

Improving sintering behaviour of BaTiO₃ by small doping additions

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The dielectric properties of BaTiO₃ ceramics are associated with its microstructure, which depends on the stoichiometric ratio, dopant nature, and ceramic processing. Optimum densification at low temperatures to reduce the amount of noble metals in electrodes for Multilayer Ceramic Capacitors (MLC) requires the use of liquid phase sintering. However, depending on the nature and amount of such a liquid phase, exaggerated grain growth is produced. In order to increase the capacitance in BaTiO₃-based multilayer capacitors, increasing the dielectric constant by careful and homogeneous development of the microstructure, is necessary. The correct distribution of dopant on the particles' surface leads to a modification of their features by reacting with surface cations such as Ba²⁺. Such a modification allows densification at low temperatures with very small amounts of liquid phase. As a consequence, good control of grain size is obtained which enhances the dielectric properties of the BaTiO₃ ceramics. The controlled microstructure also allows the reduction of the layer width in multilayer arrangements.

1. Introduction

Barium titanate-based ceramics are widely used in the electronics industry. The scientific and economic relevance of these materials are found in both the variety of applications and the modifiability of their properties as a function of the ceramic process followed. One of the most important applications of BaTiO₃-based ceramics is multilayer capacitors. Three principal areas of interest involve these materials: (a) increasing the dielectric constant to reach higher volumetric efficiency, (b) decreasing sintering temperature to reduce costs, mainly electrode ones, and (c) increase the dielectric breakdown field and the stability of the dielectric constant with the applied field. Control of the developing microstructure is the key to obtaining high reliability ceramics with better properties.

The characteristics of the ceramic powders clearly influence the developed microstructure in BaTiO₃ ceramics. Bimodal and non-uniform grain growth must be avoided if enhancement of the dielectric properties is to be attained. The dielectric properties of sintered BaTiO₃ ceramics exhibit a strong dependence on the grain size [1]. For grain sizes < 2 μm, anomalously high room-temperature permittivity values are obtained with a general broadening and flattening of the permittivity–temperature behaviour. Improvement of the dielectric properties requires grain growth to be inhibited, in order to obtain microstructures with a grain size lower than 1 μm, thus allowing reduction of the layer width in a ceramic capacitor multilayer arrangement.

Lowering the sintering temperature to reduce the amount of noble metal in electrodes requires the use of

liquid phase sintering. One possibility is the use of low melting glassy phases as binders of BaTiO₃ ceramic powders [2], but this is detrimental with respect to the high dielectric constant values required. Several additions are used to improve liquid phase sintering, and most of these lower the eutectic liquid temperature in the BaTiO₃–TiO₂ system which generally promotes exaggerated grain growth [3]. There are numerous reports on the effects of sintering temperature, dopants, and a non-stoichiometric formulation for liquid-phase-assisted BaTiO₃ sintering [4–6]. Some of the additives employed could cause rapid densification due to the formation of a reactive liquid phase in amounts above the solubility limits [7] while others increase the densification due to the precipitation of secondary phases at grain boundaries.

The dielectric breakdown field depends on the porosity, grain size, phase transitions, grain boundary phases, permittivity, and thermal environment [8]. This problem is critical for multilayer ceramic and high voltage capacitors. Some solutions use ceramic materials with compositions near the ferroelectric–antiferroelectric phase transitions. The dielectric constant also decreases as a logarithmic function of time [9]. The reduction of the ageing requires a decrease in the tetragonality of the materials by compositional modifications.

High reliability multilayer ceramic capacitors could be obtained if some of the above mentioned problems can be solved satisfactorily. However the intrinsic nature of the BaTiO₃ ceramics, or mainly the ceramic processing, limits the final properties of ceramics. Today, there is a clear trend towards the use of

wet-chemical methods for the manufacture of electronic ceramics compared to conventional processing routes [10]. One problem associated with the wet chemical routes is the formation of agglomerates, but in general, chemically prepared powders have high purity, submicron particle size, and much better compositional uniformity than those obtained by conventional processing. Recently, the adjustment of electrical properties or lower sintering temperature has been accomplished by doping the surface of the powder particles with the appropriate additives by chemical methods [11].

