

UDK 622.785.661.884

Ho₂O₃ Additive Effects on BaTiO₃ Ceramics Microstructure and Dielectric Properties

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Abstract:

Doped BaTiO₃-ceramics is very interesting for their application as PTCR resistors, multilayer ceramic capacitors, thermal sensors etc.

Ho doped BaTiO₃ ceramics, with different Ho₂O₃ content, ranging from 0.01 to 1.0 wt% Ho, were investigated regarding their microstructural and dielectric characteristics. The samples were prepared by the conventional solid state reaction and sintered at 1320 ° and 1380 °C in an air atmosphere for 4 hours.

The grain size and microstructure characteristics for various samples and their phase composition was carried out using a scanning electron microscope (SEM) equipped with EDS system. SEM analysis of Ho/BaTiO₃ doped ceramics showed that in samples doped with a rare-earth ions low level, the grain size ranged from 20-30 μm, while with the higher dopant concentration the abnormal grain growth is inhibited and the grain size ranged between 2-10 μm.

Dielectric measurements were carried out as a function of temperature up to 180 °C. The low doped samples sintered at 1380 °C, display the high value of dielectric permittivity at room temperature, 2400 for 0.01Ho/BaTiO₃. A nearly flat permittivity-response was obtained in specimens with higher additive content. Using a Curie-Weiss law and modified Curie-Weiss law the Curie constant (C), Curie temperature (T_c) and a critical exponent of nonlinearity (γ) were calculated. The obtained value of γ pointed out that the specimens have almost sharp phase transition.

Keywords: BaTiO₃, Microstructure, Sintering, Additive, Dielectric properties

1. Introduction

A modified BaTiO₃ with different additives/dopants is the most extensively investigated dielectric material due to its attractive properties that can be used on a large scale of applications. The most commercial use is for multilayers capacitors, whereas BaTiO₃ with semiconducting properties is used widely in electronic devices such as thermistors, varistors and energy converting systems. BaTiO₃ powder is usually mixed with additives in order to adjust the sintering parameters and electrical properties to the requirements of electronic

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devices [1-2]. It has been found, that the dielectric properties of polycrystalline BaTiO₃, depend in a great extent on the grain growth during sintering and on donor type and concentration [3-5].

Two types of dopants can be introduced into BaTiO₃: ions with larger ionic radii of valence 3⁺ and higher such as Ho³⁺, Er³⁺, and Dy³⁺, which replaces predominately Ba²⁺ sites in perovskite BaTiO₃ lattice, and the ions with smaller ionic radii of valence 5⁺ and higher (Nb⁵⁺), can be incorporated into the Ti⁴⁺ sublattice [6-9].

It has been shown that the three-valent ions incorporated at the Ba²⁺ -sites act as donors, which extra donor charge is compensated by ionized Ti vacancies (V_{Ti}'''), the three-valent ions incorporated at the Ti⁴⁺ -sites act as acceptors which extra charge is compensated by ionized oxygen vacancies (V_{O}^{\bullet}), while the ions from the middle of the rare-earth series show amphoteric behavior and can occupy both cationic lattice sites in the BaTiO₃ structure [10-12]. The substitution of Ho³⁺ on Ba²⁺ sites requires the formation of negatively charged defects. For the samples sintered at air atmosphere, which are the electrical insulators, the principal doping mechanism is the ionic compensation mechanism. This controversy remains concerning whether the dominate ionic mechanism is through the creation of (V_{Ba}'') or (V_{Ti}''').

The purpose of this paper was to analyze BaTiO₃ doped with various content of Ho₂O₃, sintered at different sintering temperature. The influence of dopant on the microstructure and dielectric properties (capacitance and dielectric losses) in function of frequency and temperature has been investigated.

2. Experimental procedure

In this paper, Ho₂O₃ doped BaTiO₃-ceramics were used for microstructure and electrical characterization. The samples were prepared from high purity (>99.98%) commercial BaTiO₃ powder (MURATA) with [Ba]/[Ti]=1.005 and reagent grade Ho₂O₃ powder (Fluka chemika), by conventional solid state sintering procedure. The content of additive, Ho₂O₃, ranged from 0.01 to 1.0 wt%. Starting powders were ball milled in ethyl alcohol for 24 hours using polypropylene bottle and zirconia balls. After drying at 200°C for several hours, the powders were pressed into disk of 7 mm diameter and 3 mm thickness under 120 MPa. The compacts were sintered at 1320°C and 1380 in air for four hours.

The microstructures of sintered samples were observed by scanning electron microscope (JEOL-JSM 5300) equipped with energy dispersive x-ray analysis spectrometer (EDS-QX 2000S system). X-ray diffraction (XRD) patterns were recorded with CuK α radiation in a PhilipsX'Pert diffractometer (Philips, the Netherlands). Prior to electrical measurements silver paste was applied on flat surfaces of specimens. Capacitance and loss tangents were measured using Agilent 4284A precision LCR-meter in frequency range 20 Hz-1 MHz. The dielectric constant was calculated based on capacitance, specimen thickness and electrode area. The variation of dielectric constant with temperature was measured in temperature interval from 20°C to 180°C. The dielectric parameters such as Curie temperature, Curie-Weiss temperature and Curie constant were calculated according to Curie-Weiss and modified Curie-Weiss law.

