



## Microstructure of doped barium titanate prepared from polymeric precursors

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Barium titanate is used extensively as a dielectric in ceramic capacitors, particularly due to its high dielectric constant and low dielectric loss characteristics. It can be made semiconducting by addition of certain dopants and by proper modification of grains and grain boundary properties obtaining very interesting characteristics for various applications. The synthesis method and sintering regime have a strong influence on properties of obtained barium titanate ceramics. Doped barium titanate was prepared with Nb<sup>5+</sup> and Y<sup>3+</sup> ions as donor dopants, and with Mn<sup>2+</sup> ions as acceptor dopant by polymeric precursors method. By this procedure nanosized powders were obtained after calcination. Sintering was performed in the temperature range of 1290°C to 1380°C. The microstructure of doped BaTiO<sub>3</sub> was performed using scanning electron microscopy. The influence of dopants and sintering temperature on grain size was analysed.

*Keywords: Barium titanate, doping, polymeric precursors, SEM, microstructure, grain size.*

### Microestructura de titanato de bario dopado preparado a partir de precursores poliméricos.

El titanato de bario se usa extensamente como dieléctrico en condensadores cerámicos, debido principalmente a su elevada constante dieléctrica y a sus bajas pérdidas dieléctricas. Puede hacerse semiconductor mediante la adición de ciertos dopantes y a través de modificaciones adecuadas de las propiedades de los granos y los bordes de grano se obtienen características muy interesantes para muchas aplicaciones. El método de síntesis y el régimen de sinterización tienen una fuerte influencia sobre las propiedades del titanato de bario cerámico. El titanato de bario dopado con Nb<sup>5+</sup> y Y<sup>3+</sup> como dopantes donores y con Mn<sup>2+</sup> como dopante aceptor se preparó mediante el método de precursores poliméricos. Mediante este procedimiento se obtuvieron polvos nanométricos después de la etapa de calcinación. La sinterización se realizó en el intervalo de temperaturas entre 1290°C y 1380°C. La microestructura del BaTiO<sub>3</sub> dopado se estudió usando microscopía electrónica de barrido. Se analizó la influencia de los dopantes y la temperatura de sinterización sobre el tamaño de grano.

*Palabras clave: Titanato de bario, dopado, precursores poliméricos, MEB, microestructura, tamaño de grano.*

### 1. INTRODUCTION

Up to date, barium titanate is the most extensively investigated ferroelectric material, because it is extremely interesting from the view point of practical applications (1, 2). First, because it is chemically and mechanically very stable, secondly, because it exhibits ferroelectric properties at and above room temperature, and finally, because it can be easily prepared and used in form of ceramic polycrystalline samples.

Barium titanate can be made semiconducting by addition of certain dopants and by proper modification of the grains and grain boundary properties obtaining very interesting characteristics for various applications. Since the semiconducting bulk material gives the necessary mechanical stability, the dielectric layer in grains may be very thin (a few micrometers), resulting in a large capacitance per unit area and determining the electrical characteristics. Now a days, through proper tailoring of grain boundaries, doped barium titanate ceramics are commercially available, and have been widely used for different applications. Hence, the microstructure and grain boundary play a very important role in determining the electrical characteristics (3, 4).

It is known that semiconducting barium titanate can be produced by atmospheric reduction (the formation of oxygen vacancies) or by donor doping, with trivalent ions (e.g. lanthanum, yttrium) on Ba<sup>2+</sup>-ion sites, or with a pentavalent ion (e.g. niobium, tantalum) on the Ti<sup>4+</sup>-ion sites (7). This substitution is charge compensated by a valence shift, providing a shallow donor level from which electrons can be excited into the conduction 3d band (5). The powder preparation and sintering conditions strongly affect the microstructure obtained. Thus, the abnormal grain growth observed in semiconducting BaTiO<sub>3</sub> caused by dopant concentration and their effects on BT behaviour are not fully understood (6).

In view of the above statements, our paper reports the work carried out on donor doped barium titanate with niobium and yttrium in the presence of small amount of manganese-compounds as acceptor dopant starting from organometallic precursors prepared by Pechini process. The influence of dopants on the microstructure was analysed.