1.1. Previous results

In the previous works [12,13], high density (> 98 theoretical density (D_{th})) $BaTiO_3$ ceramic materials were obtained by sintering at $1200^\circ C$ for 2 h. The improvement in densification was attained by the presence of glass forming oxides such as SiO_2 , Al_2O_3 and P_2O_5 , which promote densification at lower temperatures without exaggerating grain growth when they are homogeneously distributed among the equiaxed particles. Fig. 1 is a SEM microstructure characteristic of such samples, showing a highly densified ceramic with low porosity located at grain boundaries. A second phase could be observed in the surface of the sample after thermal etching treatment. Such a second phase corresponds to the $Ba_3(PO_4)_2$ compound as it was demonstrated by XRD analysis [14]. The secondary phase which generated this type of exuded phase, was present during the sintering step of the ceramic bodies, and its location at the grain boundaries strongly alters the evolution of the sintering stages.

1.2. Microstructural model

From the point of view of understanding such a phenomenon, the use of microstructure models is required. The most adequate approach is the brick-wall model [13,15]. In this model the main phase is separated by an interconnected intergranular secondary phase. The existence of an intergranular phase will be more important for the lower grain sizes than for the higher ones, and also depends on the amount of the secondary phase. From this model the secondary phase plays a very important role in microstructures with grain sizes lower than $2\ \mu m$.

At this point two factors must be taken into account for arriving at relevant conclusions. (a) The crystalline structure of the $BaTiO_3$ ceramics shows a reduction of the asymmetry of its unit cell lattice for grain sizes $< 1\ \mu m$, reaching a cubic structure [1,16]. In this grain size range, higher dielectric constants are expected. High internal stress and high 90° domain wall density collaborate to increase the dielectric constant values. (b) The existence of a secondary intergranular phase can be critical for the sintering mechanism and the subsequent final properties. At the grain boundaries the phase relations in the system will probably be very different to that desired by the manufacturers.

In this model the second phase (as it can be understood) is of great significance in the evolution of the

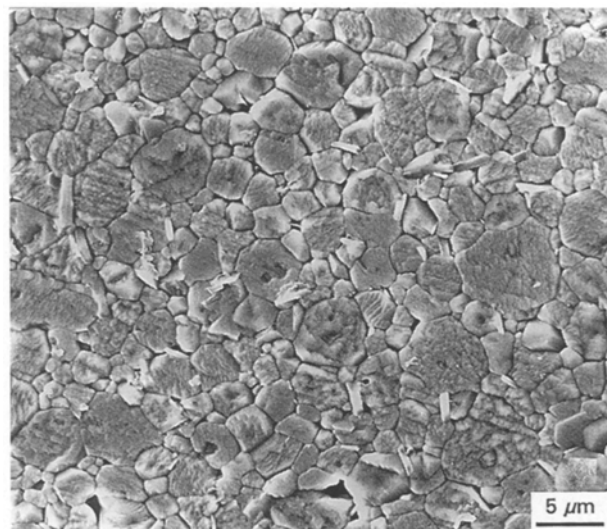


Figure 1 SEM micrographs of thermally etched $BaTiO_3$ ceramics sintered at $1200^\circ C$ for 2 h.

microstructure during the sintering treatment. This secondary phase could be associated with mass losses detected during sintering treatment [17]. These mass losses related to different chemical species that are eliminated in different temperature ranges during the sintering thermal process [18,19], as follows; (a) low temperature ($< 400^\circ C$): elimination of species acquired during ceramic processing (H_2O , $OH \dots$), (b) medium temperature ($400-900^\circ C$): CO_2 elimination from carbonates, and (c) high temperature ($> 900^\circ C$): volatilization of impurities or oxygen loss associated with the incorporation of dopants to the crystalline lattice.

Previously, the most important mechanisms studied are those related to high temperature phenomena but the surface of the $BaTiO_3$ particles is clearly influenced by those phenomena that take place at low and medium temperatures. The aim of this work is to propose a model of the sintering of $BaTiO_3$ ceramics as a function of the $BaTiO_3$ surface characteristics, particularly of the barium titanate particle surface heterogeneities, in conjunction with a correct distribution of dopants to allow the control of grain growth and reduction of sintering temperatures.