3. Microstructure characteristics

The relative density of Ho doped samples was ranged from 82% of theoretical density (TD) for 0.01Ho/BaTiO₃ samples sintered at 1320 °C to 90%TD for 0.01Ho/BaTiO₃ doped

samples sintered at 1380 °C. With the increase of dopant amount the increase of porosity is evident and density value decrease and for 1.0wt% doped samples sintered at 1320 °C the density was 76% of theoretical density.

The homogeneous microstructure with spherical shaped grains, of fairly narrow size distribution is the main characteristic of low doped ceramics sintered at 1320 °C. The average grain size in specimens doped with low content of additive (0.01wt% and 0.05wt% of Ho) has ranged between 20-30µm (Fig.1). The similar microstructure is observed in low doped ceramics sintered at 1380°C (Fig. 2).

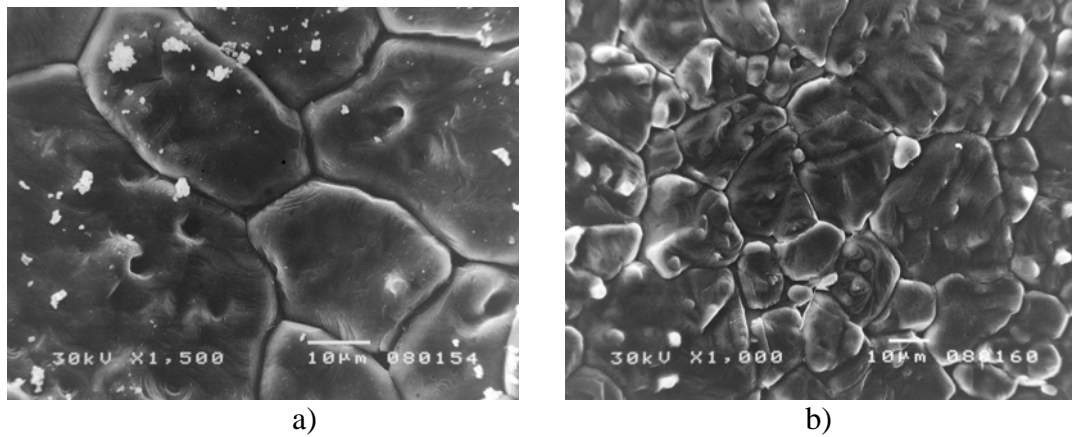


Fig. 1. SEM images of BaTiO₃ sintered at 1320°C doped with a) 0.01wt% and b) 0.05wt% of Ho₂O₃

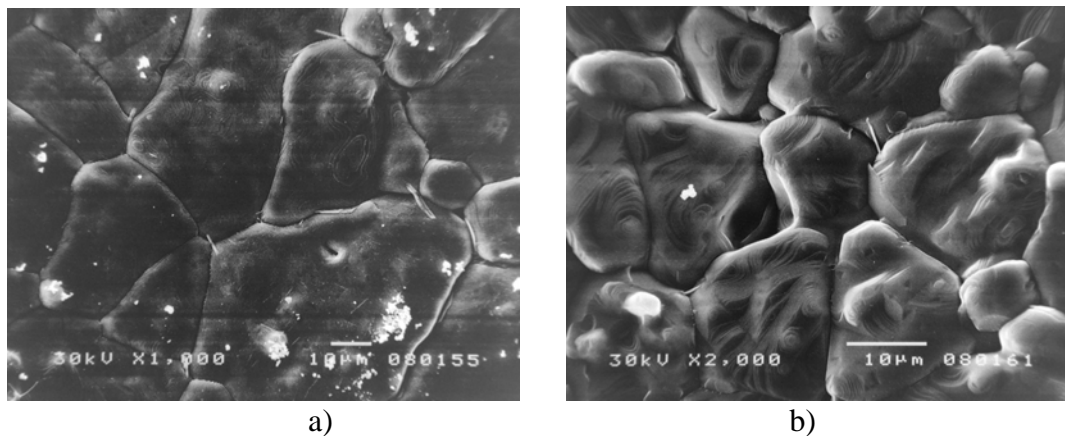


Fig. 2. SEM images of BaTiO₃ sintered at 1380°C doped with a) 0.01wt% and b) 0.05wt% of Ho₂O₃

The increase of rare-earth cations content inhibits the abnormal grain growth. By increase of dopant concentration the grain size decrease. As a result, for 0.5 wt% of dopant the average grain size was from 10µm to 15 µm, and for the samples doped with 1.0 wt% of dopant grain size decreased to the value of 2-5 µm (Fig. 3 and Fig.4) for both sintering temperatures.

