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Sintering behaviour and microstructural evolution of agglomerated spherical particles of high-purity barium titanate

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Abstract

Densification and grain growth of high-purity $BaTiO_3$ spherical particle compacts have been studied in the temperature range of 25–1300 °C by the CRH method. A rapid densification of the samples between 1000 and about 1230 °C with the formation of a continuous interconnected porosity, and a negligible grain growth took place. Above 1230 °C grains grew rapidly and the interconnected porosity progressively collapsed into isolated pores. Measurements of grain size as a function of density showed that the grain-growth behaviour change took place at about 92% of theoretical density, which coincides with the end of the intermediate-stage sintering. From the present experimental results it can be tentatively stated, for the first time in barium titanate, that a linear correlation between density and grain size in the intermediate-stage of sintering exists. In the final-stage of sintering a bloating or desintering feature was present as consequence of the loss of carbon dioxide from the barium carbonate in the barium titanate environment.

Keywords: A. Sintering; Microstructural evlution; Barium titanate

1. Introduction

Because of its dielectric constant (>1000) and ferroelectric properties, barium titanate, ($BaTiO_3$) is one of the most important material in the electronic industry [1], mainly in the manufacture of multilayer capacitors and electronic devices. Furthermore, it is being applied as a capacitor material in dynamic random access memories (DRAM) in integrated circuits. Both a high dielectric constant and good insulating properties are required for DRAM applications [2–4]. From the discovery that the relative permittivity of $BaTiO_3$ ceramics can be increased to about 3500 if the grain size is controlled at $\sim$1 μm, then a fine-grained structure is desirable to enhance the dielectric performances [5]. Therefore, the availability of $BaTiO_3$ powders with homogeneous and small particle size ($\leqslant$0.1 μm) is a crucial factor [6].

Altough many commercial ceramic undoped $BaTiO_3$ powders are available at the market, but their sintering behaviour and the characteristics of the final obtained product are in the majority of the cases very different, in spite of their apparently similar characteristics of the powders. In that way, in a detailed work Herard et al. [7,8] demonstrated the importance of the surface contamination in several commercial, undoped $BaTiO_3$ powders on the sintering behaviour and developed microstructures. Furthermore, Demartin et al. [9] studied the anomalous grain growth and desintering phenomenon during the sintering of undoped $BaTiO_3$ below and above the eutectic temperature of the TiO_2–$BaTiO_3$ system [10]. Different agglomeration level of the powders, impurities content, non-uniform particle size distribution, heterogeneity of the Ba/Ti ratio can lead to the spreading of the obtained final results on apparently similar sintered bodies and, thus, to the different dielectric properties.

Chaput et al. [11] reported that high dense and fine-grained $BaTiO_3$ bodies can be obtained at a temperature as low as 1150 °C starting from an alkoxide–hydroxide route to synthesize the $BaTiO_3$ powder, and Duran et al. [12] reached a similar result using a modified Pechini method [13]. In both cases a common fact was found, which was related to the appearance of a discontinous

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grain growth above a given densification level. Morphology and initial particle size, agglomerates nature, heating rate, and sintering temperatures were the main factors to be controlled.

The purpose of the present work was to study on a commercial high purity $BaTiO_3$ powder with a well defined morphology, (i) the densification process at the intermediate-stage of sintering; (ii) the relation between densification and grain growth; and (iii) the developed microstructure.

2. Experimental procedures

The experiments were carried out with a commercial high-purity $BaTiO_3$ powder, prepared by the hydrothermal method (41633 Lot 027 K11 Barium titanium oxide. High surface area, 99+% metalbasis, Alfa Aesar, Johnson Matthey GmbH, Kalsruhe, Germany), whose impurity levels are summarised in Table 1. The.stoichiometry BaO/TiO_2 as determined by XRF was 1.04. The as received powder was cold-isopressed at 200 MPa. The disk-shaped samples were 10 mm in diameter and 4 mm in thickness. After isopressing the green compacts were sintered at 900–1300 °C in air at a heating rate of 10 °C/min without holding, using a dilatometer (Netzsch, model 402/E7, Germany). Morphology of the as received powder was observed by Scanning Electron Microscopy, SEM (Zeiss DSM 950, Oberkochem, Germany). The particle size distribution was determined by using a counter particle laser (Mastersizer model, Malvern Instruments, Ltd, UK). The specific surface area was measured by the single-point BET method with liquid N_2 (Quantachrome MS-16 model, Syosset, NY). X-ray line broadening measurement was studied to determine crystallite size, using a Diffractometer and CuK_α radiation (D-5000 Siemens Diffractometer, Brüker, Germany).