2. $BaTiO_3$ surface powder characterization

A secondary phase located at the grain boundaries is very important due to its high reactivity and high diffusion rate. The role of particle surfaces in sintering processes is critical due to the significance of the contact point between particles. In this sense, the presence of different chemical species on particle surfaces could strongly contribute to improvement or inhibition of the sintering mechanism.

The IR (Perkin Elmer Spectrometer 520B, UK) spectra of commercial $BaTiO_3$ ceramic powders (Rhône Poulenc lot n $^\circ$.7958, Ba/Ti = 1.002, Paris, France), see Fig. 2a, shows the presence of both the carbonate and the hydroxyl groups [20]. These results have been confirmed by XPS (Electron Spectrometer

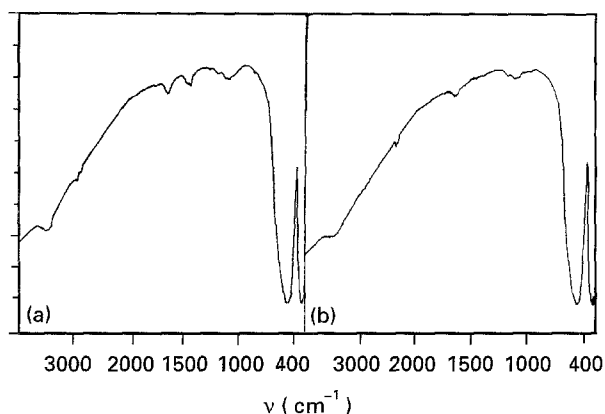


Figure 2 IR spectra of (a) commercial BaTiO₃ powders and, (b) ester phosphate modified barium titanate powders. Both ceramic powders were annealed at 700 °C for 0.5 h.

TABLE I Ba/Ti ratio for different BaTiO₃ powders

BaTiO ₃ powders	XPS surface	ICP-AES total
Solid state reaction	1.23	1.000
Chemical via	1.41	0.996

LHS-10 Leybold Heraeus, Cologne, Germany) analysis [17]. The carbonation state relating to the surface regions was produced during the annealing stage in the synthesis process, and could be eliminated by thermal treatment combined with degassing.

After oxidizing and degassing, the integrated intensity of Ba_{3d5/2} and Ti_{2p3/2} peaks of the XPS spectra, taking into account the sensitivity factors for those calculated levels, have shown a higher proportion of Ba²⁺ cations than Ti⁴⁺ cations at the particle surfaces (see Table I) and are in agreement with Hung and co-workers [21]. The XPS spectra was sampled at the surface to a depth not exceeding 2.5 nm. The powders obtained by a solid-state reaction of BaCO₃ and TiO₂ [12] had a stoichiometric ratio of Ba/Ti_{surface} = 1.23, whereas chemically prepared BaTiO₃ (Rhône Poulenc lot APM7C122, Paris, France) had Ba/Ti_{surface} = 1.41. The higher Ba²⁺ surface content of chemically prepared powders was related to its higher purity. In the case of BaTiO₃ obtained by a conventional route, the phosphor cations were incorporated into the TiO₂ particles (0.38% P₂O₅ in TiO₂ powder, ICP-AES Jobin Yvon J438VHR, France) to inhibit the anatase-rutile transformation, combined with Ba²⁺ cations. The phosphate was chemisorbed as a bidentate ligand which hinders the mobility of surface ions [22]. The reaction kinetics of barium titanate powders could be the origin of such behaviour. The barium cations react with titanium dioxide particles to form BaTiO₃, as a first reaction product [23, 24]. Ba₂TiO₄ is formed as the second reaction product from the initial barium titanate, and final decomposition of orthotitanate compound completes BaTiO₃ formation. In such a kinetic mechanism, Ba²⁺ cations migrate to TiO₂ particles, and reach the surface of those

particles. Such Ba²⁺ cations could combine with phosphates located at the surface of TiO₂ particles as secondary phases. In the case of chemically prepared BaTiO₃ powders, the kinetics are not so clear. According to the stoichiometric ratio of chemically prepared powders, the main secondary compounds are TiO₂-rich compounds in the BaTiO₃-TiO₂ system. The surfaces of chemically prepared BaTiO₃ powders show a lower carbonation state than those of conventionally prepared ones.