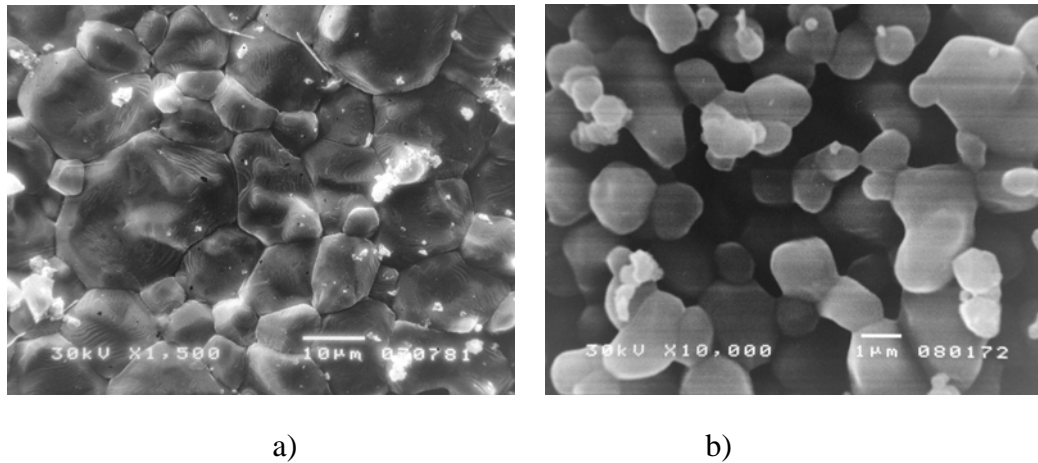


Fig. 3. SEM images of BaTiO₃ sintered at 1320°C doped with a) 0.5wt% and b) 1.0wt% of Ho

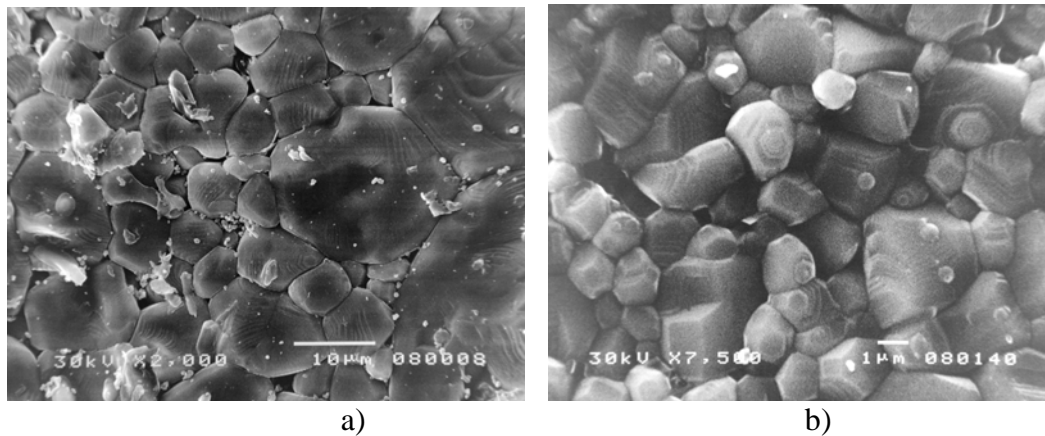


Fig. 4. SEM images of BaTiO₃ sintered at 1380°C doped with a) 0.5wt% and b) 1.0wt% of Ho

The EDS analysis of samples, doped with 0.01 wt% Ho₂O₃, did not reveal any Ho rich regions thus indicated a uniform incorporation of dopants within the samples (Fig.5a). The increase of dopant concentration leads to the appearance of Ho rich regions between grains (Fig.5b). It is important to say that EDS analysis can not detect the concentration of element less than 1 wt% unless an inhomogeneous distribution or segregation of dopant/additive is present.

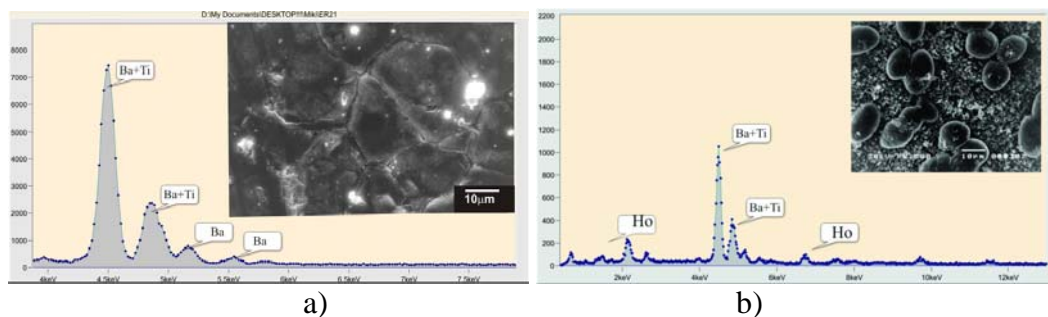


Fig. 5. SEM/EDS spectra of doped BaTiO₃ sintered at 1380 °C a) 0.01Ho-BT and b) 0.5Ho-BT- local area reach in Ho.

