Microstructural and Dielectrical Characterization of Ho Doped BaTiO$_3$ Ceramics

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Abstract: The 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. Doped BaTiO$_3$ were prepared using conventional solid state reaction and sintered at 1380°C for four hours. SEM analysis of Ho/BaTiO$_3$ doped ceramics showed that the low doped samples exhibit mainly fairly uniform and homogeneous microstructure with the grain size ranged from 20-40 µm. In the samples with the higher dopant concentration the abnormal grain growth is inhibited and the grain size ranged between 2-10 µm. Measurements of dielectric properties were carried out as a function of temperature up to 180 °C at different frequencies. The samples doped with 0.01wt % of Ho, exhibit the high value of dielectric permittivity (ε_r = 2160) at room temperature. 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 Curie temperature of doped samples were ranged from 128 to 130°C. The Curie constant for all series of samples decrease with increase of dopant concentration and the lowest values were observed on samples doped with 0.01 wt % of holmium.

Keywords: BaTiO$_3$, Microstructures, Sintering, Additive, Dielectric properties.

1 Introduction

A modified BaTiO$_3$ ceramics with different additives/dopants is one of the most important groups of functional ferroelectric material due to its attractive electrical, ferroelectric and piezoelectric properties. It is used widely in electronic devices such as multilayer capacitors, thermistors, piezoelectric sensors, energy converting systems, ultrasonic convertors, radio filters, etc. [1 – 3]. The dielectric properties of polycrystalline BaTiO$_3$ are strongly dependent on the evolved microstructure which in turn depends on the type, concentration and distribution of dopants. In order to obtain BaTiO$_3$ ceramics with a high value of

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dielectric constant it is necessary to establish high density, homogeneous and fine-grained microstructure as well as uniform distribution of dopants and additives [4, 5].

Two types of dopants can be introduced into BaTiO$_3$ lattice. Ions with larger ionic radii of valence 3$^+$ and higher replaces predominately Ba^{2+} sites, and the ions with smaller ionic radii of valence 5$^+$ and higher can be incorporated into the Ti^{4+} sublattice. Considering perovskite BaTiO$_3$ structure, the incorporation of trivalent rare-earth cations (Ho^{3+}, Dy^{3+}, Er^{3+}, Yb^{3+}) modifies the microstructural and electrical properties of doped BaTiO$_3$. For lower donor concentration (< 0.5wt %), the bimodal microstructure is formed and anomalous grain growth occurred which leads to semiconductive properties of ceramics at room temperature and PTC effect [6 – 9]. On the other side, higher donor concentration leads to dielectric properties of ceramics with high breakdown voltage. Low concentration of Ho leads to substitution of Ba^{2+} ions, which is resulted in the formation of Ba$_{(1-x)}$Ho$_x$TiO$_3$ solid solution. If concentration of additives is higher than 1.0 wt %, a substitution of Ba^{2+} or Ti^{4+} ions can be realized. However, in this case, electrical resistivity is very high [10 – 12]. The substitution of Ho^{3+} on Ba^{2+} sites requires the formation of negatively charged defects. There are three possible compensation mechanisms: barium vacancies (V$_{Ba}^{//}$), titanium vacancies (V$_{Ti}^{/////}$) and electrons (e$^/$). For samples sintered in air atmosphere, the principal doping mechanism is the ionic compensation mechanism. The controversy remains concerning whether the dominant ionic mechanism is through the creation of barium or titanium vacancies. The addition of Ho$_2$O$_3$ effectively prevents the grain growth, improves the electromechanical properties and increases the temperature region where the tetragonal phase is stable.

The aim of this paper is to study the microstructure and dielectric properties of Ho doped BaTiO$_3$ as a function of different amount of dopant concentration, temperature and frequency. The microstructure of samples was observed by scanning electron microscope (SEM). The variation of dielectric constant with temperature was measured in a temperature interval from 20°C to 180°C. The Curie-Weiss and modified Currie-Weiss laws were used to clarify the influence of dopant on the dielectric properties of BaTiO$_3$.