## 2. EXPERIMENTAL PROCEDURE

The barium titanate (BT) powders were prepared from organometallic complex based on Pechini procedure (7). Niobium (calculation was made based on 0.4 mol % of  $\text{Nb}_2\text{O}_5$ ), yttrium (calculation was made based on 0.4 mol % of  $\text{Y}_2\text{O}_3$ ) and manganese (calculation was made based on 0.05 and 0.1 mol % of manganese oxide) are used as dopants. The ratio Ba/Ti was 1:1. The Pechini process was carried out as a three-stage process for the preparation of a polymeric precursor resin. First, a mixture of cations (barium, titanium, niobium and manganese) is formed in citric acid and ethylene glycol solution; secondly, the cations become chelated; third the polymeric resin is formed and the decomposition of polymeric resin occurred during thermal treatment. The temperature for thermal treatment was determined after previous experiments (8,11). Thus, it was analyzed the presence of carbonate in mixture. Finally, the obtained organometallic complex were thermal treated at 300°C for 8 hours with heating rate of 2°/min to release organic materials of previous solutions. More details about procedure was reported earlier herein (8). After calcination at 700°C for 4 hours with heating rates of 20°C/min and milling, the powders were pressed at 175 MPa into pellets of 10 x 2.5 mm<sup>2</sup> using cold isostatic press. Sintering was performed in the range from 1290°C up to 1380°C for 2 hours. The temperature regime during sintering were adjusted for 5°C/min during heating and 10°C/min during cooling in air atmosphere. The Figure 1 shows the processing flow chart of  $\text{Nb}^{5+}$  and  $\text{Y}^{3+}$  doped BT.

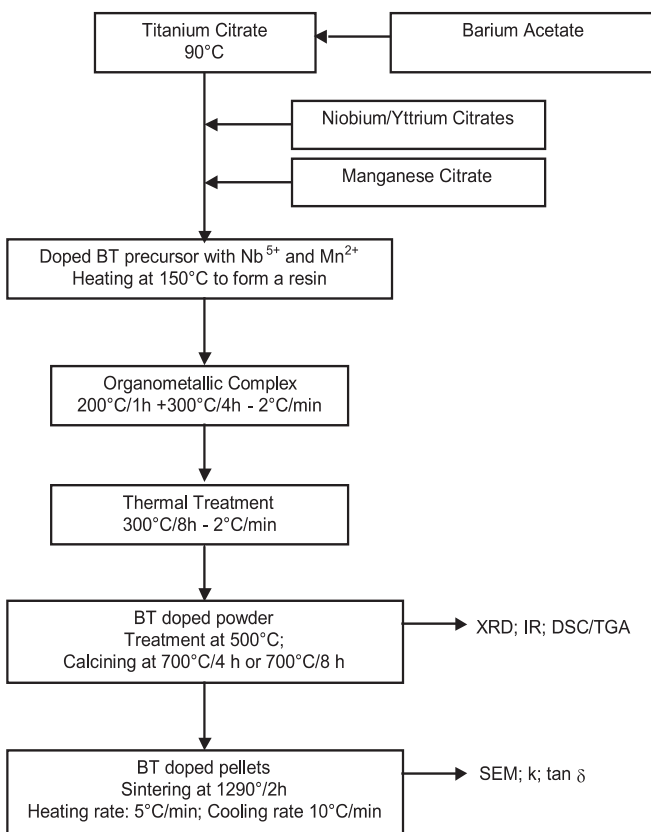


Figure 1. Flow chart of the processing  $\text{Nb}^{5+}$  and  $\text{Y}^{3+}$  doped BT.

Scanning electron microscopy (SEM) observation were carried out to identify the microstructure (Topcon SM-300). The samples for microstructure analysis were prepared by thermal etching for 20 minutes at temperature 50°C degrees low than sintering temperature.

## 3. RESULTS AND DISCUSSION

It is well known that precursor-prepared barium titanate powders may reach a high chemical homogeneity. In our study, based on the Pechini procedure, a three-stage process was employed to prepare the precursor polymeric resin of niobium and yttrium doped barium titanate. The kinetic of phase formation (analysed by XRD) and the carbonate formation (analysed by infrared to verify the presence of carbonates) were reported earlier herein (8,11). The tendency of  $\text{CO}_2$  to adsorb on to perovskite surface is well established in literature data (9-11). During our previous experiments it has been necessary to extrapolate the conditions for successful elimination of carbonates before calcination process of powders, because once the carbonate has been formed, it is very difficult to eliminate. The carbonaceous compounds were not detected in the sintered bulk of doped barium titanate (11).