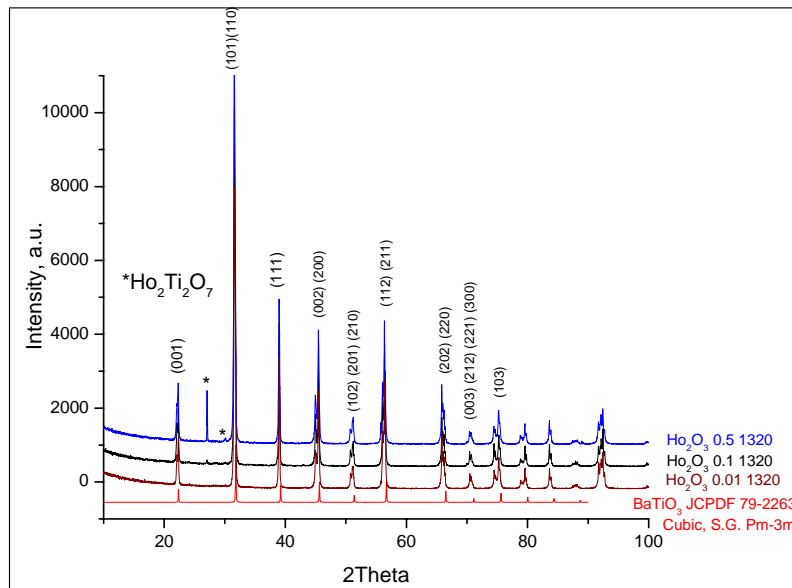


Fig. 6. X-ray analysis Ho doped BaTiO₃

X-ray analysis of 0.01Ho/BaTiO₃ samples showed only BaTiO₃ perovskite phase and uniform distribution of holmium (Fig.6). The increase of dopant content give rise to the appearance of second phase Ho₂Ti₂O₇ in 0.5Ho-BT (Fig.6). By comparison of XRD peaks of pure BaTiO₃ and doped BaTiO₃, it is evident that XRD peaks of doped samples are shifted towards to lower values of 2θ thus indicating the increase of lattice parameters, i.e. the incorporation of Ho on the Ti-sites rather than on Ba-sites in BaTiO₃ structure.

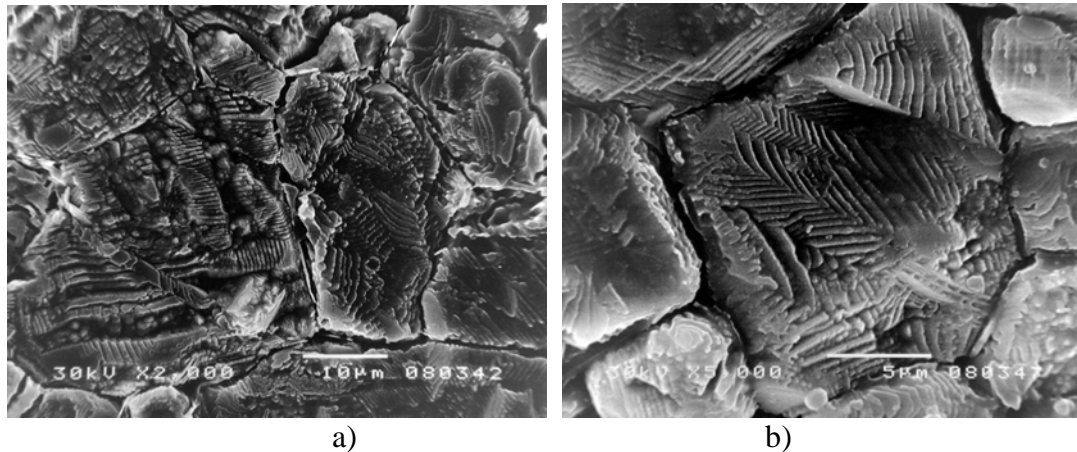


Fig. 7. Domain structure of 0.01wt% Ho/BaTiO₃ sintered at 1380 °C a) directional long domains and b) randomly oriented domains.

In samples of BaTiO₃ doped with 0.01 wt% of Ho in secondary abnormal grains the domain structure were observed. Regarding the domain structure, two types of domain structures were observed, i.e. the directional long domains that pass through the entire grain with 90° domain boundaries (Fig.7a) and randomly oriented domains within some individual abnormal grains (Fig.7b). Looking to the herring bone domain structure it can deduced that wall thickness was ranged between 0.05-0.1 μm and domain width was from 0.025 to 0.5μm.

4. Dielectric characteristics

The dielectric properties evaluation has been made by capacitance and dielectric loss measurements in the frequency range from 20 Hz to 1MHz.

The dielectric permittivity in function of frequency (Fig.8) for all investigation samples shows that, after insignificant low initial decrease in dielectric permittivity at low frequency, ϵ_r became constant for frequency greater than 5 kHz. The dielectric constant of the investigated samples ranged from 900 to 2400 at room temperature. For 0.01wt%Ho doped BaTiO₃ sintered at 1320°C dielectric constant is 2200 (Fig.8a) and for samples sintered at 1380°C dielectric constant increase and ϵ_r is 2400 (Fig.8b).