3. Surface modification of BaTiO₃ particles

More activated barium titanate particles could be attained if a hydroxycarbonate surface state is avoided. This is very difficult even if chemical synthesis processes have been carried out. The alternative is to perform a specific treatment after synthesis. An interesting example of such a process was reported by the authors [20], and consisted of the addition of ester phosphate (Merck Ref. 80251, mixture of C₄H₁₁O₄P and C₈H₁₉O₄P 40% and 60%, respectively) (0.35 wt %) to BaTiO₃ powders (Rhône Poulenc lot n° 7958, Paris, France) having a stoichiometric ratio of 1.002. These powders were thermally treated at 700 °C for 0.5 h and carbonation was avoided (Fig. 2b).

The sintering behaviour of the particles showed the most direct effect with the modification of the particle surface nature. The non-isothermal sintering experiments (Adamel Lhomargy, Paris, France) showed marked changes (Fig. 3). The chemical surface treatment increased the shrinkage rate and decreased the temperature at which the process took place. The presence of phosphor cations at the surface of the

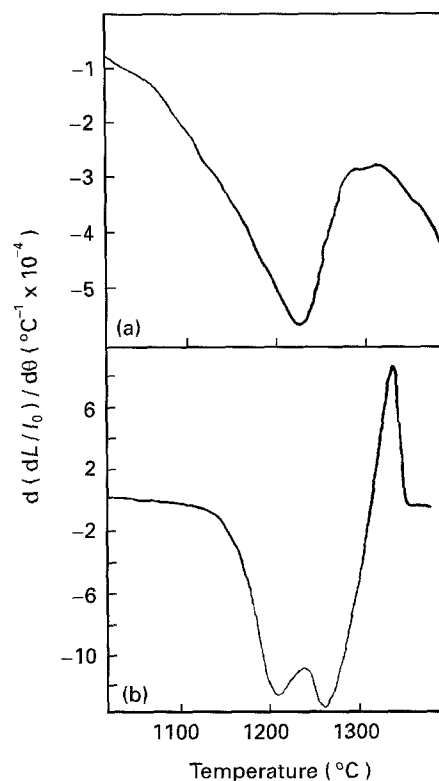


Figure 3 Shrinkage rate versus temperature of (a) pure barium titanate and, (b) ester phosphate modified barium titanate.

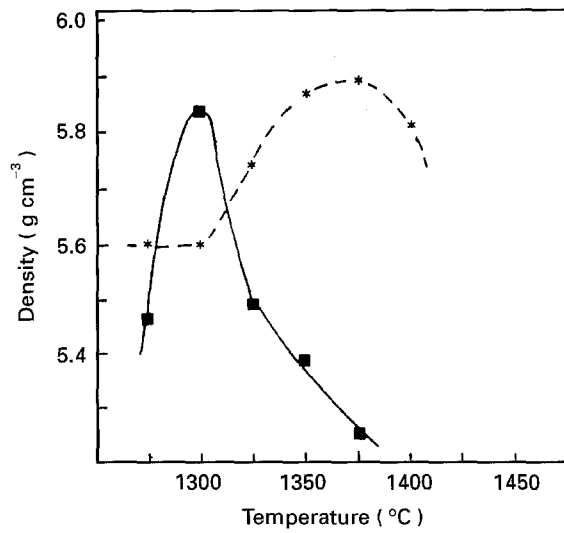


Figure 4 Apparent density as a function of the sintering temperature for (*) pure barium titanate ceramics and, (■) ester phosphate modified barium titanate ceramics.

particles produced high densification (98% D_{th} at 1300 °C for 2 h) at lower temperatures than the corresponding un-treated powders (98% D_{th} at 1375 °C for 2 h) (Fig. 4) and grain growth was avoided (Fig. 5). Exuded second phase could be observed on polished and thermally etched surfaces. The second phase was identified by XRD as $Ba_3(PO_4)_2$ [14]. Higher temperatures gave rise to the appearance of liquid phase in the system $BaO-TiO_2-P_2O_5$ which remained surrounding the barium titanate grains (Fig. 6). This liquid phase acts as a compressive phase over the $BaTiO_3$ grains due to its different thermal expansion coefficient, as can be seen in the shrinkage rate versus temperature curve (Fig. 3b). This effect decreased the anisotropic quadratic effect [25] of the sintered $BaTiO_3$ ceramics and, as a result, the dielectric constant increased to values of 3000 for grain sizes larger than 2 μm . These values did not agree with those expected from the diagram given by Arlt and co-workers [1] (dielectric constant versus $BaTiO_3$ grain size). The