After sintering, the density of the samples was measured by the Archimedes method, with water, and the pore-size distribution was studied by mercury porosimetry, (Micromeritics, Autopore II, 9215, Norgross, USA). The average grain size was measured by the interception method on the fracture surface of the sintered samples observed by SEM. At least 300 grains were measured to obtain the average grain size value.

Table 1
Impurities content of the as-received $BaTiO_3$ powder

Impurities	Concentration
Si	<165 ppm
Sr	<0.87%
Fe	<165 ppm
Pb	<165 ppm
Al	<165 ppm
C	<0.37%
Cl	<0.35 ppm

3. Experimental results.

Fig. 1 shows the morphology of the as-received powder, consisting of spherical particles with a quite broad size disrtibution between 0.3 and 20 µm, with a mean particle size diameter of 7.5 µm. Specific surface area of this powder was 12.5 m^2/g, and the equivalent diameter of the particles was 0.080 µm that coincides well with the measured by SEM. The primary particle size as measured by XRLB was 0.020 µm.

TGA measurements, not shown here, showed evidence for a weight loss of about 4% between room temperature and 1300 °C. The weight loss up to 900 °C (~3.8%) which is attributed to the loss of adsorved and removal of H_2O and CO_2 that is caused by the decomposition of contaminant barium carbonate and other volatil organic residue. CO_2 releases above 1200 °C, (~0.2%) can be due to the decomposition of $BaCO_3$ in the $BaTiO_3$ environment.

After compaction the pore size distribution of the as-received powder is fairly narrow with a peak at around 0.025 µm, and a maximum pore radius entry near 0.35 µm. It must be mentioned that on compaction almost all the spheres were broken and a smaller and homogeneous particle size of about 0.080 µm could be measured by SEM on the fracture surface of the green compacts. Therefore, given that the primary particle size as measured by XRDB was about 0.020 µm, then the particle visualised by SEM are agglomerated of at least four primary particles. The relative density of the green

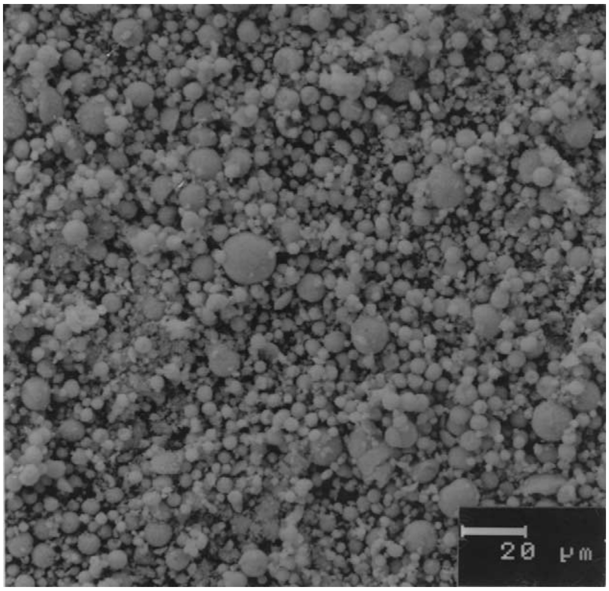

Fig. 1. Scanning electron micrograph of the as-received $BaTiO_3$ powders.

compacts was about 52% of theoretical density (D_{th}), (6.02 g/cm^3).

Fig. 2 shows the CHR densification process in which it can be seen that bulk shrinkage initiates between 900 and 1000 °C, and that an end-point density of about 98% D_{th}, is achieved at about 1350 °C. The sintering process takes place in two steps: an initial densification rate peak is present at about 1020 °C and another one at about 1250 °C. Both peaks occur below the liquid eutectic temperature for the TiO_2–$BaTiO_3$ system (~1320 °C), therefore, the densification process takes place by the conventional solid-state diffusion mechanism, at least in the temperature range of 900–1300 °C.