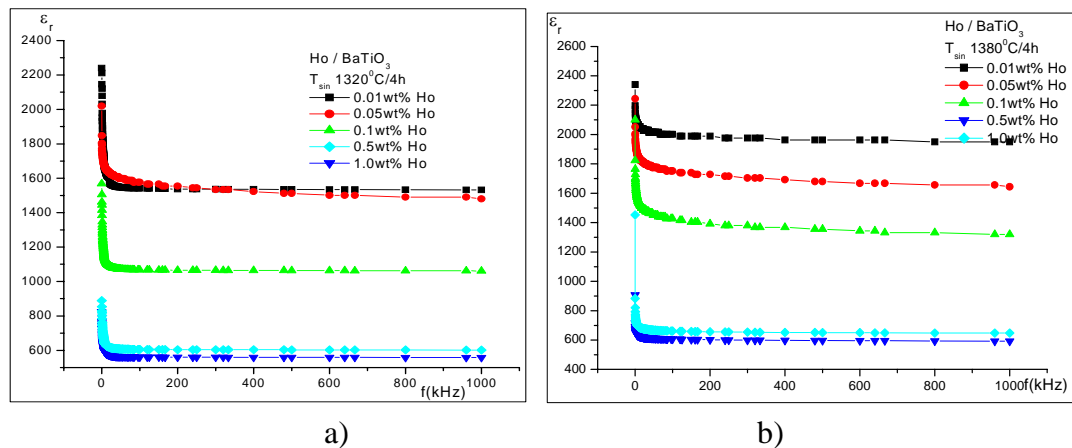


Fig. 8. Dielectric constant in function of frequency for doped BaTiO₃ sintered at a) 1320 °C and b) 1380 °C

With increase of dopant content the dielectric constant decrease for both sintering temperature and for samples doped with 1.0 wt% of Ho the dielectric constant is 900 for samples sintered at 1320°C and 1400 for samples sintered at 1380°C.

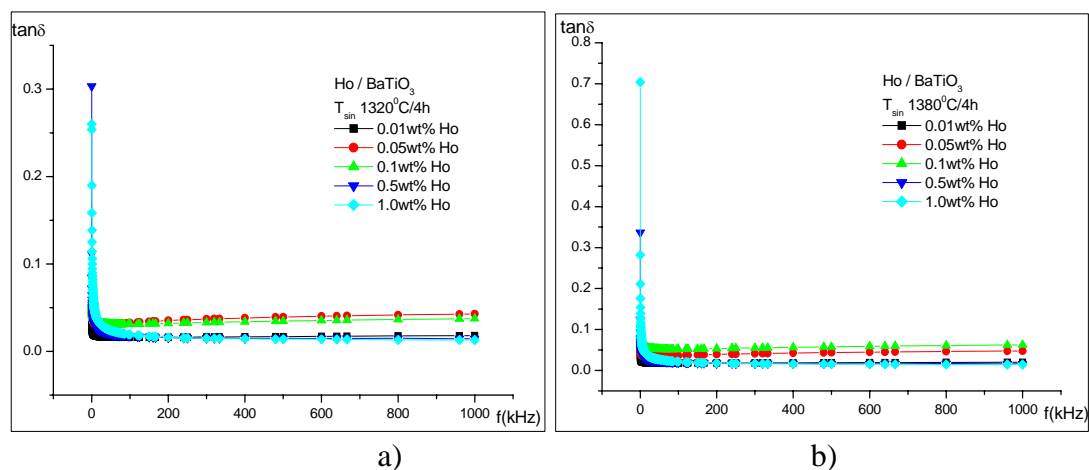


Fig.9. Dissipation losses in function of frequency for doped BaTiO₃ sintered at a) 1320 °C and b) 1380 °C

Regarding the dissipation losses (Fig.9), a liner decrease vs. frequency is measured

for all investigated samples. The corresponding curve for this sample could be separated into two regions with a change in linearity for frequency greater than 10kHz. The loss tangents values ($\tan \delta$) were in the range of 0.05 to 0.3 for samples sintered at 1320°C and from 0.05 to 0.7 for samples sintered at 1380°C.

The influence of additive type and microstructure characteristics on the dielectric behavior of Ho-doped BaTiO₃ can be evaluated through permittivity-temperature response curves (Fig. 10).

