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Secondary phases in Nb-doped $BaTiO_3$ ceramics

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Abstract

In this work, the effect of Nb_2O_5 addition on the microstructure of $BaTiO_3$ was studied. From XRD diagrams, a diminution in tetragonality parameters with an increase in dopant concentration was observed. In order to determine morphology and composition of secondary phases in niobium-doped barium titanate, EDAX and SEM analyses were carried out. It was found that a concentration of dopant higher than 0.15 mol% leads to fine-grained $BaTiO_3$ without abnormal grain growth. Otherwise, compositions of secondary phases correspond to the titanium-rich region in the BaO–TiO_2 phase diagram. Besides, the titanium content in the precipitate increases with the Nb_2O_5 addition.

Keywords: A. Grain growth; B. Microstructure; D. $BaTiO_3$ and titanates

1. Introduction

It is well known that the microstructure determines electrical properties in $BaTiO_3$ ceramics [1–5]. In order to optimise the dielectric properties, high-density and homogeneous microstructures with controlled grain size are desirable [1]. It has been shown that when dopants are introduced in the $BaTiO_3$ microstructure, fine-grained $BaTiO_3$ could be achieved (1–5 μm), leading to improved properties for electronic applications [6–8]. However, heterogeneous microstructural development is frequently observed and it has become a recognised problem in the ceramic industry. Heterogeneous microstructures involve abnormal grain growth, microcracking, unwanted compositional gradients and secondary phases precipitation [9]. All these may originate from many possible causes and affect strongly the reproducibility and quality of the electrical properties in $BaTiO_3$.

In this work, we analyse the effect of incorporating different amounts of Nb_2O_5 on the microstructural development of $BaTiO_3$. Special interest is placed in the morphology and composition of secondary phases.

2. Experimental

Samples were prepared from commercial $BaTiO_3$ powder (TAM Ceramics Inc., Sr <150 ppm as principal impurity, average grain size 0.84 μm, Ba/Ti $=1$) and 0.05, 0.15, 0.30 and 0.60 mol% of Nb_2O_5 (Fluka AG, Buchs SG, 99% purity). Raw materials were mixed in alcoholic medium by stirring in a high-speed turbine at 6000 rpm for 5 min. Then, slurries were dried at 65 °C until constant weight. After being cooled down, samples were isostatically pressed in cylinders of 8 mm in diameter. Finally, the pellets were sintered at 1350 °C for 2 h with a heating and cooling rate of 3 °C/min.

Sample densities were measured by Archimedes' Method. X-ray diffraction (XRD) analyses were carried out on sintered samples, using a Philips PW 1050/25 equipment with CuK_α radiation and a Ni filter, at 40 kV and 30 mA. In order to quantify the cell distortion, tetragonality parameters (c/a) were calculated by considering the reflections of the (111) and (200) planes of $BaTiO_3$. To analyse the microstructures, the samples were polished with SiC paper and diamond paste and thermally etched. Etched samples were analysed by scanning electron microscopy (SEM) using a Philips 505 microscope, while elemental analyses were carried out by using an EDAX (Topcon SM-300 and PGT digital spectrometer). In order to determine the average grain

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size of the microstructures, image analysis Soft Imaging System AnalySIS® 3.0 on SEM images was performed. Finally, electron paramagnetic resonance (EPR) spectroscopy on sintered and grounded samples was performed through a Bruker spectrometer (band X) with a gain of 2×10^4, a power of 5 dB and a modulation amplitude of 6.3 Gpp. Double integrated intensity of EPR signals (DII) corresponding to the detected paramagnetic species was calculated, as Murugaraj et al. reported in their article [10].

3. Results and discussion

Figs. 1 and 2 show the SEM micrographs of samples sintered at 1350 °C. From Fig. 1, pure $BaTiO_3$ and doped-$BaTiO_3$ with a Nb_2O_5 concentration $\leqslant$0.15 mol% showed abnormal grain growth (Fig. 1A–C). In these samples, coarsened grains (100 μm) embedded in a fine-grained matrix are observed. For higher dopant concentrations, the microstructures are quite different and small grains ($\leqslant$1 μm) are obtained after sintering at