The initial and intermediate stages of sintering were studied by mercury porosimetry measurements, and the evolution of the pore size distibution is shown in Fig. 3. In the temperature range of 25–1000 °C the smaller pores disappear and the larger pores grow and, as a consequence, the average pore size increased considerably from 0.023 µm in the green compacts at room temperature to 0.059 µm at 900 °C and 0.119 µm at 1000 °C. As can be observed in Fig. 4, no significant changes in the total pore volume was detected up to 1000 °C, i.e. very small densification occurs, but above that temperature it rapidly increases. Therefore, it may be assumed that up to 1000 °C most of the smaller pores have been eliminated, which coincides well with the first peak of the densification rate curve (Fig. 2) and, simultaneously, a considerable growth of pores tooks place. Since the densification was below 4%, it may be considered that the smaller pores were eliminated by surface diffusion. Above 1000 °C the average pore size continously decreases from 0.119 µm at 1000 °C to 0.107 µm at 1100 °C, 0.045 µm at 1200 °C and about 0.020 µm at 1230 °C. Above that temperature, the average pore size again increases to higher than 1 µm at 1300 °C. A maximum in the densification of about 99.3% D_{th} was achieved at 1250 °C, coinciding with the second peak in the densification rate curve (Fig. 2). As it is shown in Fig. 5, below 1000 °C the density slowly increases with increasing temperature, and in the range 1000–1250 °C

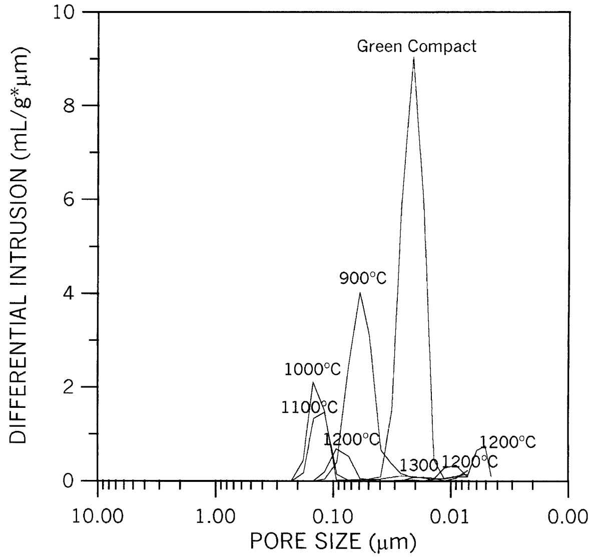

Fig. 3. Evolution of pore-size distributions in $BaTiO_3$ green compacts during sintering.

