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Role and behaviour of orthotitanate Ba_2TiO_4 during the processing of $BaTiO_3$ based ferroelectric ceramics

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Some anomalies observed in the dielectric properties of ceramics made from calcines of $BaTiO_3$ are due to the presence of Ba_2TiO_4. These effects are only negligible if the Ba_2TiO_4 concentration in the calcine is less than 1 or 2 wt %. For concentrations greater than this, Ba_2TiO_4 inhibits the growth of $BaTiO_3$ grains, shifts the Curie point towards low temperatures, decreases ϵ_r and causes large fluctuations in tan δ curves.

1. Introduction

Barium metatitanate $BaTiO_3$ manufactured by solid–solid reaction between carbonate $BaCO_3$ and titanium oxide TiO_2 is the main constituent of high constant, dielectric ceramics.

The reproducibility of the electrical characteristics of these ceramics depends notably on the degree of purity of the metatitanate. Now, the synthesis of $BaTiO_3$ is frequently accompanied by that of other titanates, Ba_2TiO_4 being most readily formed in the largest amount. The conditions of occurrence of Ba_2TiO_4 as well as its formation and destruction mechanism during the calcining of $BaTiO_3$ were studied [1, 2] and it was shown that some industrial calcines of $BaTiO_3$ contain appreciable amounts of $BaTiO_4$.

Thus, the first problem raised is to whether the anomalies observed in the dielectric properties of some ceramics made from those calcines are related or not to the presence of Ba_2TiO_4. Secondly, if this correlation is established, we must understand how the presence of Ba_2TiO_4 in a calcinate powder of $BaTiO_3$ may modify the dielectric properties of ceramics made from it.

The problem was approached in this way and the results are reported in this paper.

2. Experimental details

2.1. Materials

Ceramic bodies were made from two strains of $BaTiO_3$ prepared industrially; one which will be termed Y, was "pure" metatitanate (allowing for X-ray diffraction accuracy – Fig. 1); the second, called Z, contained orthotitanate. Other ceramics were made from artificial mixtures of $BaTiO_3$ (calcine Y) and of Ba_2TiO_4 synthesized according to a method described previously [2]. The extents of Ba_2TiO_4 in the different mixtures were 1, 2, 3, 5 and 10 wt %.

2.2. Ceramic body fabrication

The initial powders (Y or Z or mixtures $BaTiO_3$–Ba_2TiO_4) were suspended in water as a slurry. A binding agent (polyvinyl alcohol) required to shape the ceramics was then added. No other agent was used. The slurry was then injected into an atomizer to obtain a graded powder. Shaping was performed by pelleting under a pressure of about 1 tonne cm^{-2}. The pellets were then sintered at 1400° C on a platinum support for 4 h. The sintered discs were 12.8 mm in diameter and 1 mm thick.

To compactness, the ceramic bodies will be also denoted by Y and Z, designating the two powders used, or they will be identified by the per cent of Ba_2TiO_4 contained.

2.3. Electrical measurements

After sintering the discs were metallized and connections were welded on each face. The dielectric characteristics of the condenser thus obtained, i.e. the loss angle δ (evaluated by tan δ) and the

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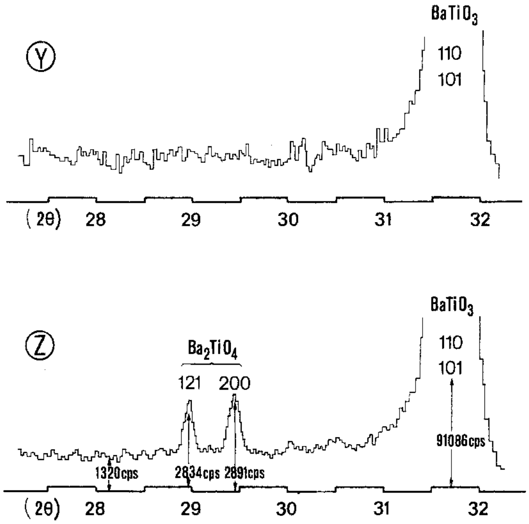


Figure 1 Partial X-ray diffractorgams related to calcines Y and Z (monochromated Cu$K\alpha_1$, Step scanning: 2/100°2θ, 800 sec).

relative dielectric constant ϵ_r were measured over the temperature range −55° C to + 140° C.