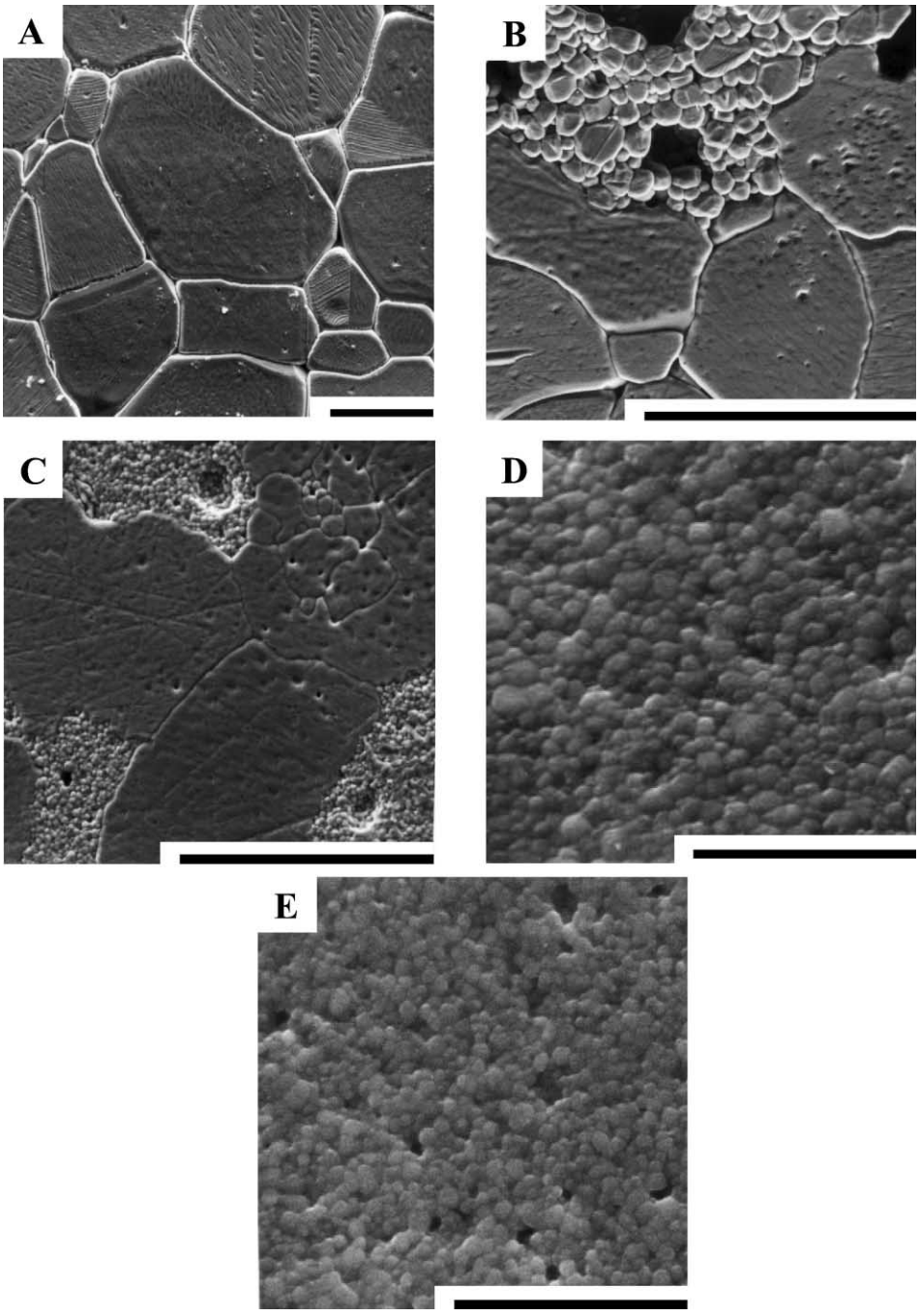

Fig. 1. SEM micrographs of the samples (A) pure $BaTiO_3$, and doped with (B) 0.05, (C) 0.15, (D) 0.30, (E) 0.60 mol% Nb_2O_5, sintered at 1350 °C for 2 h. Bar length = (A), (B) and (C) 100 μm; (D) and (E) 10 μm.