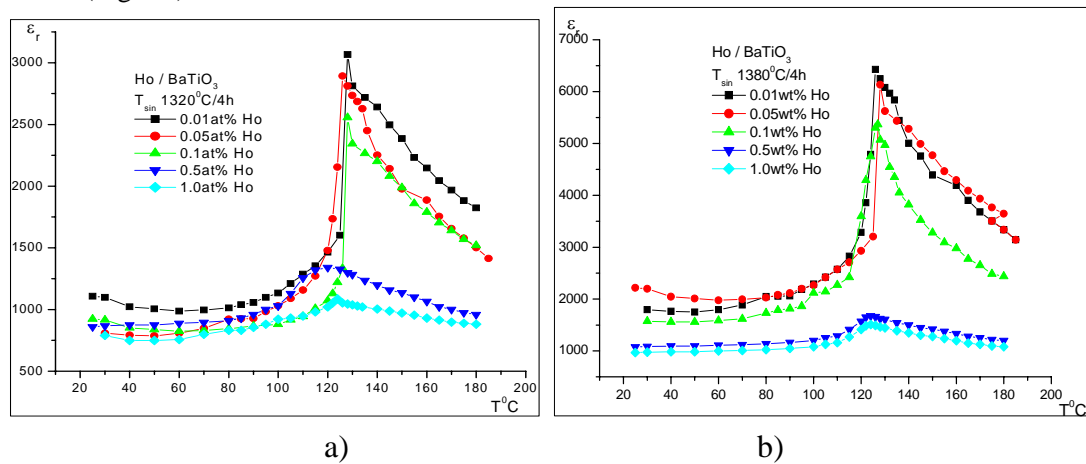


Fig. 10. Dielectric constant in function of temperature for doped BaTiO₃ sintered at a) 1320 °C and b) 1380 °C

The greatest change in dielectric constant vs. temperature for low doped samples is observed in 0.01wt% Ho doped BaTiO₃ for which the dielectric constant at Curie temperature is 6300. A relatively stable capacitance response in function of temperature up to 100°C has been noticed in all doped samples. With higher dopant concentration (0.5 and 1.0 wt%) the flatness of permittivity temperature response is observed.

The dielectric constant decrease of doped samples, with the increase of dopant concentration, can be attributed on one side to the nonhomogeneous distribution of additive throughout the specimens and on the other side to the decrease of density from 90 to 76% TD.

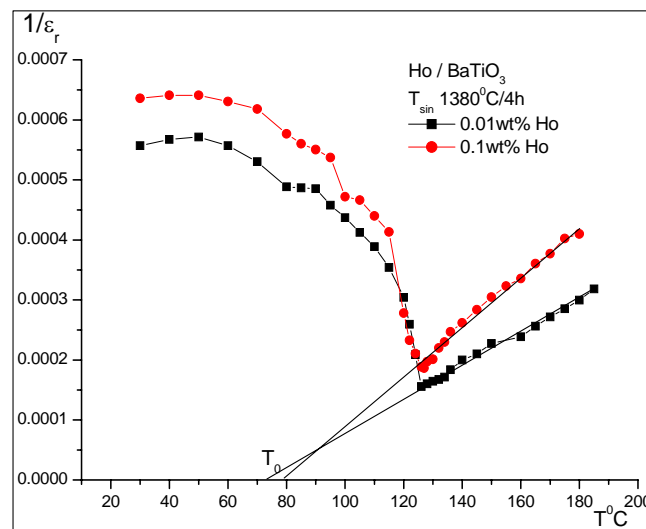


Fig. 11. Reciprocal values of ϵ_r in function of temperature.

The Curie temperature (T_C), determined from the maximum of the dielectric constant ϵ_r in the dielectric temperature characteristic, was in the range from 124 to 129°C being lower for low doped Ho-BaTiO₃.

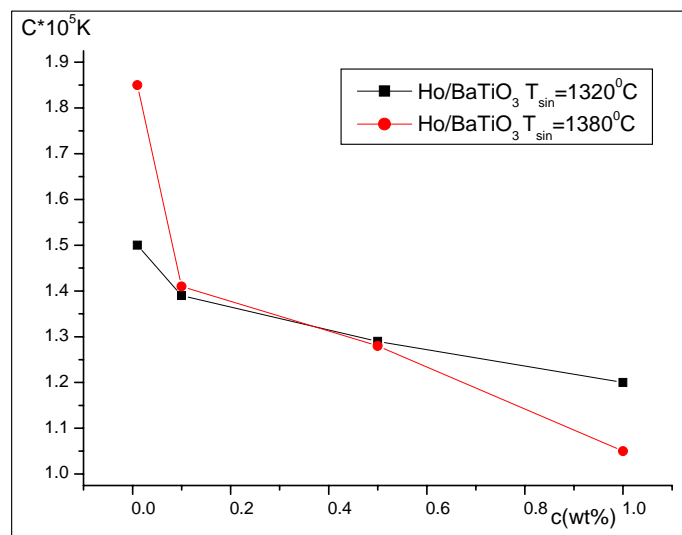


Fig.12. Curie constant in function of additive concentration.

All specimens have almost sharp phase transition and follow the Curie-Weiss law (Fig. 10). The Curie-Weiss law $\epsilon_r = C/(T - T_0)$ was used to calculate the dielectric parameters such as Curie constant (C) and Curie-Weiss temperature (T_0).

Tab. I. Dielectric parameters for Ho doped BaTiO₃.