The powders obtained after calcination were fine-grained and significantly influenced on the processes of consolidation and densification. The particles of doped BT powders could be considered, as a rough approximation, spherical in shape and with an average diameter of approximately 20 nm. These results were reported earlier (11).

It is known that dopants have a deep effect on the densification and microstructure evolution of  $\text{BaTiO}_3$ . However, in addition to the variety of functions that a dopant can display, analysis of the dopant role is rather complicated. Niobium in lower concentration enhances grain growth, while close to or above the limit of dopant solubility in barium titanate it inhibits grain growth (13). Yttrium has a prominent influence on grain growth and could enhance the grain growth. On the other hand, addition of the small amount of manganese has more expressed effect on the dielectric properties of barium titanate. In fact, the major role of both donor cations ( $\text{Nb}^{5+}$  and  $\text{Y}^{3+}$ ) and acceptor cation ( $\text{Mn}^{2+}$ ) is their ability to influence the grain boundary mobility because the charge compensation has an important effect on that. In the investigated case was chosen the same amount of donor concentration (0.4 mol %). According to literature data the concentration of 0.4 mol % is close to limit of solubility of niobium and yttrium dopants in barium titanate in observed temperature regime (14).

Niobium and yttrium have been shown different influence on the microstructure of barium titanate. Niobium is a typical donor dopant. Since the niobium ion has a different valence than that of the barium or titanium ion, substitution by niobium produce a charge imbalance. According to ionic radii,  $\text{Nb}^{5+}$  can be substitute to  $\text{Ti}^{4+}$ . It is commonly accepted in literature that manganese, because of small ionic radii, also substitutes  $\text{Ti}^{4+}$ . Because the introduction of manganese ions into barium titanate trap and increase the number of electrons, the small amount of  $\text{Mn}^{2+}$  in investigated system could compensate the charge imbalance caused by adding of  $\text{Nb}^{5+}$  in barium titanate(15-18). Otherwise  $\text{Mn}^{2+}$  could segregate at grain boundaries, contrary of niobium that can diffuse into barium titanate grains. At relatively low temperature (1290°C) and after short time of sintering (2 hours) in barium titanate

