_5 is presented in Fig. 1(d). As it can be seen, the microstructures show high percentage of porosity. This induces the fact that the sintering density is considerably lower than the theoretical density for given sintering conditions. The estimated grain size is in the range of 1–3 μm. The shapes of grains are polyhedral with rounded edges. The regions where the concentration of Nb_2O_5 is rather increased are observed. It seems that Nb is not built in the crystal lattice of $BaTiO_3$, but it is set aside forming the separate regions. In fact, a matrix of fine-grained microstructure of grain size between 1 and 3 μm contains elongated needles with size higher than 5 μm. It was reported that the incorporation of niobium substituting titanium site in the $BaTiO_3$ lattice produced the titanium displacement out of the grain.[7] The obtained results in Fig. 1 confirm insignificant influence of the increase of wt.% of Nb_2O_5 on morphology as well as on grain size for given consolidation parameters.

EDS spectra of $BaTiO_3$- ceramics samples with addition of 0.5 to 1.5 wt.% of Nb_2O_5 are shown in Fig. 2(a)–(d). The peaks of Ba, Ti, O and Nb are detected. Since the energy of electron beam was 30 KeV, the K lines of Ti and L lines of Ba are detected. The matching of these lines on EDS spectra are visible. The slight differences in the heights and the positions of peaks of corresponding elements are observed on EDS spectra[8] for all used weight percentages of the additive. The regions with increased concentration of Nb_2O_5 are observed. The corresponding EDS spectrum of this region for the 1.5 wt.% of Nb_2O_5 is shown in Fig. 2(d).

3.2. Results of dielectric characteristics

The great number of electrical measurements on the samples of $BaTiO_3$ ceramics with Nb_2O_5 of different