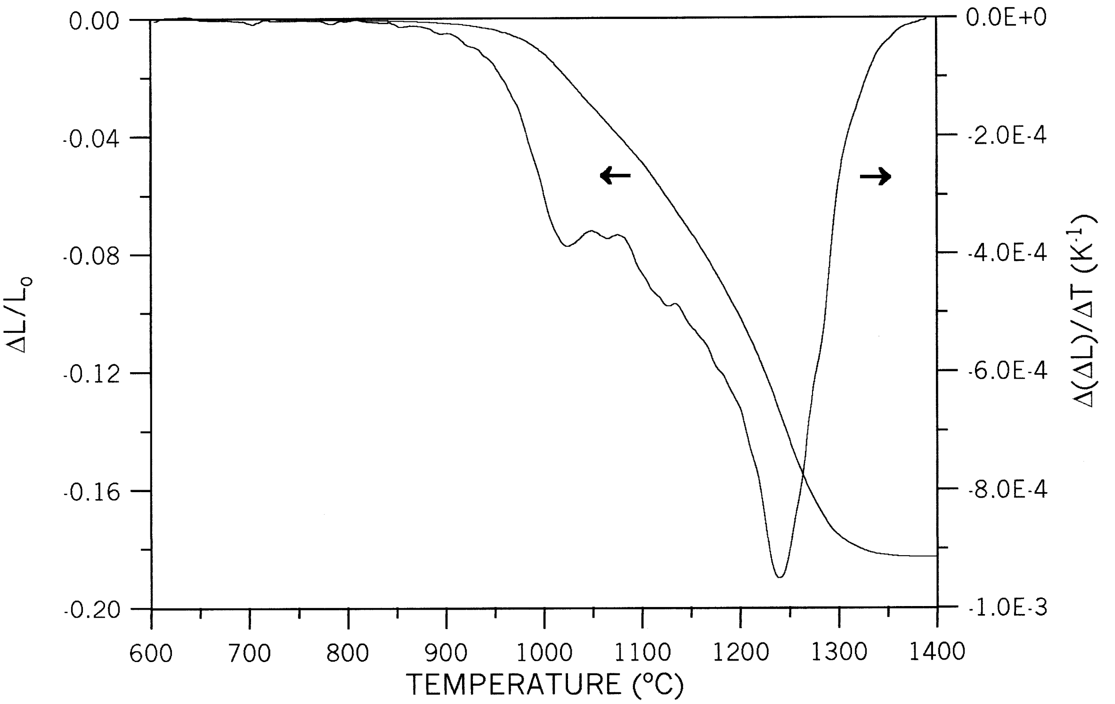

Fig. 2. CHR sintering behaviour of $BaTiO_3$ powder compacts.

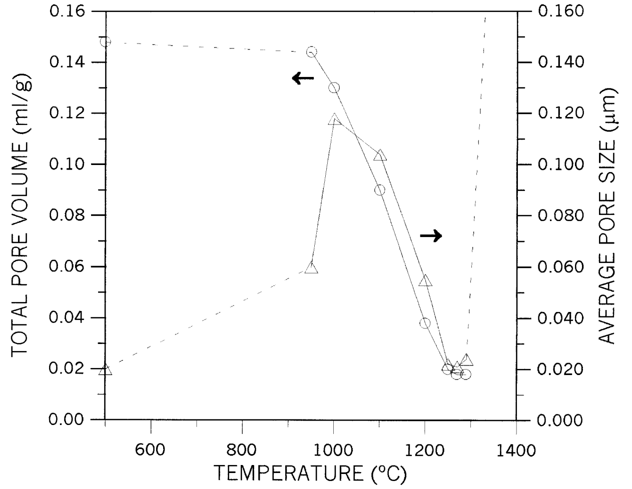

Fig. 4. Total pore volume and average pore-size versus sintering temperatures.

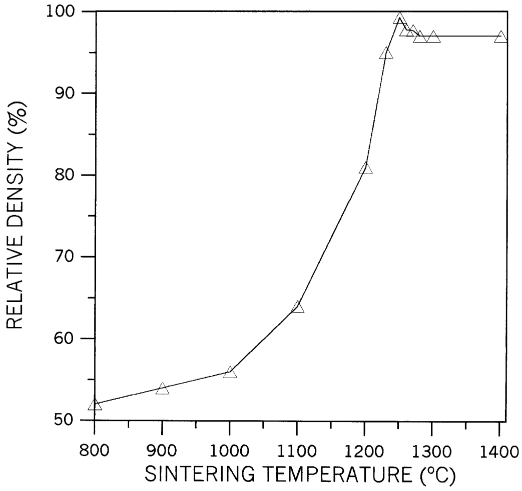

Fig. 5. Density change with sintering temperature (theoretical density of $\rho = 6.02$ g/cm^3 was used for calculation of relative densities).

it rapidly increases. Above 1250 °C a small de-densification occurred and density decreases up to about 97% D_{th} at 1300 °C.

The microstructure of $BaTiO_3$ samples sintered in the 1000° to 1300 °C temperature range are essentially composed by polygonised grains, which support the evidence of a solid-state sintering. The microstructural evolution of $BaTiO_3$ sintered samples at various relative densities is shown in Fig. 6A–F. As it can be observed, uniform microstructure was developed with a relatively slow grain growth up to a density of about 92 D_{th}, i.e., when porosity is closed, above which the appearance of a discontinuous grain growht was present in the sintered samples, i.e., within the intermediate-stage sintering the microstructures showed a quite uniform fine-grained matrix with an almost unimodal distribution of grain sizes. After heat-treatment at about 1260 °C, although the samples were near fully dense, the microstructure started to be bimodal with some relatively large grains ($\geqslant 5$ µm) growing in a fine-grained matrix ($\leqslant 1$ µm). Some large entrapped pores started to be present within the larger grains (Fig. 7). Above that temperature a generallised rapid grain growth process with a pore entrapment phenomenom occurred (see Fig. 6F).

