Ho$_2$O$_3$ Additive Effects on BaTiO$_3$ Ceramics Microstructure and Dielectric Properties

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Abstract:
Doped BaTiO$_3$-ceramics is very interesting for their application as PTCR resistors, multilayer ceramic capacitors, thermal sensors etc. Ho doped BaTiO$_3$ ceramics, with different Ho$_2$O$_3$ 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/BaTiO$_3$ 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/BaTiO$_3$. A nearly flat permittivity-response was obtained in specimens with higher additive content. Using a Curie-Weiss low and modified Curie-Weiss low the Curie constant (C), Curie temperature (Tc) and a critical exponent of nonlinearity ($\gamma$) were calculated. The obtained value of $\gamma$ pointed out that the specimens have almost sharp phase transition.

Keywords: BaTiO$_3$, Microstructure, Sintering, Additive, Dielectric properties

1. Introduction

A modified BaTiO$_3$ 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 BaTiO$_3$ with semiconducting properties is used widely in electronic devices such as thermistors, varistors and energy converting systems. BaTiO$_3$ powder is usually mixed with additives in order to adjust the sintering parameters and electrical properties to the requirements of electronic...
devices [1-2]. It has been found, that the dielectric properties of polycrystalline BaTiO$_3$, 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 BaTiO$_3$: ions with larger ionic radii of valence $3^+$ and higher such as Ho$^{3+}$, Er$^{3+}$, and Dy$^{3+}$, which replaces predominately Ba$^{2+}$ sites in perovskite BaTiO$_3$ lattice, and the ions with smaller ionic radii of valence $5^+$ and higher (Nb$^{5+}$), can be incorporated into the Ti$^{4+}$ sublattice [6-9]. It has been shown that the three-valent ions incorporated at the Ba$^{2+}$ -sites act as donors, which extra donor charge is compensated by ionized Ti vacancies ($V_{Ti}''''$), the three-valent ions incorporated at the Ti$^{4+}$ -sites act as acceptors which extra charge is compensated by ionized oxygen vacancies ($V_{O}''$), while the ions from the middle of the rare-earth series show amphoteric behavior and can occupy both cationic lattice sites in the BaTiO$_3$ structure [10-12]. The substitution of Ho$^{3+}$ on Ba$^{2+}$ 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 BaTiO$_3$ doped with various content of Ho$_2$O$_3$, 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, Ho$_2$O$_3$ doped BaTiO$_3$-ceramics were used for microstructure and electrical characterization. The samples were prepared from high purity (>99.98%) commercial BaTiO$_3$ powder (MURATA) with [Ba]/[Ti]=1.005 and reagent grade Ho$_2$O$_3$ powder (Fluka chemika), by conventional solid state sintering procedure. The content of additive, Ho$_2$O$_3$, 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 $^\circ$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$^\circ$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$\alpha$ 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$^\circ$C to 180$^\circ$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/BaTiO$_3$ samples sintered at 1320 $^\circ$C to 90%TD for 0.01Ho/BaTiO$_3$ 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 ferly 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](image)

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. 2. SEM images of BaTiO3 sintered at 1380°C doped with a) 0.01wt% and b) 0.05wt% of Ho2O3](image)
Fig. 3. SEM images of BaTiO$_3$ sintered at 1320°C doped with a) 0.5wt% and b) 1.0wt% of Ho

Fig. 4. SEM images of BaTiO$_3$ 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% Ho$_2$O$_3$, 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 BaTiO$_3$ 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 BaTiO$_3$

X-ray analysis of 0.01Ho/BaTiO$_3$ samples showed only BaTiO$_3$ perovskite phase and uniform distribution of holmium (Fig.6). The increase of dopant content give rise to the appearance of second phase Ho$_2$Ti$_2$O$_7$ in 0.5Ho-BT (Fig.6). By comparison of XRD peaks of pure BaTiO$_3$ and doped BaTiO$_3$, it is evident that XRD peaks of doped samples are shifted towards to lower values of 2$\theta$ thus indicating the increase of lattice parameters, i.e. the incorporation of Ho on the Ti-sites rather than on Ba-sites in BaTiO$_3$ structure.

Fig. 7. Domain structure of 0.01wt% Ho/BaTiO$_3$ sintered at 1380 °C a) directional long domains and b) randomly oriented domains.

In samples of BaTiO$_3$ 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 1 MHz.

The dielectric permittivity in function of frequency (Fig. 8) for all investigated samples shows that, after insignificant low initial decrease in dielectric permittivity at low frequency, \( \varepsilon_r \) 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 BaTiO\(_3\) sintered at 1320°C dielectric constant is 2200 (Fig. 8a) and for samples sintered at 1380°C dielectric constant increase and \( \varepsilon_r \) is 2400 (Fig. 8b).

![Fig. 8. Dielectric constant in function of frequency for doped BaTiO\(_3\) sintered at a) 1320°C and b) 1380°C](image)

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 BaTiO\(_3\) sintered at a) 1320°C and b) 1380°C](image)

Regarding the dissipation losses (Fig. 9), a linear 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 δ) 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.](image)

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 εᵣ in function of temperature.](image)
The Curie temperature ($T_C$), determined from the maximum of the dielectric constant $\varepsilon_r$ in the dielectric temperature characteristic, was in the range from 124 to 129°C being lower for low doped Ho-BaTiO$_3$.