2   Experimental Procedure

The samples of modified BaTiO$_3$ ceramics doped with 0.01, 0.1, 0.5 and 1.0 wt % Ho$_2$O$_3$ were examined. The samples were prepared by a conventional solid state sintering procedure starting from reagent grade Ho$_2$O$_3$ and BaTiO$_3$ powder. Starting powders were ball milled in ethyl alcohol for 24 hours. After drying at 200°C for several hours, the powders were pressed into disk under 120 MPa. The compacts were sintered at 1380°C in air atmosphere for four

hours. The microstructure of the sintered samples were observed by scanning electron microscope JOEL-JSM 5300 equipped with EDS (QX 2000S) system. X-ray diffraction (XRD) patterns were recorded with Cu$_{K\alpha}$ radiation in a Philips X'Pert diffractometer. Electrical contacts were prepared by silver paste. The calculation of dielectric constant was performed by measured values of capacitance, samples thickness and electrode area. The variation of dielectric constant with temperature was measured in temperature interval from 20°C to 180°C by using LCR meter Agilent 4284A at different frequencies (0.1 kHz, 1 kHz, 10 kHz, 100 kHz and 1 MHz). The dielectric parameters such as Curie temperature (T_C), Curie-Weiss temperature (T_0) and Curie constant (C) were calculated according to Curie-Weiss and modified Curie-Weiss law.

3   Results and Discussion

3.1 Microstructure characteristics

The relative density of Ho doped samples was ranged from 82% to 91% of theoretical density (TD). With the increase of dopant amount the increase of porosity is evident and density value decrease, so the largest density was for 0.01 wt % doped samples (91% TD). The SEM study showed that the samples of Ho doped BaTiO$_3$ ceramics have spherical shaped grains. The specimen average grain size doped with low content of additive (0.01 wt % and 0.1 wt % of Ho) ranged between 20–40 µm (Fig. 1). By increasing dopant concentration the grain size decreases. As a result, for 0.5 wt % of dopant the average grain size is from 10 µm to 15 µm, and for the samples doped with 1.0 wt % of Ho grain size is from 2 µm to 5 µm (see Fig. 2).


| (a) | (b) |
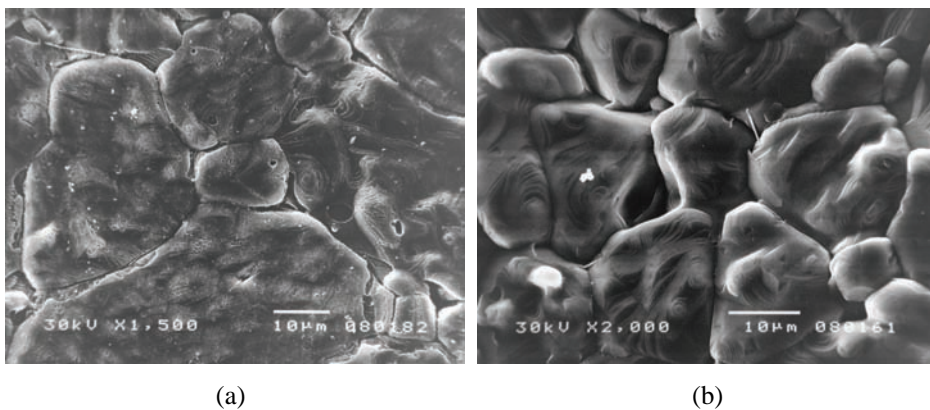
Fig. 1 – SEM *images of* (a) 0.01 *wt % and* (b) 0.1 *wt %* Ho/BaTiO$_3$ *sintered at* 1380°C.

(a)   (b)
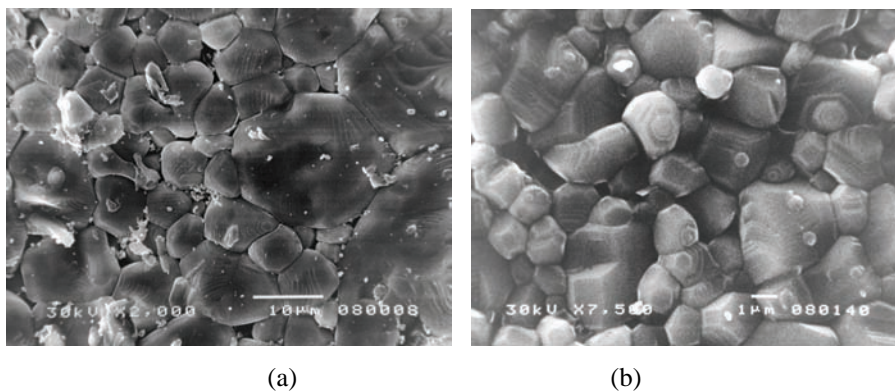
Fig. 2 – SEM *images of* (a) 0.5 *wt % and* (b) 1 *wt %* Ho/BaTiO$_3$ *sintered at* 1380°C.