Fig. 8 shows the grain size-relative density variation for the barium titanate sintered samples. It shows that the average grain size increases slowly below 92% D_{th}, therefore the end of the intermediate-stage of sintering can be located around that density, and it is characterised by a transition from a continuous pore channels to isolated pores. Above 92% D_{th} grains grew from about 0.7 µm to about 2.0 µm at 99.3% D_{th}, and more than 20 µm at 1300 °C in which the density decreased up to 97% D_{th}. From the above results it could be assumed that at the intermediate-stage of sintering of $BaTiO_3$ spherical particles compacts a possible linear correlation between density and grain size exists.

4. Discussion

According to the whole of the above obtained results, it might be stated that during intermediate-stage of sintering of high purity $BaTiO_3$ spherical particle compacts a simultaneous process of densification and grain growth takes place. Such an approach is consistent with the model used by Zhao and Harmer [14] to explain the effects of pore size distribution on the final-stage sintering behaviour of high-purity alumina powders. In the present study, it could be considered that the sintering of $BaTiO_3$ spherical particle compacts proceeds through three steps. In the first one, below 1000 °C, both densification and grain growth show a very small increase. In the second step, between 1000 and about 1230 °C, a rapid densification takes place with a simultaneous slow grain growth and, finally, in the third step, above 1230 °C, a slight desintering phenomenon but with a rapid grain growth occurred (Figs. 5 and 6). Such a densification behaviour may be explained as follows: in the first step with relatively little change in density, from 52 to 56% D_{th}, the pore size distribution was strongly narrowed Fig. 3. That means that the pores smaller than 0.023 µm shrank or disappear and those larger than 0.023 µm grew with a small increasing in density. Given that the total pore volume slightly decreased, it must be assumed that those pores with size smaller than the critical disappeared, according to the concept of equilibrium pore size proposed by Kingery and Francois [15]. As a result, the average pore size increases (see Fig. 4). Therefore, it can be stated that a pore growth process is predominant at this stage of sintering and, probably, at the beginning of the intermediate-stage.

In the second step or intermediate-stage of sintering, i.e. above 1000 °C, both the total pore volume and the