![Fig.12. Curie constant in function of additive concentration.](image)

All specimens have almost sharp phase transition and follow the Curie-Weiss law (Fig. 10). The Curie-Weiss law $\varepsilon_r=C/T-T_0$ 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 BaTiO$_3$.

<table>
<thead>
<tr>
<th>Sample Ho/BT (wt%)</th>
<th>$\varepsilon_r$ at 300K</th>
<th>$\varepsilon_r$ at $T_C$</th>
<th>$T_C$ [°C]</th>
<th>Curie constant [K]</th>
<th>$T_0$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 ($T_{sin}$=1320)</td>
<td>2200</td>
<td>3000</td>
<td>125</td>
<td>1.50 x 10$^5$</td>
<td>65</td>
</tr>
<tr>
<td>0.05 ($T_{sin}$=1320)</td>
<td>2000</td>
<td>2800</td>
<td>124</td>
<td>1.45 x 10$^5$</td>
<td>65</td>
</tr>
<tr>
<td>0.1 ($T_{sin}$=1320)</td>
<td>1550</td>
<td>2500</td>
<td>125</td>
<td>1.39 x 10$^5$</td>
<td>70</td>
</tr>
<tr>
<td>0.5 ($T_{sin}$=1320)</td>
<td>1000</td>
<td>1500</td>
<td>126</td>
<td>1.29 x 10$^5$</td>
<td>75</td>
</tr>
<tr>
<td>1.0 ($T_{sin}$=1320)</td>
<td>900</td>
<td>1000</td>
<td>129</td>
<td>1.20 x 10$^5$</td>
<td>80</td>
</tr>
<tr>
<td>0.01 ($T_{sin}$=1380)</td>
<td>2400</td>
<td>6300</td>
<td>124</td>
<td>1.85 x 10$^5$</td>
<td>75</td>
</tr>
<tr>
<td>0.05 ($T_{sin}$=1380)</td>
<td>2300</td>
<td>6100</td>
<td>125</td>
<td>1.66 x 10$^5$</td>
<td>70</td>
</tr>
<tr>
<td>0.1 ($T_{sin}$=1380)</td>
<td>2200</td>
<td>6000</td>
<td>126</td>
<td>1.41 x 10$^5$</td>
<td>75</td>
</tr>
<tr>
<td>0.5 ($T_{sin}$=1380)</td>
<td>1900</td>
<td>1600</td>
<td>127</td>
<td>1.28 x 10$^5$</td>
<td>88</td>
</tr>
<tr>
<td>1.0 ($T_{sin}$=1380)</td>
<td>1400</td>
<td>1500</td>
<td>128</td>
<td>1.05 x 10$^5$</td>
<td>70</td>
</tr>
</tbody>
</table>
The Curie constant (C) decreases with the increase of additive amount and have an extrapolated Curie-Weiss temperature (T₀) 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⋅10⁵) was measured in 0.01 Ho-BaTiO₃-ceramics sintered at 1380°C. The Curie constant C and the Curie-Weiss temperature T₀ values were given in Table I.

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

To quantify the diffuseness i.e. the diffuse phase transformation of εᵣ at Tₘₐₓ the equation proposed by Uchino and Nomura [13] has been used:

\[
\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_{\text{max}}} = \left(\frac{T - T_{\text{max}}}{C'}\right)^\gamma
\]

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

![Fig.13](image13.png)

**Fig.13.** The modified Curie-Weiss plot ln(1/εᵣ - 1/εₘₐₓ) vs. ln (T−Tₘ) for selected samples.

![Fig.14](image14.png)

**Fig.14.** The critical exponent γ in function of additive concentration.
The critical exponent gamma ($\gamma$) was calculated from the best fit of curve $\ln(1/\varepsilon_r - 1/\varepsilon_m)$ vs. $\ln (T-Tm)$ [13, 14] were the $\gamma$ represent the slope of curve (Fig 13).

The critical exponent $\gamma$ is in the range $1\leq\gamma\leq2$, 1 for a sharp phase transformation and 2 for diffuse phase transformation. For BaTiO$_3$ single crystal $\gamma$ is 1.08 and for modified BaTiO$_3$ gradually increases up to 2 for diffuse phase transformation.

In our case the critical exponent $\gamma$ 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 $\gamma$ 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 Ho$_2$O$_3$ on BaTiO$_3$ 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 $\mu$m and that with 1.0 wt% ranged from 2-5 $\mu$m. 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 $\gamma$ 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

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References


Садржај: Допирана BaTiO₃ керамика је нашла велику примену за добијање PTCR отпорника, вишеслојних керамичких кондензатора и температурних сензора. У раду испитиване су микроструктурне и диелектричне карактеристике Ho допиране BaTiO₃ керамике. Концентрација адитива, Ho₂O₃, кретала се од 0.01 до 1.0wt%. Узорци допиране BaTiO₃ керамике добијени су конвенционалном методом синтезирања у чврстој фази и синтезовани на 1320 °C и 1380 °C у трајању од 4h.

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

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

Кључне речи: BaTiO₃, микроструктура, синтезовање, адитиви, диелектричне карактеристике.