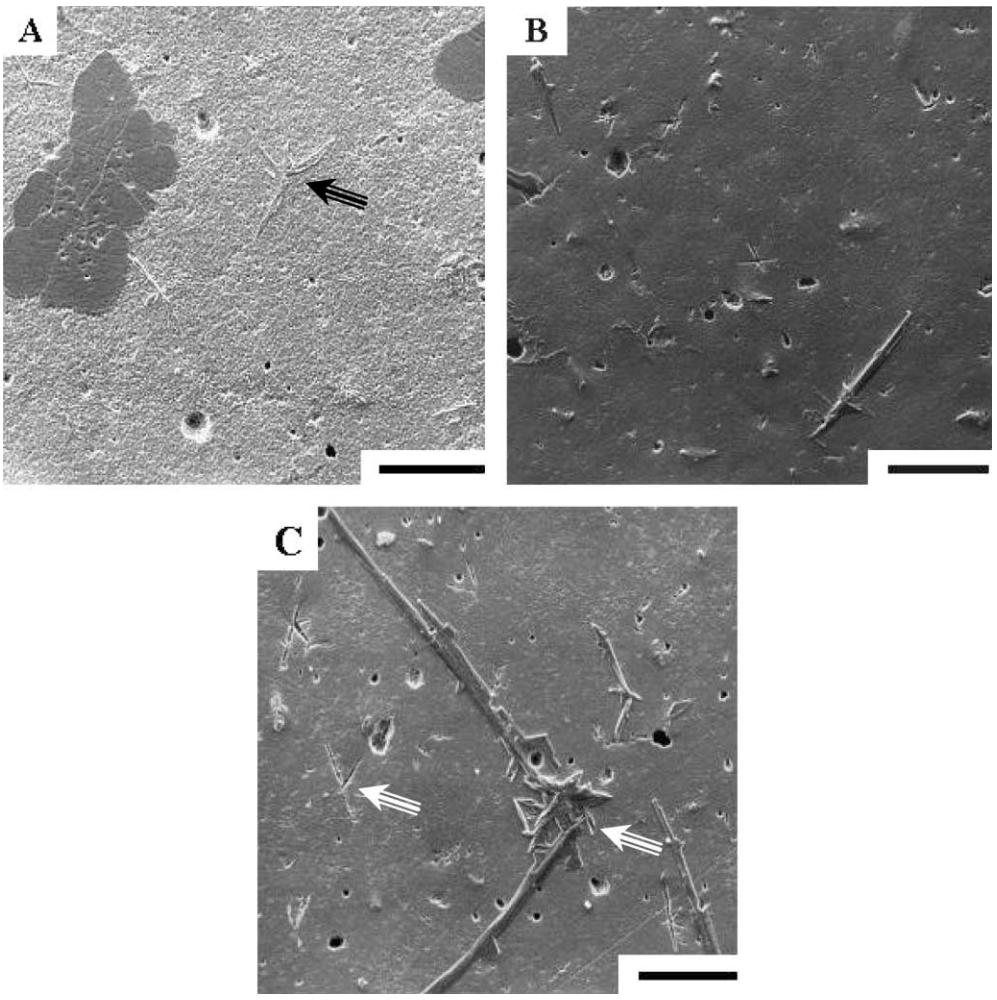

Fig. 2. SEM micrographs showing regions with secondary phases and etching prints (both phenomena indicated by arrows), corresponding to $BaTiO_3$ doped with (A) 0.15, (B) 0.30, (C) 0.60 mol% Nb_2O_5 sintered at 1350 °C for 2 h. Bar length = 100 μm.

1350 °C. On the other hand, in samples doped with Nb_2O_5 concentrations higher than 0.05 mol%, the development of a second phase with the appearance of elongated needles (100–200 μm) took place (Fig. 2A–C). In $BaTiO_3$ doped with 0.15 mol% Nb_2O_5, the needles are formed only in the fine-grained regions, as indicated by the arrow. From Fig. 2B and C, some etching prints are observed, which are possibly originated by the secondary phases during the etching treatment.

In Fig. 3, the density values of $BaTiO_3$ ceramics against dopant concentration data are showed. From Fig. 1A and B, it is possible to observe that low dopant concentrations (0.05–0.15% Nb_2O_5) lead to abnormal grain growth along with intra and intergranular porosity. This phenomenon is responsible for the decrease in the density values (Fig. 3) with respect to the pure-$BaTiO_3$. On the other hand, the highest density measured for the sample doped with 0.30% Nb_2O_5 is associated to a more uniform and fine-grained microstructure. However, the secondary phases presumably act as structural defects and generate microcracks, especially in the sample

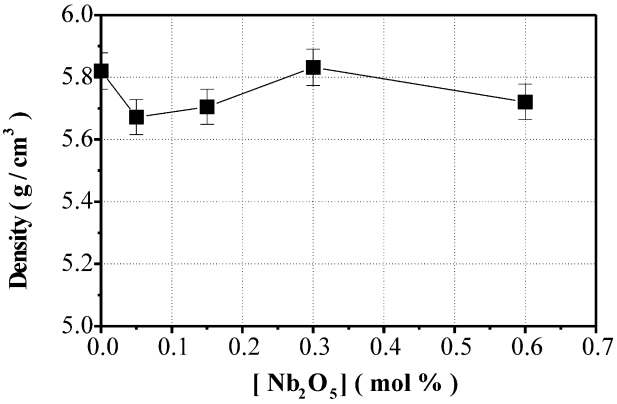

Fig. 3. Density vs. dopant concentration curve.

doped with 0.60 mol% Nb_2O_5. Consequently, density values do not increase when dopant concentration increases above 0.30 mol %.