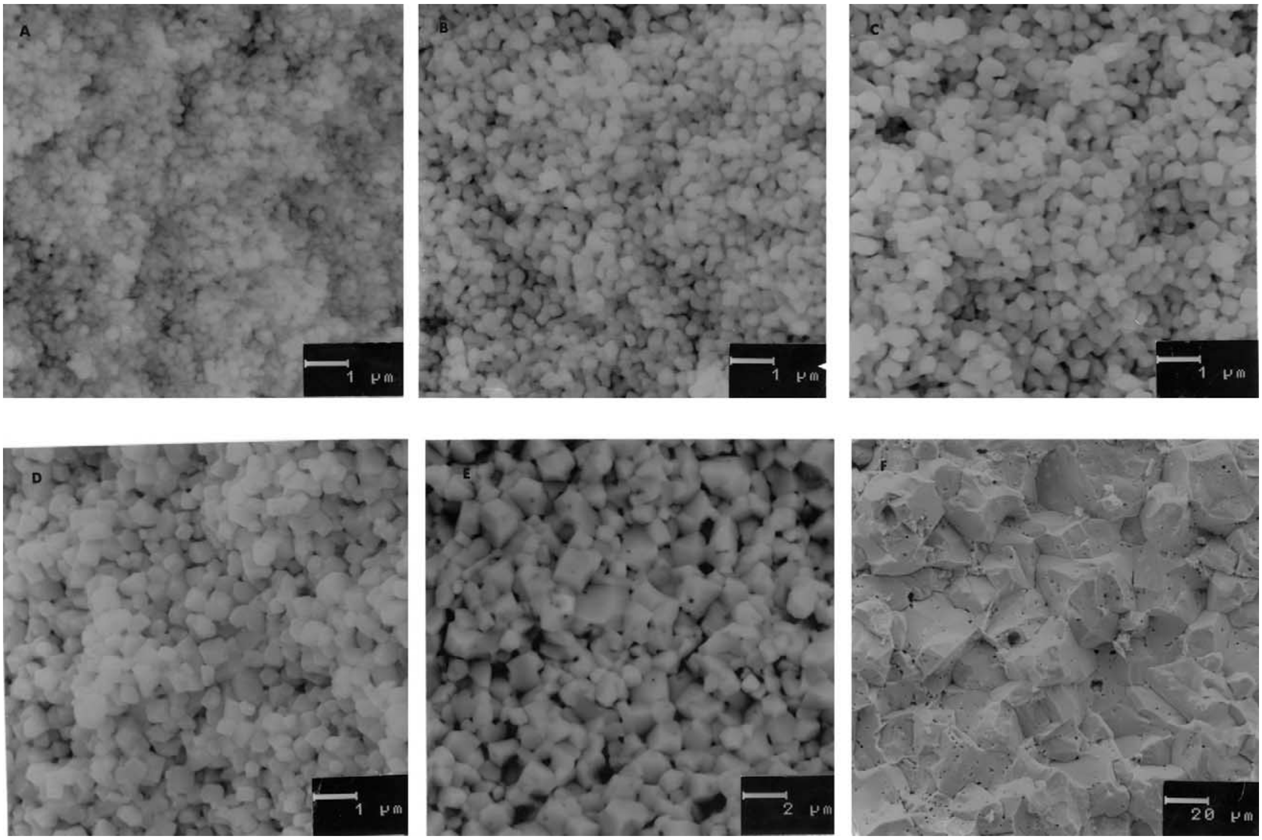

Fig. 6. SEM micrographs of fractured surfaces of $BaTiO_3$ samples sintered at different temperatures without holding: (A) 900 °C; (B) 1000 °C; (C) 1100 °C; (D) 1200 °C; (E) 1230 °C; (F) 1300 °C.

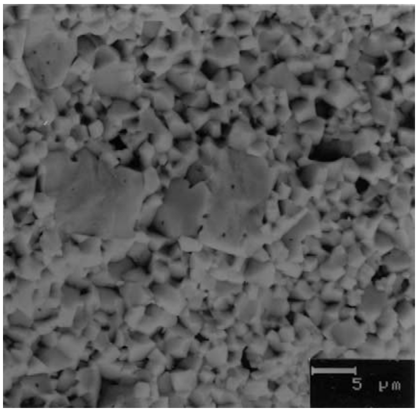

Fig. 7. SEM micrograph of fractured surface of a $BaTiO_3$ sample sintered at 1260 °C showing the appearance of abnormal grain growth.

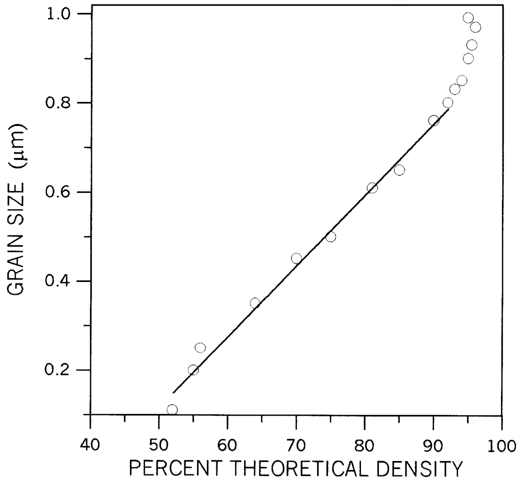

Fig. 8. Density versus grain size during intermediate-stage sintering showing a transition at about 92% D_{th}.