2.4. Analysis

All the samples, industrial calcine mixtures and ceramic bodies made by firing, were investigated by X-ray diffraction. The purpose of these investigations was, on the one hand, to identify Ba_2TiO_4 and a possible displacement of its characteristic diffraction lines during thermal treatment and, on the other, to assess the extent of formation of Ba_2TiO_4 in industrial powders. Therefore the diffractograms were rather finely recorded over a range of 2θ which contained two strong lines of Ba_2TiO_4 (1 2 1 and 2 0 0) and a strong reflection of $BaTiO_3$ (mixed lines 110, 101 – Fig. 1). The recording conditions were as follows: step scanning (1/100 °2θ – 800 sec) – Cu$K\alpha_1$ monochromated radiation. The background was recorded each side of the peaks sufficient to allow good precision. The corrected experimental values of the Lorentz polarization factor and of the background were then treated to obtain the area of each orthotitanate peak; this area increased almost linearly with the Ba_2TiO_4 concentration (Fig. 2).

A morphological study of all the samples before and after firing was carried out in an SEM at the surface of the ceramics and on out sections. Electron probe microanalysis (EPMA) was used to identify and locate the different phases. Some observations by transmission electron microscopy (TEM) were made on sections made thin by ionic abrasion.

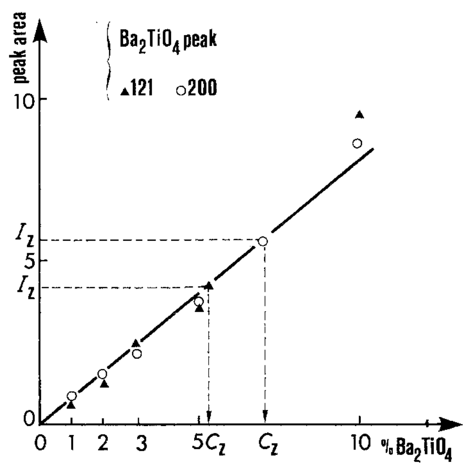


Figure 2 Variation of the area of the diffraction peaks against the percentage of Ba_2TiO_4 added to a $BaTiO_3$ calcine.

3. Results

3.1. Comparison of the dielectric properties of ceramics Y and Z

The straight line plot in Fig. 2 shows the variation of the area of the 121 and 200 diffraction peaks of orthotitanate against the percentage of Ba_2TiO_4 added to a strain of $BaTiO_3$. This plot allows the amount of Ba_2TiO_4 contained in the industrial calcine Z to be deduced, the proportion C_Z being comprised between 5 and 7%. For calcine Y, the amount of orthotitanate contained is very low, much less than 1% since the specific bands of this phase have not been detected in the recording conditions used (Figs. 1 and 2).

The results of the dielectric measurements made on ceramics Y and Z are listed in Fig. 3; they show appreciable differences.

From room temperature up to about 100° C ceramic Z shows ϵ_r and tan δ values for larger than those obtained for ceramic Y.

In contrast, at higher temperatures (120° C) constant ϵ_r is lower for ceramic Z and the Curie point is slightly shifted towards low temperatures. Finally the variation of tan δ with temperature is far more irregular for ceramic Z than for Y.

3.2. Comparison of the dielectric properties of the ceramics prepared from mixtures of orthotitanate and metatitanate

At temperatures below the Curie temperature the dielectric constant increases with increasing Ba_2TiO_4 content. The maximum value of ϵ_r at the Curie point, however, falls with increasing