The EDS analysis of samples shows uniform distribution for small concentration of Ho, while the increase of dopant concentration leads to the appearance of Ho rich regions between grains (Fig. 3). It is important to notice that EDS analysis can't resolve the concentration of element less than 1 wt % unless an inhomogeneous distribution or segregation of dopant/additive is present.
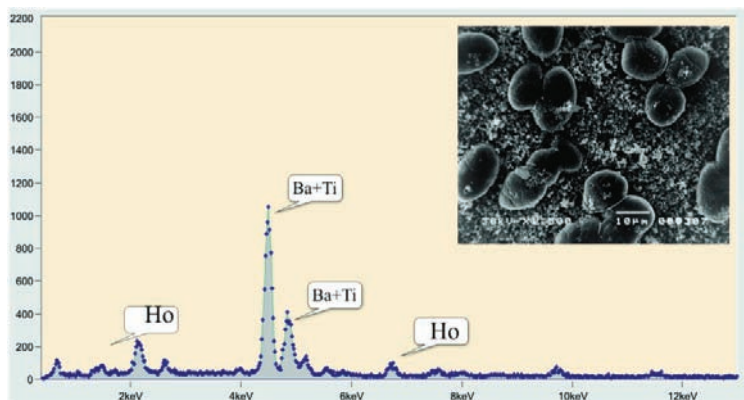

Fig. 3 – SEM/EDS *image of 0.5 wt %* Ho/BaTiO$_3$.

X-ray analysis of 0.01 Ho/BaTiO$_3$ samples shows only BaTiO$_3$ perovskite phase and uniform distribution of holmium (Fig. 4). The increase of Ho content leads to the second phase Ho$_2$Ti$_2$O$_7$ in samples doped with 0.5 wt % Ho. Comparing 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 *2θ*. This indicates the increase of lattice parameters, i.e. the incorporation of Ho on the Ti-sites rather than on Ba-sites in BaTiO$_3$ structure.
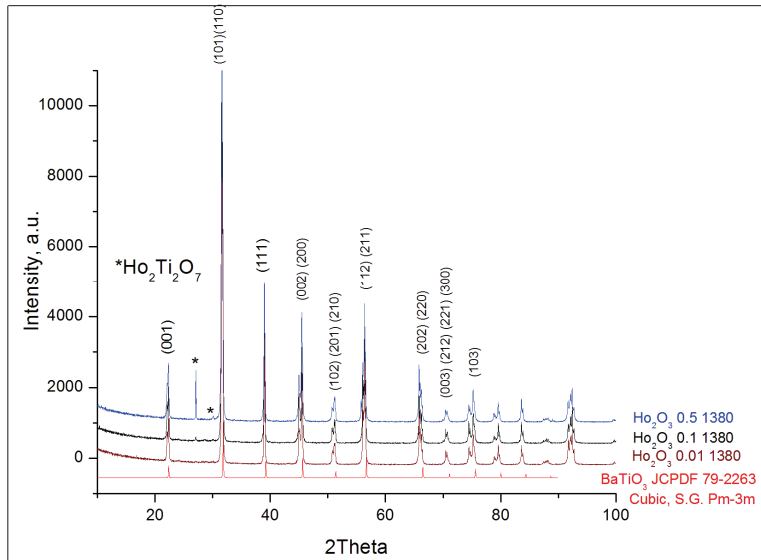
**Fig. 4** – *X-ray diffraction pattern for* Ho/BaTiO₃ *samples*.

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 and randomly oriented domains within some individual abnormal grains (Fig. 5). Looking to the herring bone domain structure it can be deduced that wall thickness was ranged between 0.05–0.1 µm and domain width was from 0.25 to 0.5 µm. EDS analysis showed that secondary abnormal grains with domain structure does not include Ho.