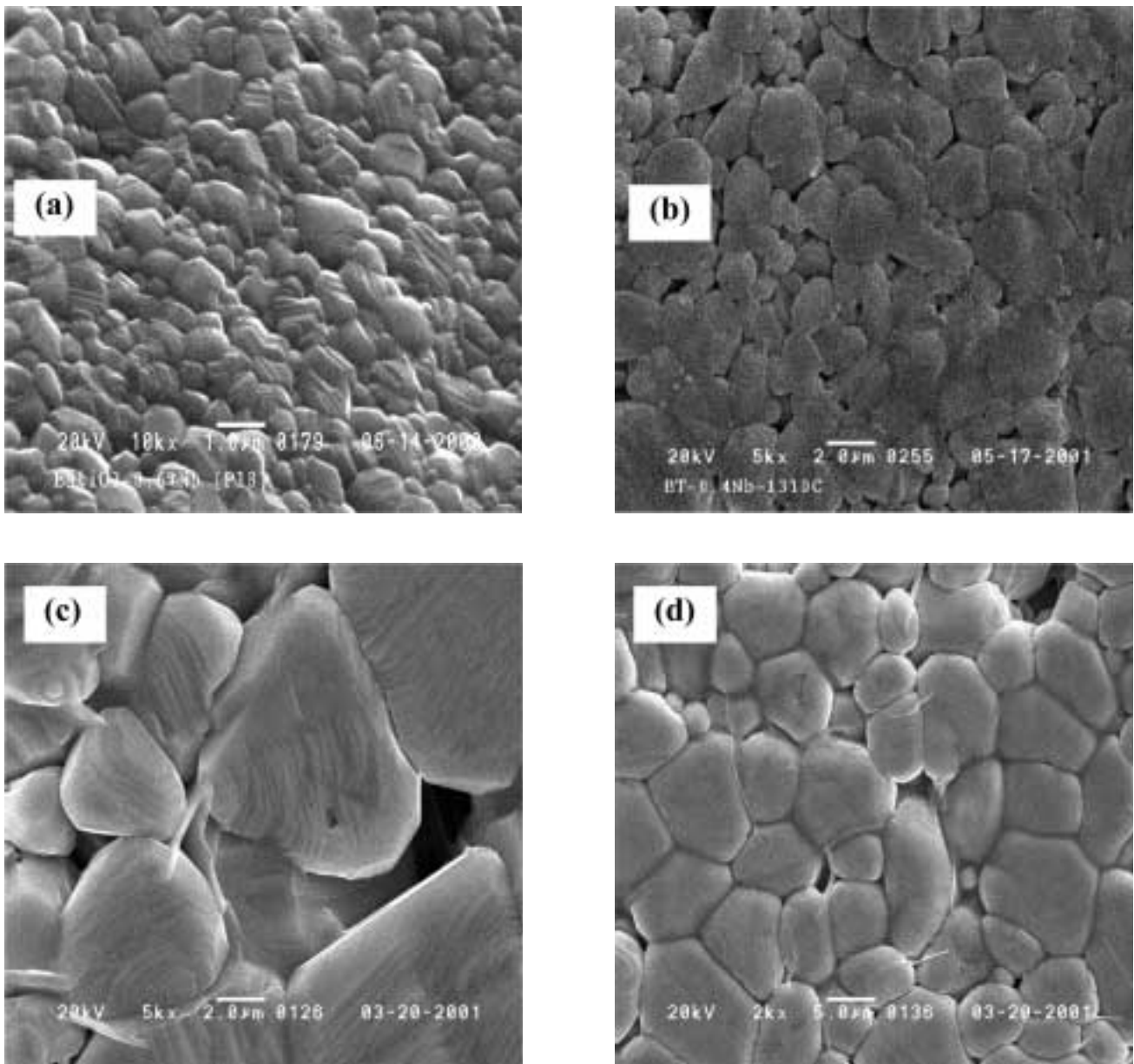


Figure 2. Microstructure of barium titanate doped with 0.4 mol % niobium and 0.01 mol% manganese at sintering temperature: a) 1290°C, b) 1310°C, c) 1330°C, d) 1380°C.

doped with 0.4 mol % of niobium significant grain growth was not observed. The grain size was about 500 nm (Fig. 2a). Contrary, the microstructure of niobium doped barium titanate sintered at 1310°C (Fig. 2b), 1330°C (Fig. 2c) and 1380°C (Fig. 2d) showed a rather significant grain growth. The microstructure was not rather uniform and grains with various sizes were observed. After sintering at 1310°C, besides a small amount of grains of 500 nm, the most of the grains were approximately of 2  $\mu\text{m}$ . Microstructure after sintering at 1330°C and 1380°C was fine-grained, less uniform than at the lower sintering temperature and consisted of grains sized in rough approximation of 6  $\mu\text{m}$ , and 7  $\mu\text{m}$ , respectively. Besides, the presence of small amount of liquid phase and inter-grain porosity was also observed. Meanwhile, the abnormal grain growth is not noticed. Generally, the abnormal grains may nucleate from the dense agglomerates of calcinated powders causing the chemical inhomogeneity and reducing the liquid

phase formation temperature. The temperature is lower than the  $\text{BaTiO}_3\text{-Ba}_6\text{Ti}_{17}\text{O}_{40}$  eutectic temperature resulting in the shrinkage of the intra-agglomerate pores, increase of volume fraction and size of abnormal grains. The pores could be trapped in the abnormal grains besides fine grain microstructure. Finally, the result is non-homogeneous microstructure (15-18). In the niobium doped barium titanate prepared from polymeric precursors this kind of anomaly was not mentioned. This point out that change-over in the abnormal grain growth with sintering temperature or the so-called doping anomaly in barium titanate and the evidence of abnormally large grains was not observed. The small amount of liquid phase enhanced the grain growth, but did not influenced on the generation of dendrite morphology in the fine grains region.