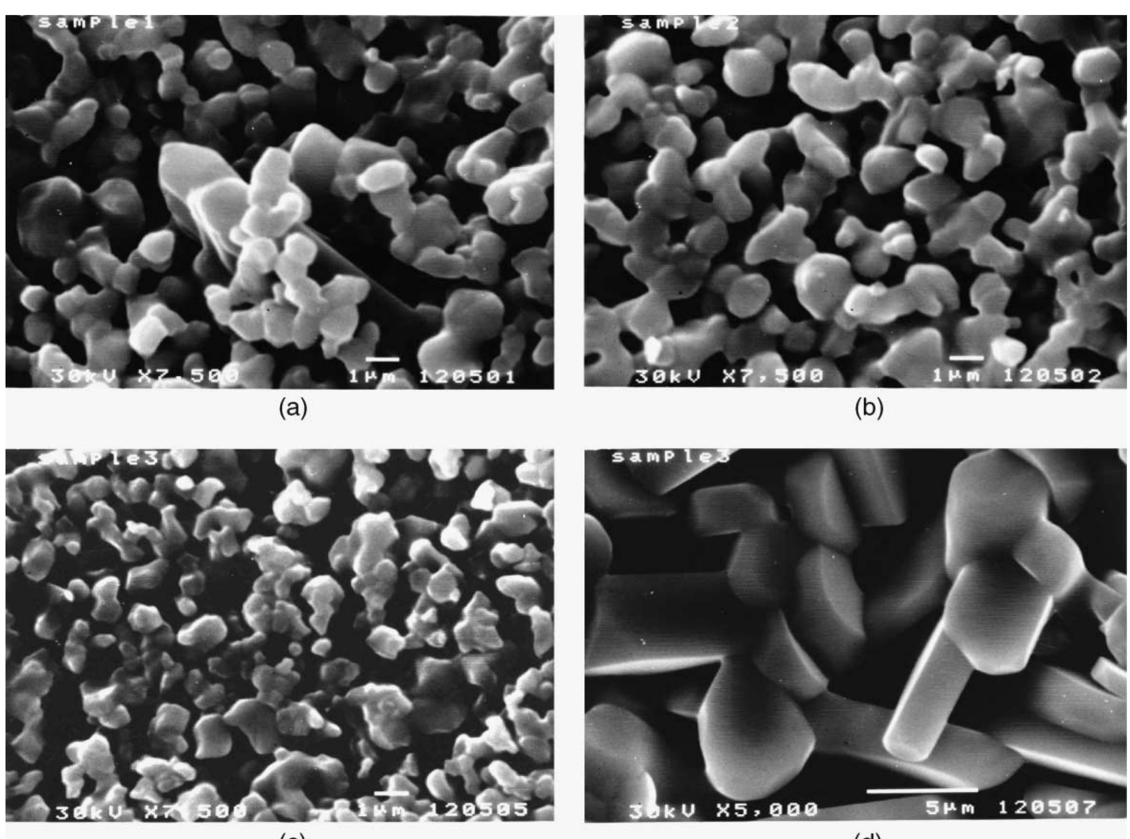

Fig. 1. The SEM microphotographs of $BaTiO_3$ ceramics with Nb_2O_5: (a) 0.5 wt.% (×7500); (b) 1 wt.% (×7500); (c) 1.5 wt.% (×7500); (d) the Nb_2O_5-rich region (×5000).

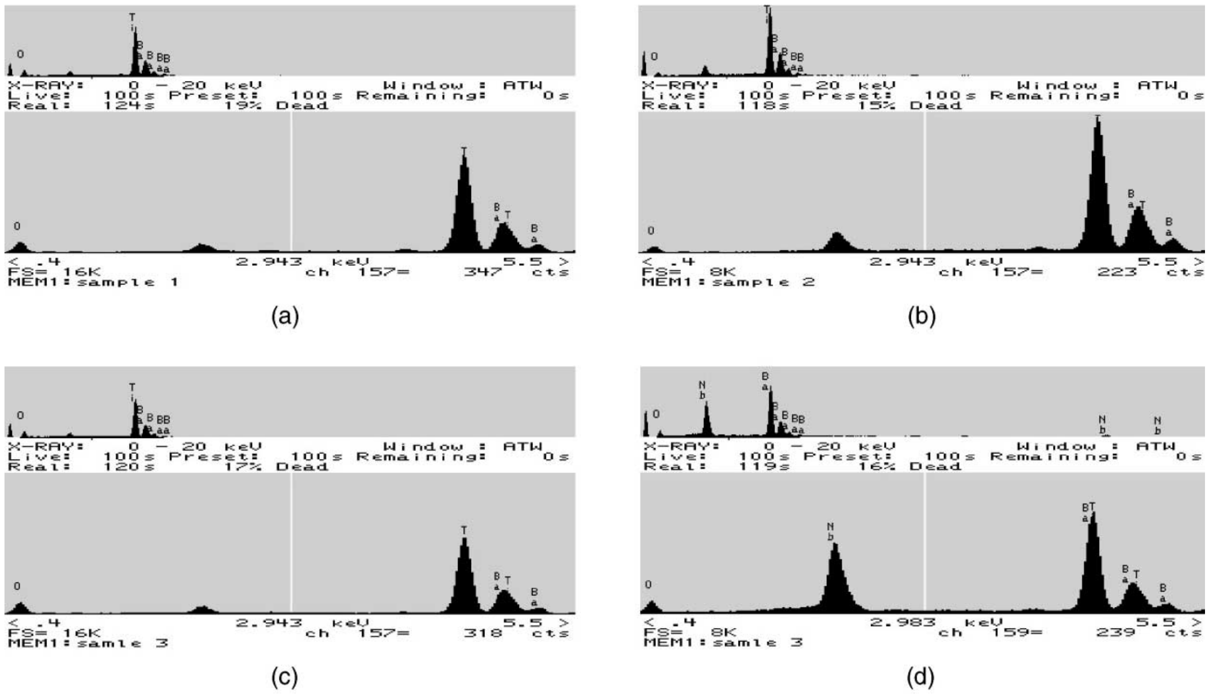

Fig. 2. EDS spectra of $BaTiO_3$ ceramics with Nb_2O_5: (a) 0.5 wt.%; (b) 1 wt.%; (c) 1.5 wt.%; (d) 1.5 wt.% (the Nb_2O_5-rich region).

