Core – Shell structures in Sb – doped BaTiO₃

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In this work, fine – grained microstructures have been obtained after sintering BaTiO₃ doped with an organic precursor of antimonium. In this compound, the development of a core – shell structure in the grains takes place influencing on the final grain size and electrical properties of the material. Samples were characterised by Scanning Electron Microscopy (SEM), X – ray diffraction (XRD) analysis, and dielectric constant – temperature curves. Strong inhibition of the grain growth is observed in Sb-doped BaTiO₃. Besides, dielectric constant vs temperature curves show the contribution of two regions, corresponding to the grain boundaries and the grain bulk. According to the observed properties, the contribution belonging to the shell region becomes more important as the dopant content and the sintering temperature rise.

Key words: processing, barium titanate, core – shell structures.

Estructura Core-Shell en materiales de BaTiO₃ dopados con Sb

En el presente trabajo se han obtenido materiales de BaTiO₃ dopados con antimonio a partir de un precursor orgánico que presentaron una microestructura homogénea y con tamaño de grano pequeño. En este compuesto se desarrolla una estructura de tipo “core-shell” en los granos que afecta tanto al tamaño de grano final como a las propiedades eléctricas del material. Las muestras fueron analizadas mediante Microscopía Electrónica de Barrido, difracción de rayos-X y la respuesta de la constante dieléctrica frente a la temperatura. Se observó una fuerte inhibición del crecimiento cristalino con la incorporación de antimonio. La respuesta de la constante dieléctrica frente a la temperatura presenta dos contribuciones, una asociada al borde de grano y otra al interior de grano. De acuerdo con las propiedades observadas, la contribución del borde de grano (región “shell”) crece en importancia a medida que la concentración de dopante y la temperatura de sinterización aumentan.

Palabras clave: procesamiento, titanato de bario, estructura “core-shell”.

1. INTRODUCTION

It is known that some additives are capable of flattening the dielectric constant vs temperature response of BaTiO₃ ceramics (1-3). In these materials, a compositional gradient along each grain leads to a core – shell type structure. This phenomenon and the development of small grains provide the mentioned particular electrical features. Several authors reported the formation of grain core – grain shell structures in chemically modified BaTiO₃, specially in materials doped with Nb (4) or Mg (5). Moreover, surface doping of BaTiO₃ has been shown to improve the development of grain boundary structures and changes the dopant concentration needed to control grain growth (6). Therefore, core – shell characteristics and consequently electrical properties, which depends on the dopant, its concentration and the thermal treatment applied, may be favoured by surface doping.

This work focusses on the microstructural development and dielectric properties of Sb – doped BaTiO₃ ceramics obtained by surface doping. The main purpose is to show evidence of the core-shell structures in Sb – doped BaTiO₃, considering the electrical properties of these materials.

2. EXPERIMENTAL PROCEDURE

Samples of antimonium - doped barium titanate were prepared from technically pure BaTiO₃ powder (Elmic BT100, Rhône Poulenc, particle size 0.84µm, Ba/Ti 1.000, main

impurity Sr<0.05%) and a solution of Sb[O(CH₃)₃(CH₃)₃] (Sb – butoxide, Aldrich) as dopant precursor. Concentrations of dopant equivalent to 0.05, 0.15, 0.30 and 0.60 % mol of Sb₂O₃ were studied. The starting materials were homogenised in isopropilic medium with a high – speed turbine. Dried powders were isostatically pressed at 200 MPa and sintered at temperatures ranged from 1300 to 1400°C for 2 hours in air.

Average grain size was estimated by Scanning Electron Microscopy (SEM) (Philips 505) on fractured, polished, and etched samples of the BaTiO₃ – based ceramics. Lattice parameters were calculated from the XRD profiles performed on the ground samples. Then, XRD patterns corresponding to the reflections of the (200) and (002) planes were scanned between 44° and 47° at 0.125°/minute, using a Philips PW 1050/25 equipment with CuKα radiation and a Ni filter at 40KV and 20 mA. Finally, constant dielectric measurements were performed on electroded samples, from room temperature to 150°C using a Hewlett Packard meter 4284A at 1 KHz and 1 V.

3. RESULTS AND DISCUSSION

SEM microphotographs in Figure 1 points to two important aspects. First, BaTiO₃ doped with Sb-butoxide leads to the development of uniform grain – size microstructure. Second, Sb incorporation inhibits the grain growth during

Figure 1. SEM microphotographs (A) undoped BaTiO₃ and doped with (B) 0.05, (C) 0.15, (D) 0.30, (E) 0.60 % mol of Sb – butoxide. Sintered at 1350°C.

sintering, when the dopant concentration increases from 0.05 (grain size 6 μm) to 0.60 % mol (grain size 1- 2 μm).

In Figure 2, tetragonality (c/a) vs. dopant concentration representation for Sb-doped BaTiO₃ is shown. In these samples, the incorporation of Sb⁵⁺ in B sites of the perovskite together with the decrease of the final grain size drive to a monotonous decrease of the c/a ratio when increasing the dopant concentration.

Microstructure development as well as the tetragonality parameters are related with the electrical properties of the Sb – doped BaTiO₃ samples. In Figure 3, dielectric constant (ϵ) vs temperature curves for all the samples are presented. It is possible to observe that the sample with the lowest dopant concentration show the Curie – Weiss behaviour. However,

two contributions to the ϵ vs T curve are detected for the next set of samples. Chazono H. et al and Toshitaka O. et al (7,8) reported that these characteristics reflect the development of a core – shell microstructure in the BaTiO₃ grains. The shell region consist of BaTiO₃ exhibiting a gradient of dopant concentration decreasing towards the grain bulk. In this region, tetragonality diminishes towards the grain boundaries, while ionic defects like barium vacancies increases in this sense. On the contrary, the core region contains slightly doped BaTiO₃, with high tetragonal characteristics and low concentration of ionic defects.

In Figure 3, contribution of the core region is reflected by a sharp peak around 112°C, while the response of the shell zone appears as a wide region of ϵ at lower temperature. As

the dopant concentration increases, antimony ions diffuse into the core region. Then, the Curie point corresponding to this zone diminishes from 112°C (for 0.05% mol of dopant) to ≈88°C (for 0.60% mol of dopant). Besides, contribution of the shell region to the ϵ vs T curve also increases with the dopant content. A similar effect to the above described is found when the sintering temperature is increased (Figure 4).

4. CONCLUSIONS

Uniform microstructures are obtained by doping BaTiO_3 with Sb-butoxide. In this case, surface doping of the BaTiO_3 particles improved the efficiency of the doping process. Strong inhibition of the grain growth is attained in Sb-doped BaTiO_3 sintered at 1350°C when increasing the dopant concentration from 0.05 to 0.60% mol. Dielectric constant vs. temperature curves indicate the development of core-shell structures in Sb-doped BaTiO_3 based materials. The contribution of the shell region increases with the dopant content and sintering temperature, being this effect related to incorporation and diffusion of the Sb cations into the BaTiO_3 lattice.

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Figure 2. Tetragonality (c/a) vs dopant concentration curve for Sb-doped samples sintered at 1350°C.

Figure 3. Dielectric constant vs temperature curves for Sb-doped BaTiO_3 , sintered at 1350°C.

Figure 4. Dielectric constant vs temperature curves for BaTiO_3 doped with 0.60% mol of Sb, sintered at different temperatures.