From SEM results it is possible to deduce that heterogeneous dopant distribution in the system does not allow a successful microstructural control in the slightly

doped $BaTiO_3$ ceramics (Fig. 1B and C). This is because at low dopant concentration, it is difficult to get a system in which each particle of $BaTiO_3$ contacts a Nb_2O_5 particle before the sintering treatment. Consequently, some $BaTiO_3$ particles are far from the dopant particles. At 1350 °C, for the niobium ions to access into the $BaTiO_3$ particles, large diffusion paths are required. In order to get a homogeneous distribution of the dopant in the system, it would be necessary to keep the samples at high temperature for longer times. When the system contains a non-homogeneous dopant distribution, the dopant enriched regions present limited grain growth and high secondary phases precipitation. Conversely, the dopant deficient regions show exaggerated grain growth and strong intragrain porosity (Fig. 1B and C).

In samples doped with 0.30 and 0.60% Nb_2O_5, the dopant amount is high enough to favour a better distribution of Nb_2O_5 particles among the $BaTiO_3$ particles. Then, microstructural control by the dopant is completely achieved.

From EPR results (Fig. 4), an important effect of the donor dopant on the defect profile is observed. Depending on the donor concentration in the $BaTiO_3$ lattice, several neutrality conditions are established. For low Nb_2O_5 concentrations ($\leqslant$0.15 mol%), an electronic compensation regime takes place [11]:

$$2\ BaO + Nb_2O_5 \rightarrow 2\ Ba_{Ba} + 2\ Nb_{Ti}^{\cdot} + 6O_O + \frac{1}{2}\ O_2\ (g) + 2e' \quad (1)$$

As the donor concentration increases, there is an eventual shift from electronic to vacancy compensation [11]. In this situation, the increasing rate of V_{Ba}'' becomes faster than that of electrons [12], as indicated in the following equations:

$$BaO + Nb_2O_5 \rightarrow Ba_{Ba} + V_{Ba}'' + 2Nb_{Ti}^{\cdot} + 6O_O \quad (2)$$

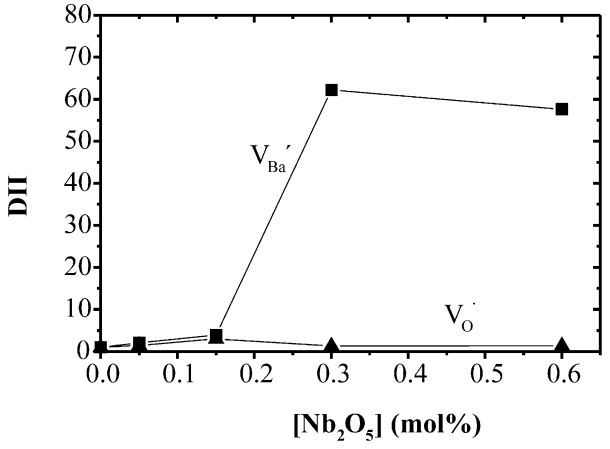

Fig. 4. Double integrated density (DII) corresponding to V_{Ba} and $V_O^{\bullet}$ defects vs. Nb_2O_5 concentration.

$$V''_{Ba} \rightarrow V'_{Ba} + 1e' \quad (3)$$

From Fig. 4, the strong increase in DII of V'_{Ba} for a dopant concentration of 0.30% Nb_2O_5 indicates the transition from an electronic to a vacancy compensation regime. In our materials, an important grain-growth restriction at 0.30% Nb_2O_5 was also detected. These phenomena support the hypothesis that kinetics of vacancy diffusion and the dopant tendency to accumulate at the grain boundaries control the boundary mobility [12].