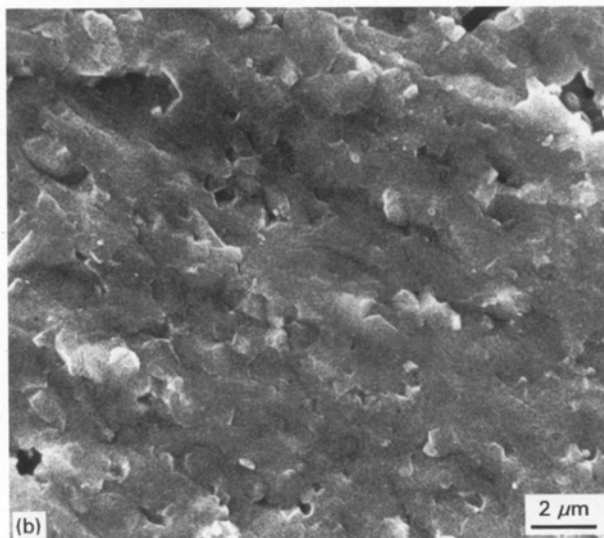
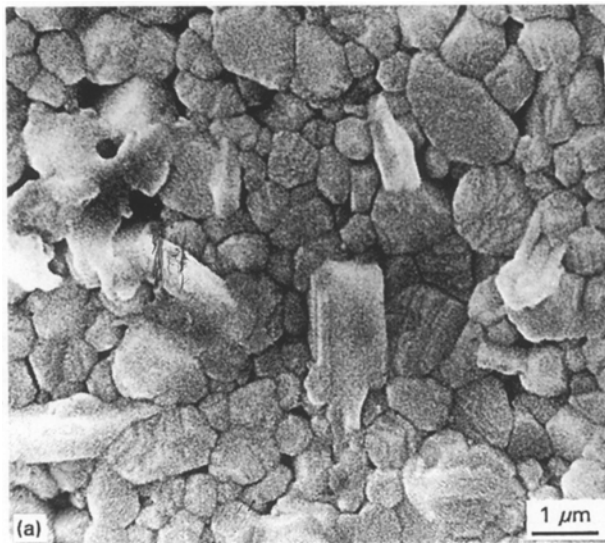


Figure 5 SEM micrographs of ester phosphate modified barium titanate ceramic sintered at 1300 °C for 2 h. (a) Polished and thermally etched surface showing exuded secondary crystalline phase, $Ba_3(PO_4)_2$, and, (b) fresh fracture surface showing intergranular fracture behaviour.

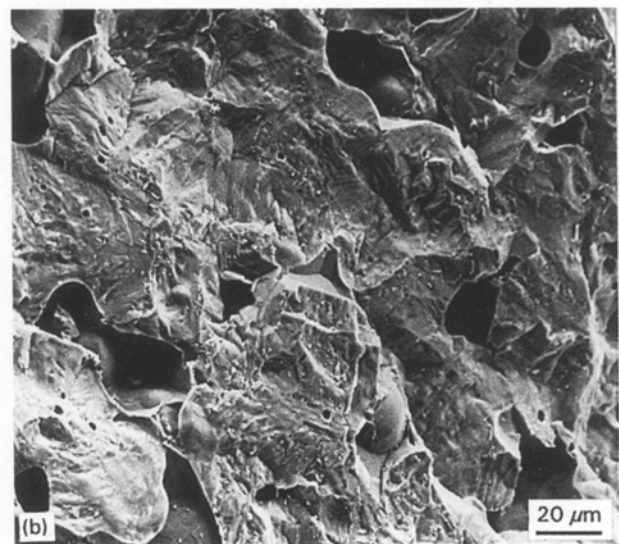
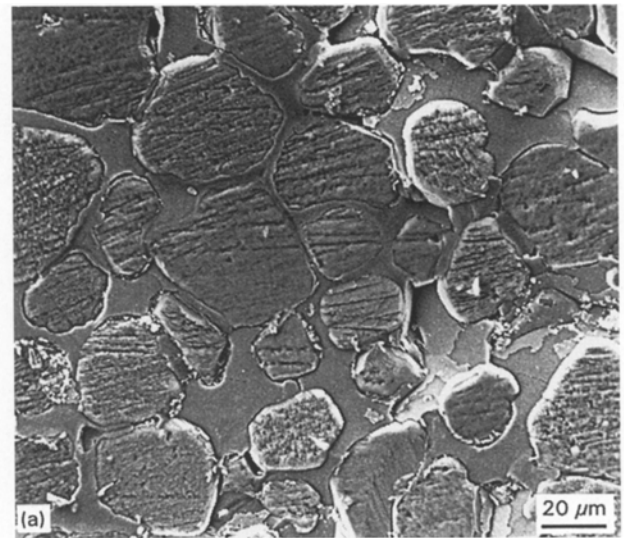