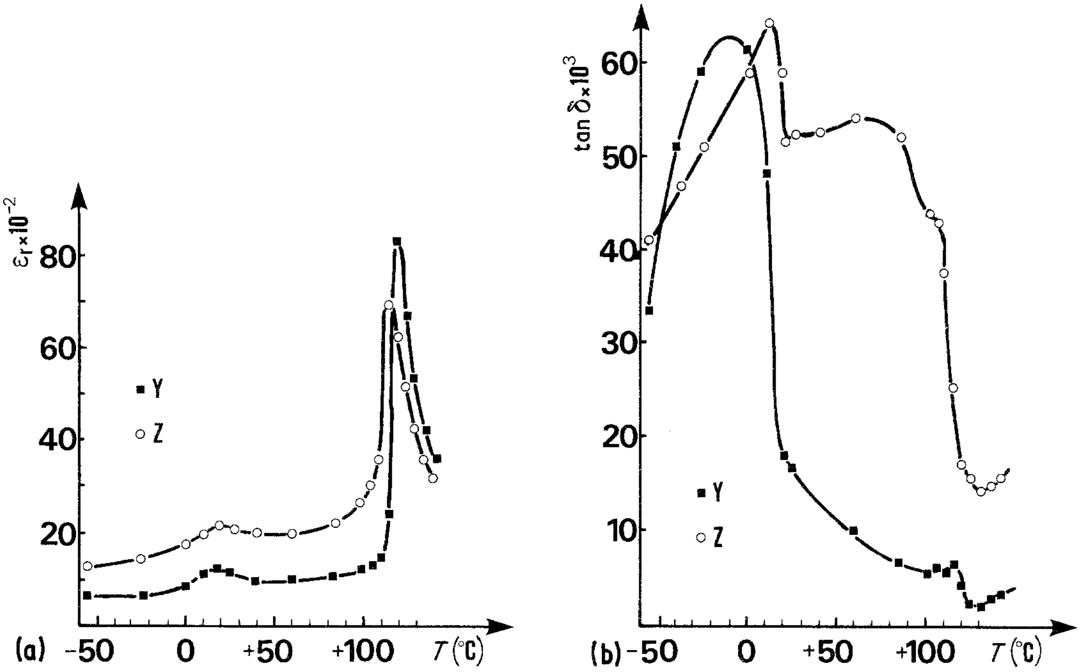


Figure 3 Dielectric characteristics ϵ_r and δ of two ceramics Y (containing only $BaTiO_3$) and Z (containing $BaTiO_3$ and some per cents of Ba_2TiO_4). δ is the loss angle and ϵ_r is the relative dielectric constant.

Ba_2TiO_4 content and the Curie point itself is displaced to lower temperatures (Figs. 4a and b).

Concerning the variation of tan δ (Fig. 4c) no significant change is noticed when the amount of Ba_2TiO_4 in the mixture is less than 5% but for amounts of 5 and 10% there is a large fluctuation in the curve.

3.3. Composition of the dielectric after sintering

Ceramics bodies similar to those used for electrical measurements were ground and then analysed in X-ray diffraction. It was then noted that the orthotitanate present in the powder Z and in the 1 and 2% mixtures had disappeared during ceramic curing. Allowing for measurement accuracy the diffractograms only show the presence of metatitanate $BaTiO_3$.

For ceramics prepared from 5 and 10% mixtures of Ba_2TiO_4, the latter also disappeared but an extraneous phase, characterized by a single band, poorly visible, ($d = 0.307$ nm) was detected but could not be identified.

4. Discussion and further results

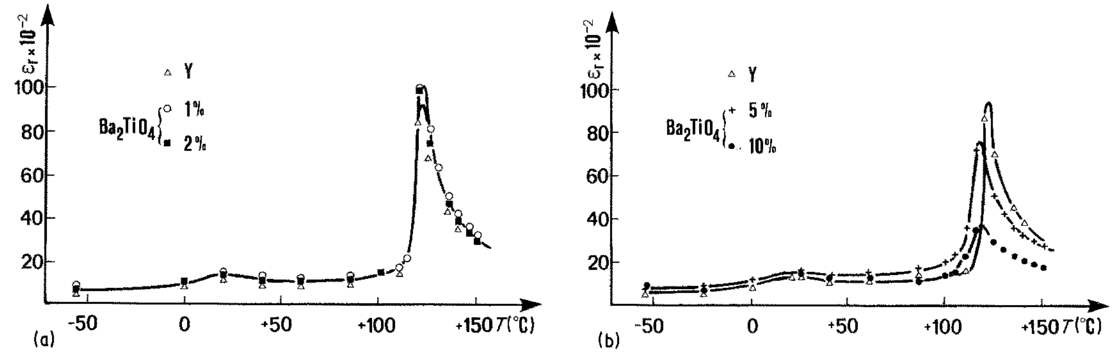
The absolute values of ϵ_r and tan δ obtained with ceramics resulting from Ba_2TiO_4 and $BaTiO_3$ mixtures are different from those found for ceramics prepared from Z, but the changes observed with respect to the results obtained for a pure $BaTiO_3$ based ceramic follow the same trend.

It should be noted that this difference may be due to the fact that in the case of mixtures there can only be juxtaposition of $BaTiO_3$ and Ba_2TiO_4 grains whereas in a calcine such as Z these two phases coexist in grains which were undergoing transformation when calcining was stopped [2].

Nevertheless, from the results of dielectric measurements, it is obvious that the presence of Ba_2TiO_4 in a calcinate powder of $BaTiO_3$ is the origin of the changes in the characteristics of the dielectric prepared from this powder. The threshold below which the presence of Ba_2TiO_4 seems to bring about only negligible effects is about 1 to 2%.