(a)   (b)
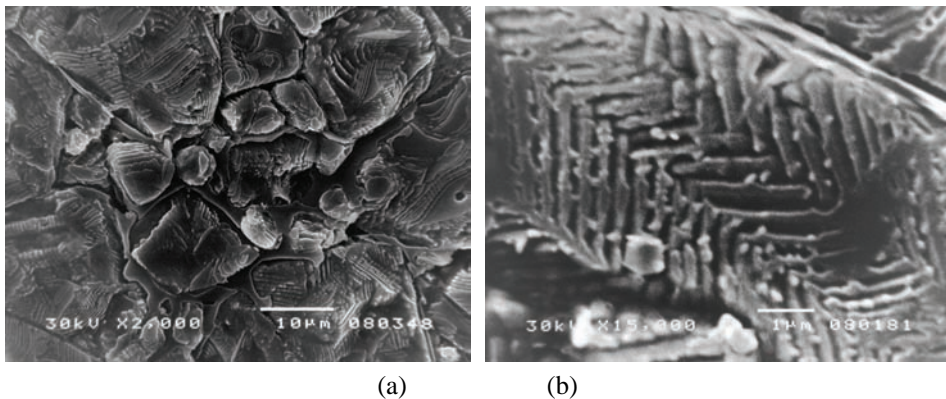
Fig. 5 – *Domain structure of* 0.01 *wt % Ho/BaTiO₃ sintered at* 1380°C
(a) *randomly oriented domains and* (b) *directional long domains*.

3.2 Electrical characteristics

The effects of additives and microstructure on the dielectric behavior of modified BaTiO$_3$ can be analyzed through permittivity-temperature dependence. The samples were measured in a temperature interval from 20°C to 180°C at different frequencies: 0.1 kHz, 1 kHz, 10 kHz, 100 kHz and 1 MHz. The temperature dependencies of permittivity at different frequencies and for different additive concentration are shown in Figs. 6 and 7.
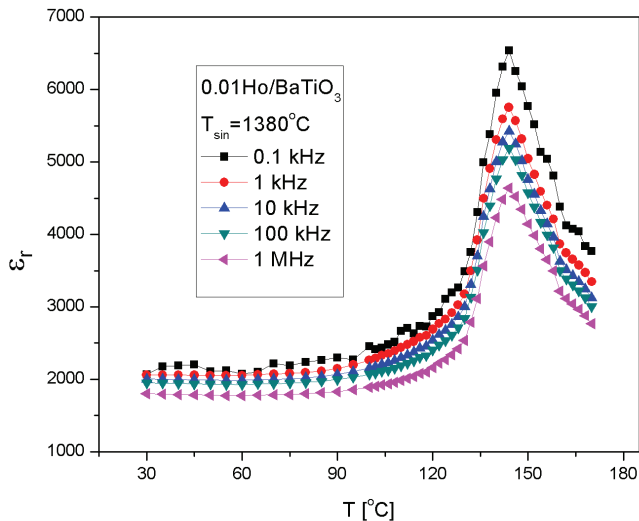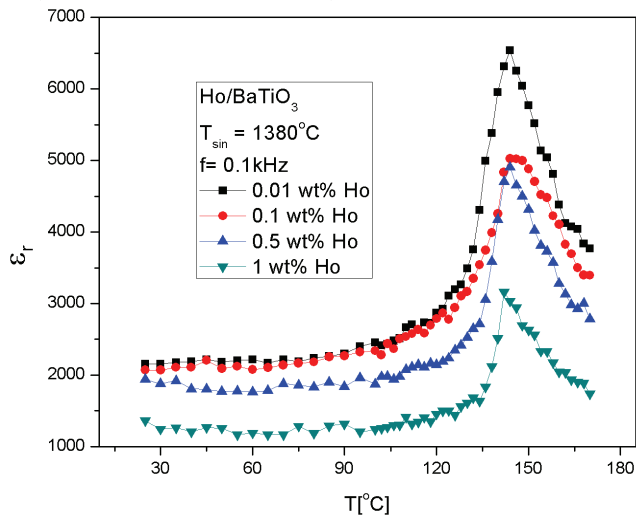