weight percentages were done. In this paper, the results of relative dielectric constant, capacitance, dissipation factor and impedance as a function of different additive's concentration (0.5, 1 and 1.5 wt.%) and sample's densites ($\rho_1 = 4 \times 10^3$ kg/m^3, $\rho_2 = 5.3 \times 10^3$ kg/m^3 and $\rho_3 = 5.6 \times 10^3$ kg/m^3) will be given. According to measured values, the diagram of relative dielectric constant (ε) vs. wt.% of Nb_2O_5 is presented in Fig. 3. Three different curves were obtained, each corresponding to the specified sample's density: the first one to ρ_1, the second curve to ρ_2 and the third one to ρ_3. The curves 1 and 2 show the minimum value of dielectric constant for 1 wt.% of Nb_2O_5, while the curve 3 shows the decrease of dielectric constant in the whole region of additive's concentration.

The diagram of capacitance vs. frequency for $BaTiO_3$ ceramics with 1.5 wt.% of Nb_2O_5 is shown in Fig. 4. The three different curves obtained on graph corresponds to sample's densities ρ_1, ρ_2 and ρ_3, given above. As it can be seen, the increase of sample's densities causes the decrease of the capacitance values, although the shape and tendency of curves are the same. In the frequency region from 5 to 20 KHz the capacitance value is stable with a slight decrease towards higher frequencies. Thus, for given sample's densities ρ_1, ρ_2 and ρ_3 the capacitances are approximately 0.67, 0.5 and 0.38 nF, respectively.

In Fig. 5, the diagram of dissipation factor vs. frequency for $BaTiO_3$ ceramics with 1.5 wt.% of Nb_2O_5 is shown. The decline of dissipation factor towards higher frequencies can be noticed for each curve which corresponds to given sample's density. Also, the highest sample's density the highest dissipation factor value.

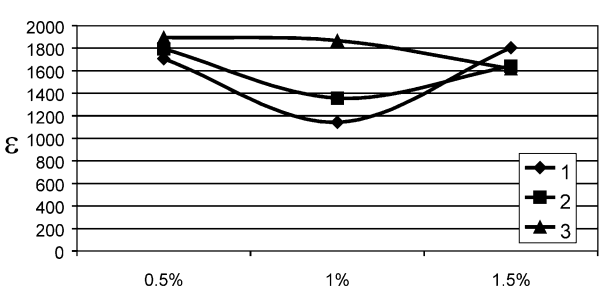

Fig. 3. The relative dielectric constant vs. wt.% of Nb_2O_5 for $BaTiO_3$ ceramics [1, 2, 3 refers to sample's densities ρ (10^3 kg/m^3): 4, 5.3 and 5.6, respectively].

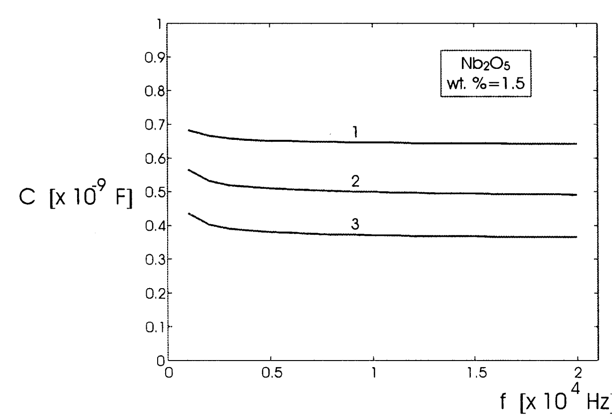

Fig. 4. The capacitance vs. frequency for $BaTiO_3$ ceramics with 1.5 wt.% of Nb_2O_5 (the frequency range 1–20 kHz).