Sample Ho/BT (wt%)	ϵ_r at 300K	ϵ_r at T_c	T_c [°C]	Curie constant [K]	T_0 [°C]
0.01 ($T_{sin} = 1320$)	2200	3000	125	$1.50 \cdot 10^5$	65
0.05 ($T_{sin} = 1320$)	2000	2800	124	$1.45 \cdot 10^5$	65
0.1 ($T_{sin} = 1320$)	1550	2500	125	$1.39 \cdot 10^5$	70
0.5 ($T_{sin} = 1320$)	1000	1500	126	$1.29 \cdot 10^5$	75
1.0 ($T_{sin} = 1320$)	900	1000	129	$1.20 \cdot 10^5$	80
0.01 ($T_{sin} = 1380$)	2400	6300	124	$1.85 \cdot 10^5$	75
0.05 ($T_{sin} = 1380$)	2300	6100	125	$1.66 \cdot 10^5$	70
0.1 ($T_{sin} = 1380$)	2200	6000	126	$1.41 \cdot 10^5$	75
0.5 ($T_{sin} = 1380$)	1900	1600	127	$1.28 \cdot 10^5$	88
1.0 ($T_{sin} = 1380$)	1400	1500	128	$1.05 \cdot 10^5$	70

The Curie constant (C) decreases with the increase of additive amount and have an extrapolated Curie-Weiss temperature (T_0) down to lower temperature (Fig.11 and Fig.12). In 0.01 wt % doped samples, that exhibit a high density, the Curie constant is higher compared to the high doped samples. It is believed that the value of Curie constant is related to the grain size and porosity of samples. The highest value of C ($C=1.85 \cdot 10^5$) was measured in 0.01 Ho-BaTiO₃-ceramics sintered at 1380°C. The Curie constant C and the Curie-Weiss temperature T_0 values were given in Table I.

In order to investigate the Curie-Weiss behavior the modified Curie-Weiss law is used.

To quantify the diffuseness i.e. the diffuse phase transformation of ϵ_r at T_{max} the equation proposed by Uchino and Nomura [13] has been used:

$$\frac{1}{\epsilon_r} - \frac{1}{\epsilon_{r \max}} = \frac{(T - T_{\max})^\gamma}{C'} \tag{1}$$

where: (γ) is the critical exponent of nonlinearity and C' is a Curie like constant.

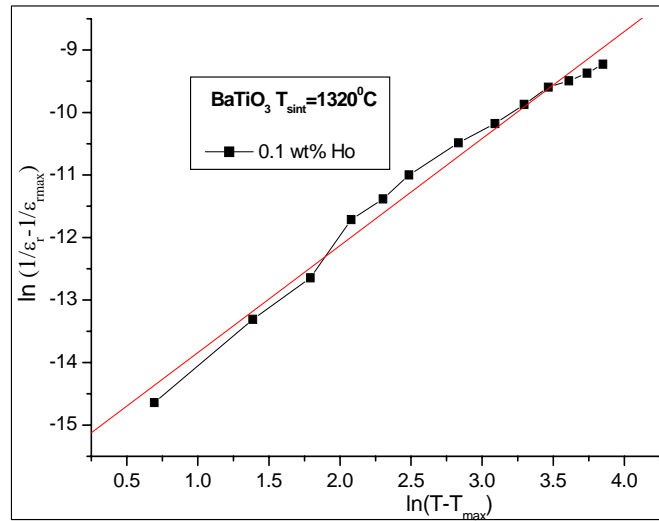


Fig.13. The modified Curie-Weiss plot $\ln(1/\epsilon_r - 1/\epsilon_m)$ vs. $\ln(T - T_m)$ for selected samples.

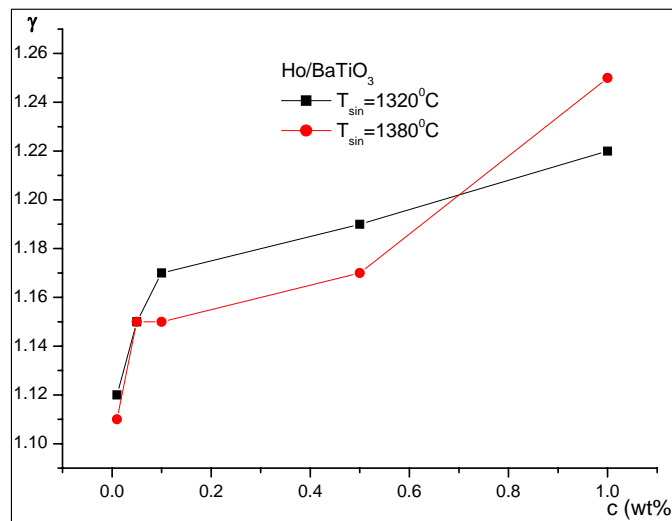


Fig.14. The critical exponent γ in function of additive concentration.

The critical exponent γ was calculated from the best fit of curve $\ln(1/\epsilon_r - 1/\epsilon_m)$ vs. $\ln(T-T_m)$ [13, 14] where γ represents the slope of curve (Fig 13).

The critical exponent γ is in the range $1 \leq \gamma \leq 2$, 1 for a sharp phase transformation and 2 for diffuse phase transformation. For BaTiO₃ single crystal γ is 1.08 and for modified BaTiO₃ gradually increases up to 2 for diffuse phase transformation.

In our case the critical exponent γ is in the range from 1.12 to 1.25, and slightly increases with the increase of additive concentration (Fig. 14). The obtained value of γ and the curves given in Fig. 7 pointed out that the specimens have almost sharp phase transition.