(a)
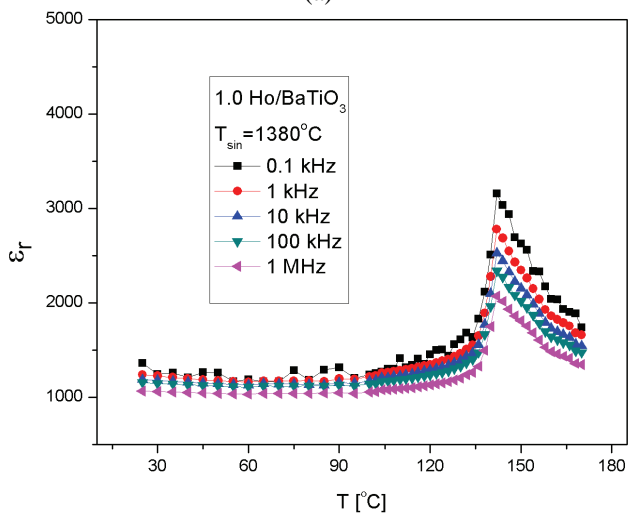
(b)

Fig. 6 – *Temperature dependence of dielectric relative permittivity of* Ho/BaTiO$_3$ *ceramic at different frequencies for samples* (a) 0.01 *wt % of* Ho *and* (b) 1.0 *wt % of* Ho.

The dielectric constant for all samples decreases with increase of frequency. The highest value of permittivity is observed at 0.1 kHz. The dielectric constant decreases with increase of dopant concentration, too. The samples with 0.01Ho/BaTiO$_3$ have the highest value of dielectric constant (ε_r = 2160) at room temperature and the highest variation of permittivity with temperature at Curie temperature (ε_r = 6540) (see Fig. 7). With increase of additive content, the change of dielectric constant with temperature is less pronounced and the flatness of permittivity temperature response can be observed for 0.5 and 1.0 wt % Ho doped samples. The lowest value of dielectric constant (ε_r = 1238) was noticed in samples doped with 1 wt % of Ho. The lower values of dielectric constant in the samples with higher concentration can be attributed to the decrease of density from 91 to 82 % *TD*, as well as to the nonhomogeneous distribution of additive throughout the specimens. Generally the pronounced permittivity response and a sharp phase transition from ferroelectric to paraelectric phase at Curie temperature are characteristic for low doped samples (0.01 and 0.1 wt % of Ho).

Fig. 7 – *Temperature dependence of dielectric relative permittivity of doped* BaTiO$_3$ *ceramics for different concentration of* Ho *at f* = 0.1 *kHz.*

The dielectric loss tangent (*tan δ*) values for all investigated samples were in the range from 0.08 to 0.002. The main characteristic for all specimens is that *tan δ* decreases with increasing of frequency. The temperature dependence of dielectric loss at different frequencies for 1.0 wt % of Ho sample is given in Fig. 8. A similar dependence was obtained for the other concentrations of holmium.
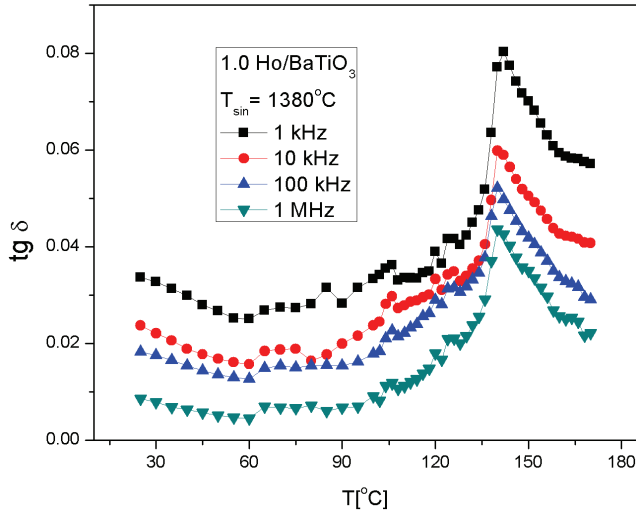
Fig. 8 – *Temperature dependence of dissipation losses of doped*
BaTiO$_3$ *ceramics for different frequencies* (*c = 1 wt % of* Ho).

The permittivity for all samples can be characterized by the Curie-Weiss law:

$$\varepsilon_r = C / T - T_0, \tag{1}$$

where *C* is the Curie constant and T_0 Curie-Weiss temperature, which is close to the Curie temperature. The Curie-Weiss temperature (T_0) and the Curie constant (*C*) was obtained by fitting the plot of inverse value of dielectric constant vs. temperature (Fig. 9). The values of dielectric parameters are given in **Table 1**.