Figure 6 SEM micrographs of ester phosphate modified barium titanate ceramic sintered at 1375 °C for 2 h. (a) Polished and thermally etched surface showing secondary amorphous phase surrounding barium titanate grains and, (b) fresh fracture surface showing transgranular fracture behaviour of the barium titanate grains.

existence of secondary phases, the consequence of impurities or doping, could be the reason for such a difference.

4. Advanced model for sintering BaTiO₃ ceramics

A new model for sintering BaTiO₃ ceramics based on the effects of surface heterogeneity reported is proposed. The advanced method is schematically compared with conventional doping method in Fig. 7.

The conventional method starts with the mixture of BaTiO₃ particles and the corresponding dopant ones. The BaTiO₃ particles showed a hydroxycarbonated state on their surfaces. The dopants are heterogeneously distributed due to the physical limitations of mechanical mixing methods. As the temperature rises, the hydroxycarbonated state disappears and gives rise to non-stoichiometric ratio on BaTiO₃ particle surfaces, $Ba/Ti_{\text{surface}} > 1$. The excess of Ba²⁺ requires higher sintering temperatures and this increase of temperature is greater as the degree of carbonation rises. The dopants react with the surface of the BaTiO₃ particle and thereafter with barium titanate compound. In this sense, dopant addition and several solid solution limits on BaTiO₃ system must be re-examined taking into account this idea. On the other hand, the dopants that are heterogeneously distributed could provoke exaggerated grain growth. Also, secondary phases remain at grain boundaries or triple point junctions. As a result, complete solid solution of dopants probably does not take place.

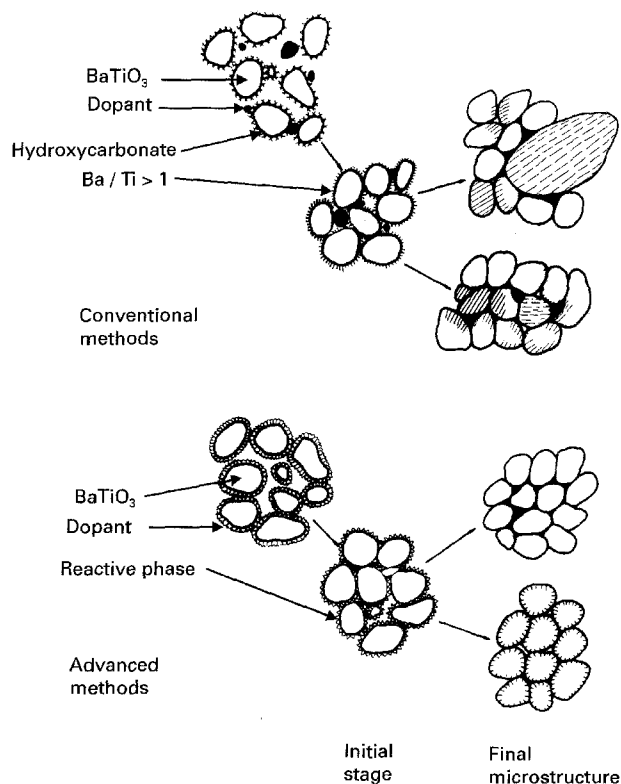


Figure 7 Schematic representation of the advanced method proposed to improve sintering in barium titanate ceramics in comparison with conventional doping method.