5. Conclusions

In this article the investigations of the influence of Ho₂O₃ on BaTiO₃ ceramics microstructure and corresponding electrical properties have been presented. Our investigations showed that ceramic densities varied from 76% of theoretical density (TD), for high doped samples sintered at 1320°C, to 93%TD for the low doped samples sintered at 1380°C. The average grain size in specimens doped with low content of additives is ranged between 20-30 μm and that with 1.0 wt% ranged from 2-5 μm . The increase of rare-earth cations content inhibits the abnormal grain growth. The dielectric constant of the investigated samples ranged from 900 to 2400 at room temperature. The decrease in dielectric constant in doped samples with the increase of dopant concentration was explained by nonhomogeneous distribution of additive throughout the specimens. All specimens have almost sharp phase transition and follow the Curie-Weiss law. The critical exponent γ is in the range from 1.12 to 1.25, and increases with the increase of additive concentration. The obtained results enable further optimization of electrical properties of barium-titanate based materials especially from synthesis-structure-properties point of view.

Acknowledgements

This research is a part of the project „Directed synthesis, structure and properties of multifunctional materials“ (172057). The authors gratefully acknowledge the financial support of Serbian Ministry of Education and Science for this work.

References

1. S.Wang, G.O.Dayton, J. Am. Ceram. Soc. 82, [10], (1999) 2677–2682.
2. C.Pithan, D.Hennings, R.Waser, International Journal of Applied Ceramic Technology, 2; 1, (2005) 1–14.
3. P.Kumar, S.Singh, J.K.Juneja, C.Prakash, K.K.Raina, Ceramics International, 37, (2011) 1697–1700.
4. Z.C.Li, B.Bergman, J. E. Ceram. Soc. 25, (2005) 441-445.
5. V. Mitic, V.Paunovic, D.Mancic, Lj.Kocic, Lj.Zivkovic, V.B.Pavlovic, Ceramic Transactions, 204, (2009) 137-144.
6. N.H. Chan, D.M.Smyth, J. Am. Ceram. Soc. 67: 4, (1984) 285-288.
7. V.Paunovic, Lj.Zivkovic, V.Mitic, Science of sintering, 42, 1 (2010) 69-79.
8. R.Zhang, J.F.Li, D.Viehland, J. Am. Ceram. Soc. 87: 5, (2004) 864-870.
9. P.W.Rehrig, S.Park, S.Trolier-McKinstry, G.L.Messing, B.Jones, T.ShROUT, J. Appl. Phys. 86: 3, (1999) 1657-1661.

10. V.Mitić, Z. Nikolić, V.Pavlović, V.Paunović, M.Miljković, B. Jordović, Lj. Zivković, Journal of the American Ceramic Society, Vol. 93[1], 2010, 132-137.
11. D.Makovec, Z.Samardzija, M.Drofenik, J.Am.Ceram.Soc. 87: 7, (2004) 1324-1329.
12. D.Lu, X.Sun, M.Toda, Japanese Journal of Applied Physics, 45: 11 (2006) 8782-8788.
13. K. Uchino and S. Namura, Ferroelectric Lett. 44, (1982). 55–61
14. I. Isupov, Ferroelectric, 90, (1989) 113–8.

Садржај: Допирана BaTiO_3 керамика је нашла велику примену за добијање *PTCR* отпорника, вишеслојних керамичких кондензатора и температурних сензора. У раду испитиване су микроструктурне и диелектричне карактеристике *Ho* допираних BaTiO_3 керамика. Концентрација адитива, Ho_2O_3 , кретала се од 0.01 до 1.0wt%. Узорци допираних BaTiO_3 керамика добијени су конвенционалном методом синтеривања у чврстој фази и синтеровани на 1320 °C и 1380 °C у трајању од 4h.

Величина зрна и микроструктурне карактеристике различитих узорака као и њихов фазни састав испитивани су *SEM* и *EDS* анализом. *SEM* анализа *Ho/BaTiO₃* допираних керамика показала је да је за узорке допираних нижом концентрацијом адитива карактеристична хомогена микроструктура са величином зрна од 20-30µm. За узорке допираних вишом концентрацијом адитива карактеристична величина зрна кретала се од 2-10µm.

Диелектричне карактеристике мерене су у температурном интервалу 20-180 °C. За узорке допираних ниском концентрацијом адитива (0.01 wt%) и синтероване на 1380 °C карактеристична је висока вредност диелектричне константе ($\epsilon_r=2400$) на собној температури. Релативно мала промена диелектричне константе са температуром карактеристична је за узорке допираних високом концентрацијом адитива. Коришћењем Кири-Вајсовог и модификованог Кири-Вајсовог закона израчунати се Киријева константа (*C*), Киријева температура (*T_c*) и критични експонент нелинеарности (γ). Добијени резултати за γ показују да је за све испитиване узорке карактеристичан оштар фазни прелаз.

Кључне речи: BaTiO_3 , микроструктура, синтеровање, адитиви, диелектричне карактеристике.