Table 1
Dielectric parameters for Ho/BaTiO$_3$ (0.1 kHz, T_{sin}= 1380°C).

| Ho/BaTiO$_3$ [wt %]	$_r$ at 300K	$_r$ at T_C	T_0 [°C]	C [K 10^5]	γ
0.01	2160	6540	107.6	2.13	1.01
0.1	2070	5020	100.9	2.08	1.05
0.5	1940	4900	110.3	1.49	1.15
1	1238	2779	102.9	1.10	1.19

The Curie constant (*C*), as well as the Curie-Weiss temperature (T_0), decreases with increase of additive concentration for all series of samples, which is consistent with microstructure characteristics. The lowest value of T_0

(100.9°C) was measured in samples doped with 0.1 wt % of Ho. T_0 has very low value, whereas T_C has values similar with T_C for non-doped BaTiO$_3$. The highest values of C (2.13·10^5 K) was measured in 0.01 Ho/BaTiO$_3$ ceramics samples (see Fig. 10).
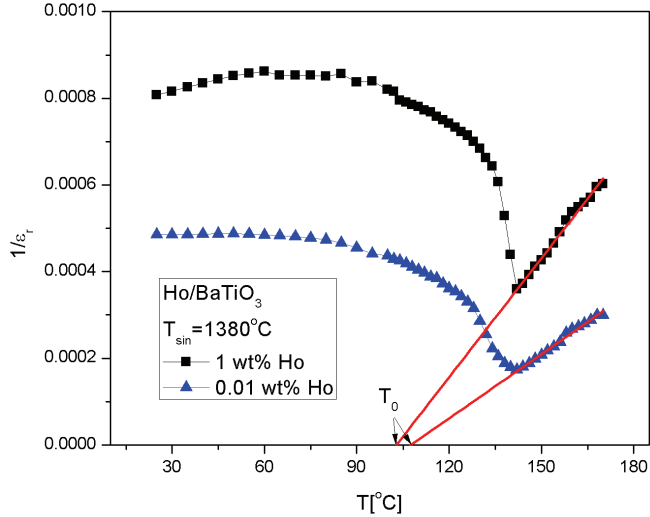
Fig. 9 – *Temperature depenedence of reciprocal value of* ε$_r$
*for* 0.01 *wt % and* 1 *wt % of* Ho *doped* BaTiO$_3$.
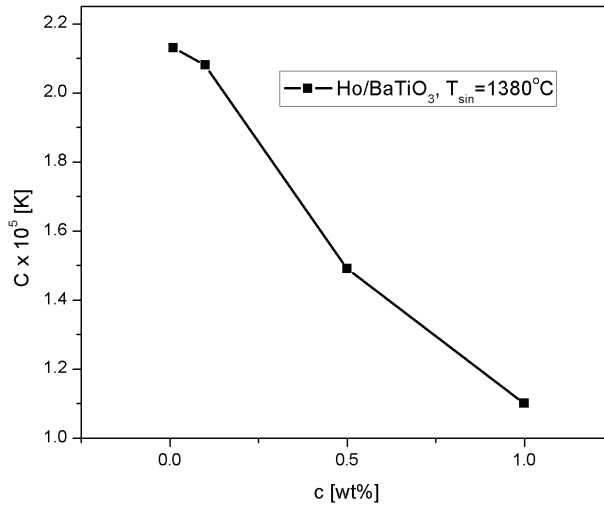
Fig. 10 – *Curie constant as a function of additive concentration.*