Unlike conventional doping methods for BaTiO₃ ceramics, advanced preparation methods provide the correct distribution of the dopants on BaTiO₃ particles. These dopants avoid carbonation by combining with Ba²⁺ cation excess. The correct distribution of the dopants normally requires chemical processing. The isoelectric point of specimens can be checked to confirm that homogeneous distribution has been achieved. Hydrated surfaces have not necessarily been avoided. The presence of OH⁻ in the green bodies could favour the reactivity at low temperature between Ba²⁺ cations and dopants by hydrothermal reactions. At the initial stage of sintering, a reactive phase is formed at the grain boundaries. When the temperature rises, this reactive phase, generally a liquid phase, acts as a lubricant medium during this stage and high densification values can be attained. The elimination of the carbonation reduces the sintering temperature and produces an increase of the shrinkage rates. The amount of liquid phase is small and, therefore, the mass transport is minimized. The secondary phase could be located at the grain boundaries or triple point junctions, or absorbed in BaTiO₃ grains to form a solid solution with good distribution of the dopants along the grains, as compared to conventional doping methods which produce high and low doping regions.

At this point it is necessary to remark that the non-homogeneous, conventional doping methods could behave similarly to satisfy the requirements of advanced methods if a reactive phase was formed at the first sintering stage, and it is distributed by high surface diffusion before the complete sintering takes place. This hypothesis implies that the dopants react



Figure 8 TEM micrograph of X7R capacitor ceramics based on niobium-cobalt modified BaTiO₃ powders with 0.2 wt % silica addition sintered at 1225°C for 2 h.

with surface cations at a temperature lower than the initial sintering stage at which undoped powders start, and also that the bulk diffusion coefficient would be very low in comparison with the surface diffusion coefficient at this temperature.

This proposed advanced method allows increased sinterability of the BaTiO₃ ceramic powders and, as a consequence, lowering of the sintering temperatures and enhanced quality of the final ceramic bodies through the formation of better microstructures.

By following this model, 98% D_{tb} BaTiO₃ ceramics were obtained at temperatures 50–100 °C lower than those needed for conventional sintering [26–30]. In most cases, this reduction of sintering temperature resulted in a microstructure with a smaller grain size and the consequent improvement of the dielectric properties. As an example, TEM examination of the microstructure attained for X7R capacitor material obtained by co-precipitating dopants on synthetic BaTiO₃ [27], revealed the existence of the grain core–grain shell structure (Fig. 8). Grain cores show typical ferroelectric domains patterns whereas grain shells consist of nonferroelectric materials. No evidence of secondary intergranular phases was observed so the different dopants were incorporated into the grain boundaries.

5. Conclusions

Carbonation and hydration are common states on ceramic particle surfaces that are obtained by calcining treatment. The Ba²⁺ rich surface particles move locally the stoichiometry to BaO-rich compounds in the BaO–TiO₂ system, and these compounds sinter at higher temperatures and longer times than the stoichiometric or TiO₂-rich ones, which lead to heterogeneous microstructure with exaggerated grain growth and pinhole porosity.

More activated barium titanate particles could be obtained if the hydroxycarbonate surface state is avoided by applying specific treatments after synthesis.

The advanced model for sintering of BaTiO₃ ceramics implies the correct distribution of dopants on BaTiO₃ particles, and the adequate distribution could generally be attained by chemical methods. These dopants avoid carbonation by combining with the Ba²⁺ cation excess. The reduction of the carbonation decreases the sintering temperature and produces an increase in densification. A reactive metastable phase is formed at the grain boundaries in the initial stage of sintering. This reactive phase, generally a liquid phase, acts as a lubricant medium during this first stage of sintering and highly dense bodies could be attained.

This proposed advanced method increases sinterability of the BaTiO₃ ceramic powders and, as a consequence, a lowering of the sintering temperatures thus enhancing the quality of the final ceramic bodies through a better developed microstructure. The improvement of dielectric properties is thus attributed to

the grain growth control and the compensating balance between donor and acceptor dopants which can be reached.

Acknowledgements

This work was supported by the Spanish Inter-ministerial Commission of Science and Technology (MAT94-0807) and partially by a grant from Rhône Poulenc Química. The authors wish to express their thanks to Professor Jose L. Garcia-Fierro for XPS measurements and to Professor M. Yoshimura for helpful discussions.

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Received 14 September 1994

and accepted 22 June 1995