average pore size decreased (Fig. 4). Simultaneously, density rapidly increases and the grain size also increases but slowly (Figs. 2 and 8). During this sintering-stage many pores with convex surfaces and co-ordination number higher than the critical shrank and those one with co-ordination number lower than the critical disappeared. As a result, the total pore volume decreases. In that way, and in a progressive manner, many areas with interconnected porosity changes to a configuration with isolated pores located in three or four grain junctions (Fig. 6C). As the density increases all the interconnected porosity areas disappear giving rise to a configuration with only isolated pores (Fig. 6E). Such a situation is maintained until a density near to 92% D_{th}. In that density region, i.e., between 56 and about 92% D_{th}, grain growth was very slow and, thus, grains grew from 0.3 μm to only about 0.7–0.8 μm, and within such a regime of slow grain growth it could be stated, for the first time in the case of barium titanate, that the grain size is linearly proportional to density and independent of the sintering temperature, Fig. 8. Although such a statement is consistent with the suggestions of Gupta [16] and Coble [17], but more experimental data are necessary to be sure of such a correlation. A similar result was reported by Hsieh and Fang [18] who suggested that discontinuous grain growth did not occurs up to a relatively density of 99% D_{th}, i.e., well within the final-stage of sintering of $BaTiO_3$ samples. Our results are more consistent with the suggestions of Xue and Brook [19,20]. Summarising, in a not completly uniform ceramic matrix as is the present case, those regions in which the interconnected porosity firstly collapsed grains will grow more rapidly giving rise to a discontinuous grain growth situation (Fig. 7): Once the continuous pore network completly collapsed in all the ceramic matrix then a generalised exaggerated grain growth will take place. Such a phenomenon takes place in the present case above about 92% D_{th}, i.e., when the porosity was closed.

Above 1230 °C, i.e., after the end of the intermediate-stage of sintering, both a rapid grain growth from about 2.0 μm at 1250 °C to more than 20 μm at 1300 °C, and a desintering phenomenon took place, which extended up to 1400 °C. In that temperature range a decreasing of density and a strong increasing of the pore size occurred (Figs. 5 and 6). Although a rapid grain growth process is consistent with the final-stage of sintering, but the simultaneous presence of a desintering phenomenon can't be explained on the only basis of an increasing of the grain size. Above 1000 °C a weight loss of about 0.2% could be measured up to 1300 °C, of which 0.1% of the weight is lost between 1200 and 1300 °C. Just above 1200 °C a gas releasing and simultaneously the beginning of abnormal grain growth took place. There is a short temperature interval (1230–1250 °C) in which the abnormal grain growth with a pore entrapment began, and all the pores have concave surface curvature, with the consequent decreasing in the pore co-ordination number. From a thermodynamic point of view the driven force for densification is enhanced supporting, thus, the Xue and Brook analysis [20]. However, above 1250 °C the abnormal grain growth process is predominant on the gas release phenomenon, and being the grain boundary mobility extremely high the generated pores are entrapped at the interior of the grains giving rise, thus, to a desintering or bloating phenomenon, i.e., given that the porosity is closed the pores become very difficult to be eliminated. As a result the final density decreases (Fig. 5).

5. Summary

On the basis of the above mentioned discussions on the evolution of pore and grain morphologies during the sintering of spherical particle compacts of high-purity $BaTiO_3$, we can advance the following final considerations:

1. A pore growth process predominated at the initial and at the beginning of the intermediate stages of sintering, with negligible both densification and grain growth.
2. The intermediate stage of sintering for spherical particle compacts of high purity $BaTiO_3$ were established by means of density measurements and microstructural studies of sintered samples at different temperatures. A slow grain growth along such a sintering stage was found.
3. At the intermediate-stage of sintering a linear correlation between density and grain growth up to 92% D_{th} seems to exist. This finding is in agreement with results previously reported on grain growth during intermediate-stage of sintering for other oxides [17].
4. Near fully dense barium titanate bodies (99.3 D_{th}) could be obtained just above the intermediate-stage of sintering, but the appearance of larger grains could not be avoided. This is related to the presence of some agglomerates in the green microstructure.
5. In the final-stage of sintering a rapid and exaggerated grain growth with entrapment of pores takes place. Gas release from the decomposition of barium carbonate in the barium titanate environment, and the high mobility of the grain boundaries were the cause for the desintering phenomenon present at this stage. This result is in contrast with previous studies but the discrepancy can be explained through the differences in the Ba/Ti ratio.

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