Another possible mechanism for the ionic compensation regime is the generation of titanium vacancies, besides the barium vacancies formation:

$$6\ BaO + 3\ Nb_2O_5 \rightarrow 6\ Ba_{Ba} + V''_{Ba} + 6\ Nb_{Ti}^{\cdot} + V''''_{Ti} + 2l\ O_O \quad (4)$$

However, from the EPR results, we have no experimental evidence for the V''''_{Ti} or the V''''_{Ti} formation. On the other hand, the low $V_O^{\bullet}$ concentration detected for all the Nb_2O_5-doped samples comes from the "freeze-in" of intrinsic oxygen defects.

It is known that incorporation of niobium substituting in titanium site in the $BaTiO_3$ lattice produces the titanium segregation out of the grains [13]. This phenomenon promotes the grain growth inhibition and is responsible for the secondary phases formation. Needles are only observed on the fine-grained matrix, owing to the high Nb incorporation and Ti segregation in these regions. This phenomenon is favoured by sintering at temperatures above the eutectic temperature in the $BaTiO_3$–TiO_2 system (1332 °C). Formation of a liquid phase during sintering increased the dopant distribution, resulting in a more homogeneous system. EDAX analysis carried out on the fine-grained region of barium titanate doped with 0.15–0.60% Nb_2O_5 shows a Ba/Ti elemental ratio of 49/51. However, EDAX analysis performed on the needles showed a higher content of titanium respect to barium ions. The composition of the secondary phase corresponds to a non-stoichiometric compound between $Ba_6Ti_{14}Nb_2O_{39}$ (in samples with low concentration of Nb_2O_5) and $Ba_6Ti_{17}O_{40}$ (in samples with high concentration of Nb_2O_5). As dopant concentration increases, the predominant secondary phase becomes richer in titanium. In the slightly doped $BaTiO_3$ sample (0.15% Nb_2O_5), the actual dopant concentration in some regions overcomes the nominal composition. In this case, the dopant locally saturates the $BaTiO_3$ lattice and the excess Nb contributes to the $Ba_6Ti_{14}Nb_2O_{39}$ phase formation. For higher Nb_2O_5 concentrations (0.30–0.60% mol), the uniform dopant distribution allows its complete incorporation into the $BaTiO_3$ lattice. As most of the Nb^{5+} ions solubilise into the $BaTiO_3$ lattice, there is an important segregation of titanium in the whole system. In this case, the titanium

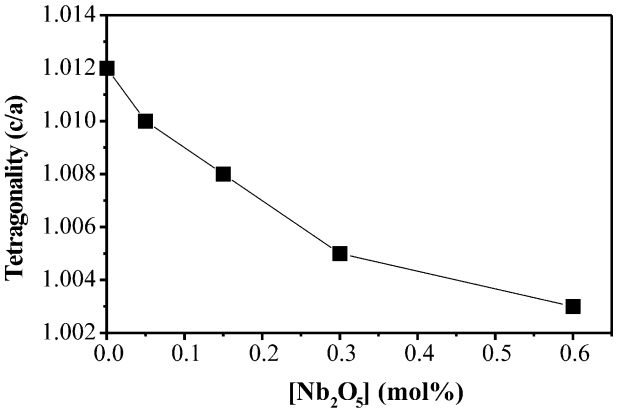

Fig. 5. Tetragonality parameter (c/a) vs. dopant concentration curve.

ions contribute to the second phase formation, which becomes close to the composition $Ba_6Ti_{17}O_{40}$. Due to the high incorporation of Nb^{5+} in the $BaTiO_3$ lattice, an important shrinkage of the host lattice takes place. This phenomenon is reflected by a noticeable decrease in the tetragonality of $BaTiO_3$ as the nominal composition becomes higher in the dopant (see Fig. 5).

4. Conclusions

In this work, the microstructural development of Nb-doped $BaTiO_3$ ceramics was analysed, focusing the study on the secondary phases formation. The Nb_2O_5 addition strongly influences the grain growth of $BaTiO_3$. Starting from 0.30 mol% Nb_2O_5, niobium inhibits the grain growth of $BaTiO_3$. This is in agreement with an extraordinary jump in the barium vacancies concentration. In this case, a shift from electronic to vacancy compensation takes place by increasing the dopant concentration. These results support the previously made hypothesis that the kinetic of vacancy diffusion and the dopant tendency to accumulate at the grain boundaries control the boundary mobility on sintering and, consequently, the grain growth.

As result of the dopant incorporation, an important titanium segregation is observed, followed by secondary phases precipitation. In this work, secondary phase compositions correspond to non-stoichiometric compounds close to $Ba_6Ti_{14}Nb_2O_{39}$ and $Ba_6Ti_{17}O_{40}$.

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