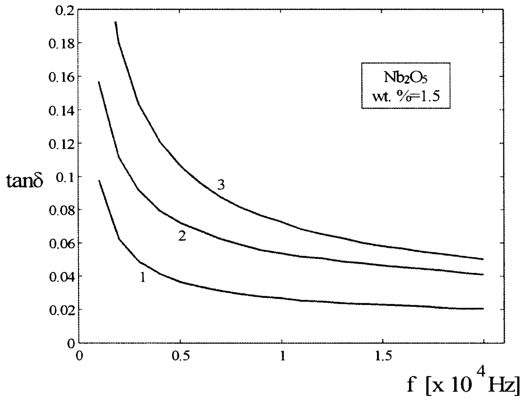

Fig. 5. Dissipation factor vs. frequency for $BaTiO_3$ ceramics with 1.5 wt.% of Nb_2O_5 (the frequency range 1–20 kHz).

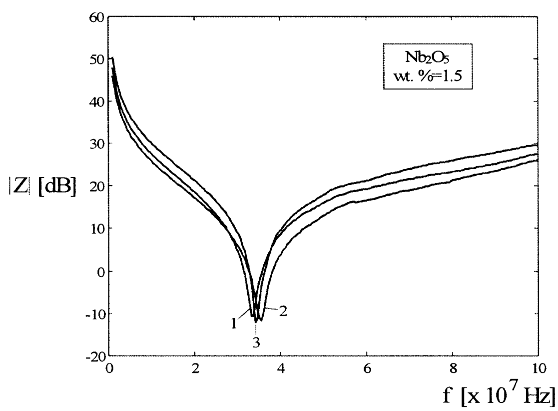

Fig. 6. The magnitude of impedance vs. frequency for $BaTiO_3$ ceramics with 1.5 wt.% of Nb_2O_5 (the frequency range 1–100 MHz).

The magnitude of impedance vs. frequency for $BaTiO_3$ ceramics with 1.5 wt.% of Nb_2O_5 is presented in Fig. 6. The resonant peaks are between 30 and 40 MHz. The increase of sample's densities up to 5.3×10^3 kg/m^3 shift the resonant peak towards higher frequencies. This expands the frequency region of $BaTiO_3$ ceramics for capacitor's application. Further increase of density influences the shift of resonant peak toward left side, being inconvenient for condenser's use. Thus, the optimal frequency characteristic here is obtained for the density $\rho_2 = 5{,}3\times10^3$ kg/m^3 (curve 2, Fig. 6), where the resonant frequency is approximately 35.5 MHz.

4. Conclusion

In this paper, the influence of Nb_2O_5 of the concentration up to 1.5 wt.% on $BaTiO_3$ ceramics microstructural and dielectric properties has been investigated. The results obtained by SEM and EDS methods have shown that the specimens are not well consolidated, specially in the previous process of powders mixing, forming and finally in the process of sintering. In this way, some $BaTiO_3$ particles could be far from the additives particles requiring large diffusion paths for the access of niobium ions to $BaTiO_3$ grains. It is known that such diffusion phenomena require rigorous thermal treatments in order to obtain homogeneous additive distribution by ionic diffusion at high temperature. Meanwhile, when the contact between additive and $BaTiO_3$ particles is closed, the diffusion is easier resulting in a homogeneous niobium distribution and a possible secondary phase generation. Here, the regions of Nb_2O_5-rich phase have been observed. These regions have the morphology of needles and could be the result of titanium substitution by niobium in the $BaTiO_3$ lattice and segregation of the titanium ions out of the $BaTiO_3$ grains.[5]

The diagrams of relative dielectric constant, capacitance, dissipation factor and impedance are given as a function of used additive's concentration, sample's densities and in frequency domain for $BaTiO_3$ ceramics with 1.5 wt.% of Nb_2O_5. Considering given results, the optimal frequency characteristics is obtained for the sample's density of 5.3×10^3 kg/m^3.

The research realized in this paper is a step towards further study of the influence of Nb_2O_5 on ferroelectric, dielectric and particularly core–shell properties of barium-titanate ceramics.

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