On the other hand,  $\text{Y}^{3+}$  is the donor dopant and replaces the  $\text{Ba}^{2+}$  ions at A-site perovskite lattice resulting in the n-type



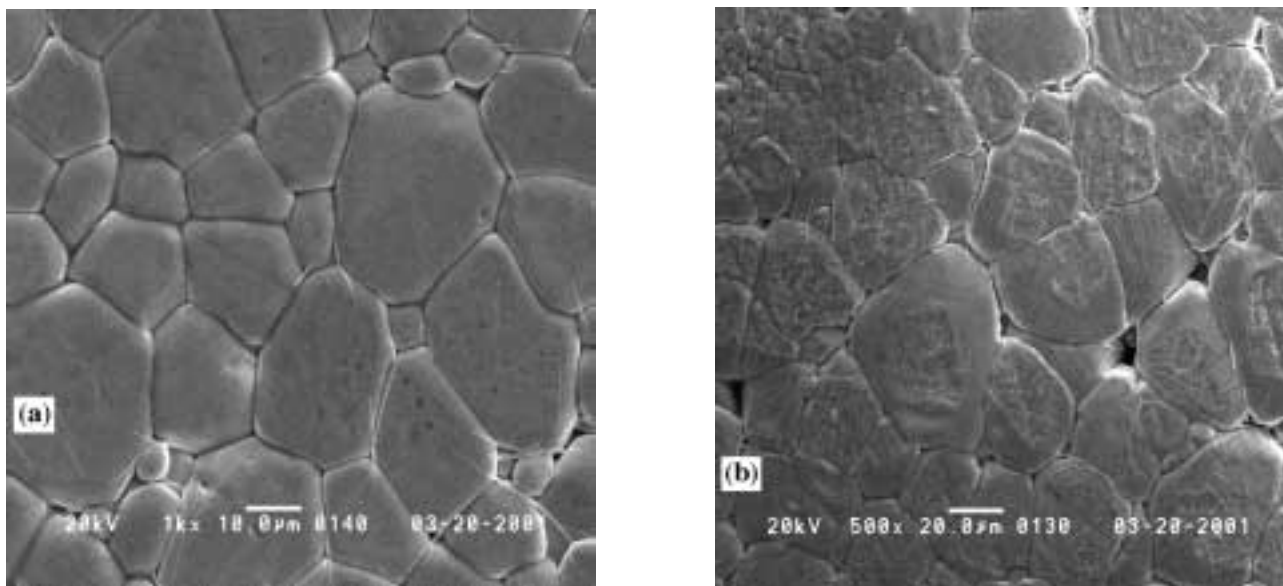


Figure 3. Microstructure of barium titanate doped with 0.4 mol % yttrium and 0.5 mol% manganese at sintering temperature: a) 1330°C, b) 1380°C.

conduction. With  $Mn^{2+}$  as an acceptor dopant, yttrium dopant influences on the boundary mobility. The behaviour of this type of material is closely related to the specific properties of grain boundaries and near boundary regions, in which the properties are different from the bulk.

The microstructure of yttrium doped barium titanate showed the coarse-grained structure comparing with fine-grained niobium doped barium titanate (Fig. 3). Otherwise, the presence of large grains, larger than 100  $\mu m$  were not noticed. According to literature data, extremely large grains without presence of any liquid phase is indicative for yttrium doped barium titanate above sintering temperature of 1350°C. This seems to indicate that the solid state diffusion mechanism is the main sintering mechanism. Meanwhile, the presence of manganese cations besides yttrium cations probably influenced both the change of the grain size of doped barium titanate and the mechanism of sintering. Taking into account that manganese cations replace  $Ti^{4+}$  cations, the small amount of excess of titanium rich phase is possible above the  $BaTiO_3$ - $Ba_6Ti_{17}O_{40}$  eutectic temperature. Thus, the rather small amount of liquid phase can change the morphology of yttrium doped barium titanate grains. The grain size of yttrium doped barium titanate sintered at 1330°C (Fig. 3a) was approximately 22  $\mu m$ . After sintering at 1380°C, the grains growth was observed with grain size in rough approximation of 32  $\mu m$  (Fig. 3b).

#### 4. CONCLUSIONS

$Nb^{5+}$  and  $Y^{3+}$  doped barium titanate in the presence of manganese ions was synthesized by polymeric precursor method from citrate solutions. The microstructure development of niobium doped barium titanate was fine-grained with grains in the range from 500 nm up to 7  $\mu m$ , depending on the sintering temperature. The microstructure of yttrium doped barium titanate was coarse-grained with grain size from 22 up to 32  $\mu m$  depending on sintering temperature. In niobium and yttrium doped barium titanate the abnormal grain growth was not observed.

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