In order to investigate the Curie Weiss behavior, the modified Curie-Weiss law was used [13, 14]:

$$1/\varepsilon_r = 1/\varepsilon_{r\max} + (T - T_{\max})^{\gamma}/C', \tag{2}$$

where ε_r is dielectric constant, $\varepsilon_{r\max}$ maximum value of dielectric constant, $T_{\max}$ temperature where the dielectric constant has its maximum, γ critical exponent for diffuse phase transformation, and C' the Curie-Weiss-like constant. The critical exponent γ was calculated from the best fit of curves $\ln(1/\varepsilon_r - 1/\varepsilon_{r\max})$ vs. $\ln(T - T_{\max})$ (Fig. 11).
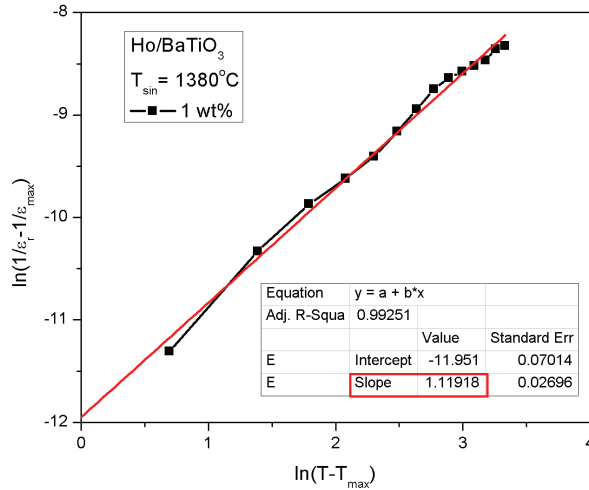
Fig. 11 – *The modified Curie-Weiss plot* $\ln(1/\varepsilon_r - 1/\varepsilon_{r\max})$ *vs.* $\ln(T - T_{\max})$ *for* 1*wt %* Ho *doped ceramic sample.*
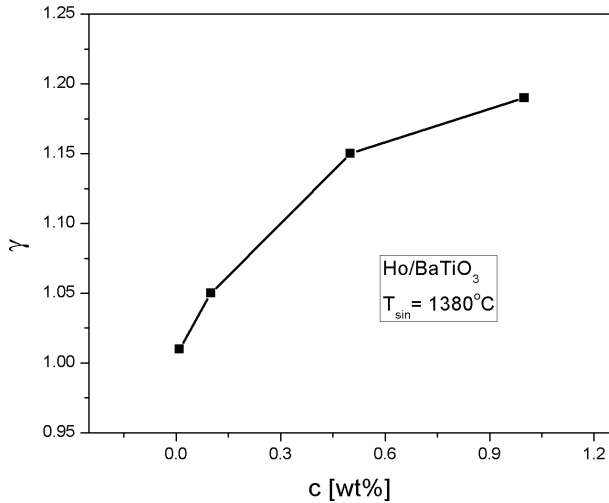
Fig. 12 – *The critical exponent* γ *as a function of additive content.*

For low concentration of dopant the critical exponent γ is in a range from 1.01 to 1.05 for 0.01 wt % and 0.1 wt % Ho doped BaTiO$_3$ samples, respectively. The low values of γ could be predicted from the shape of ε_r vs. T plots which show the sharp phase transition from ferroelectric to paraelectric phase at Curie point. The critical exponent γ slightly increase of additive concentration, pointed out a diffuse phase transformation for heavily doped samples (see Fig. 12). The highest value of γ (1.19) was calculated for 1.0 wt % Ho doped samples.

4   Conclusion

In this article the influence of the Ho dopant content on microstructure and electrical properties of HoBaTiO$_3$ ceramics sintered at 1380 ^{O}C has been investigated. The main characteristic of low doped samples is the abnormal grain growth with the average grain size range between 20-40 µm. The increase of concentration of additives in samples causes decrease of average grain size, so, all samples have a small grained microstructure. The EDS analysis of samples with lower concentration of additive indicated a uniform incorporation of dopants within the ones. For the samples with 0.5 wt % and greater concentration of additives, XRD analysis showed the incorporation of Ho on the Ti-sites rather than on Ba-sites in BaTiO$_3$ structure. The highest value of dielectric permittivity at room temperature and the greatest change of permittivity as a function of temperature show the sample with lowest concentration of additives. At room temperature the value of relative dielectric permittivity for 0.01 wt % Ho/BaTiO$_3$ sample is 2160. In samples with higher concentration of additives, the changes of permittivity as a function of temperature are weakly pronounced ($\varepsilon_{rmax} / \varepsilon_{rmin} \approx 2$). The Curie constant ($C$) decreases with increase of additive concentration and the highest values exhibit the sample with 0.01 wt % of Ho. The critical exponent γ is in range from 1.0 to 1.19, and increases with the increase of additive concentration.

5   Acknowledgment

6   References

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