The remaining question concerns the way in which the orthotitanate present in the $BaTiO_3$ before sintering, may change the properties of the resulting ceramic while it totally disappears during curing. In an attempt to answer this question a series of observations with SEM and EPMA was undertaken with all the ceramic bodies prepared.

The SEM and EPMA observations of the surface of the ceramics made from the 1% Ba_2TiO_4 mixture shows that the $BaTiO_3$ grains are coated with a substance rich in barium but containing no titan-



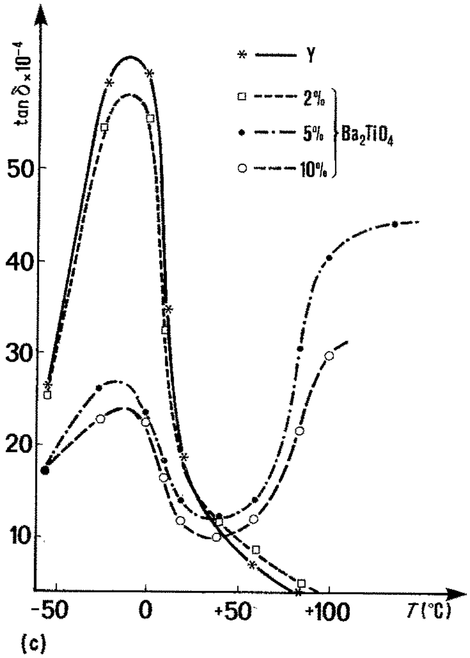


Figure 4 Dielectric characteristics ϵ_r and δ of $BaTiO_3$ ceramics containing various per cents of Ba_2TiO_4. (a) and (b) $\epsilon_r = f(T)$, and (c) $\tan\delta = f(T)$.

ium (Figs. 5a, b and c). This phenomenon is to be related to what has been observed in the macroscopic study of the $BaTiO_3$–Ba_2TiO_4 interface [2]. Indeed, after thermal treatment of a reaction couple of TiO_2, $BaTiO_3$ and Ba_2TiO_4 pellets it has been observed that the transformation of Ba_2TiO_4 brings about the occurrence of a phase termed "BaO", which coats the $BaTiO_3$ grains near the contact surface between $BaTiO_3$ and Ba_2TiO_4. Another interesting result has been obtained by observing 1% ceramics, the presence of Ba_2TiO_4 does not seem to affect the sintering of metatitanate grains. In fact the grain size is the same in a Y and 1% ceramic (Figs. 6a and b).

When the extent of orthotitanate reaches 2%, the $BaTiO_3$ grains are still of the same size but, on the one hand, they are irregular and, on the other, the substance "BaO" no longer occurs as clearly at the grain periphery (Fig. 6c).

Larger addition of Ba_2TiO_4 affects considerably the morphological evolution of $BaTiO_3$ grains. The evidence shows that grain growth is progressively inhibited with increasing proportions of Ba_2TiO_4.

In compositions containing 5 or 10% Ba_2TiO_4 the grains have remained comparable in size with the initial calcine crystallites. In addition the examination of cross-sections allowed identification of the accumulation, as small blocks, of a phase that might be likened to that already termed "BaO" (Figs. 5d, e and f).

The examination of ceramic Z, by the above mentioned techniques, supplemented by TEM analysis, shows the same features as those of ceramics made from 5 or 10% mixtures of Ba_2TiO_4.

1. Intergrain sintering of $BaTiO_3$ does not occur. The sizes of $BaTiO_3$ grains in the ceramic after curing are the same as those of the crude powder grains (Fig. 6f).

2. There is no segregation of phase "BaO" at grain boundaries, but formation of random blocks (Figs. 5g, h and i).

It thus seems that the presence of a proportion of orthotitanate no exceeding 2% in the $BaTiO_3$ powders does not affect appreciably the sintering of ceramic grains, whereas it limits it strongly for amounts higher than 5%. These observations confirm those related to the electrical properties of these ceramics. Indeed, on the one hand, the $\tan\delta = f(T)$ and $\epsilon_r = f(T)$ curves obtained from ceramics resulting mixtures with a low content of Ba_2TiO_4 differ little from those characterizing the dielectric formed by calcine Y, on the other, the characteristics $\tan\delta$ and ϵ_r of ceramics resulting from mixtures at 5 and 10% and from calcine Z shift appreciably from those of ceramic Y.

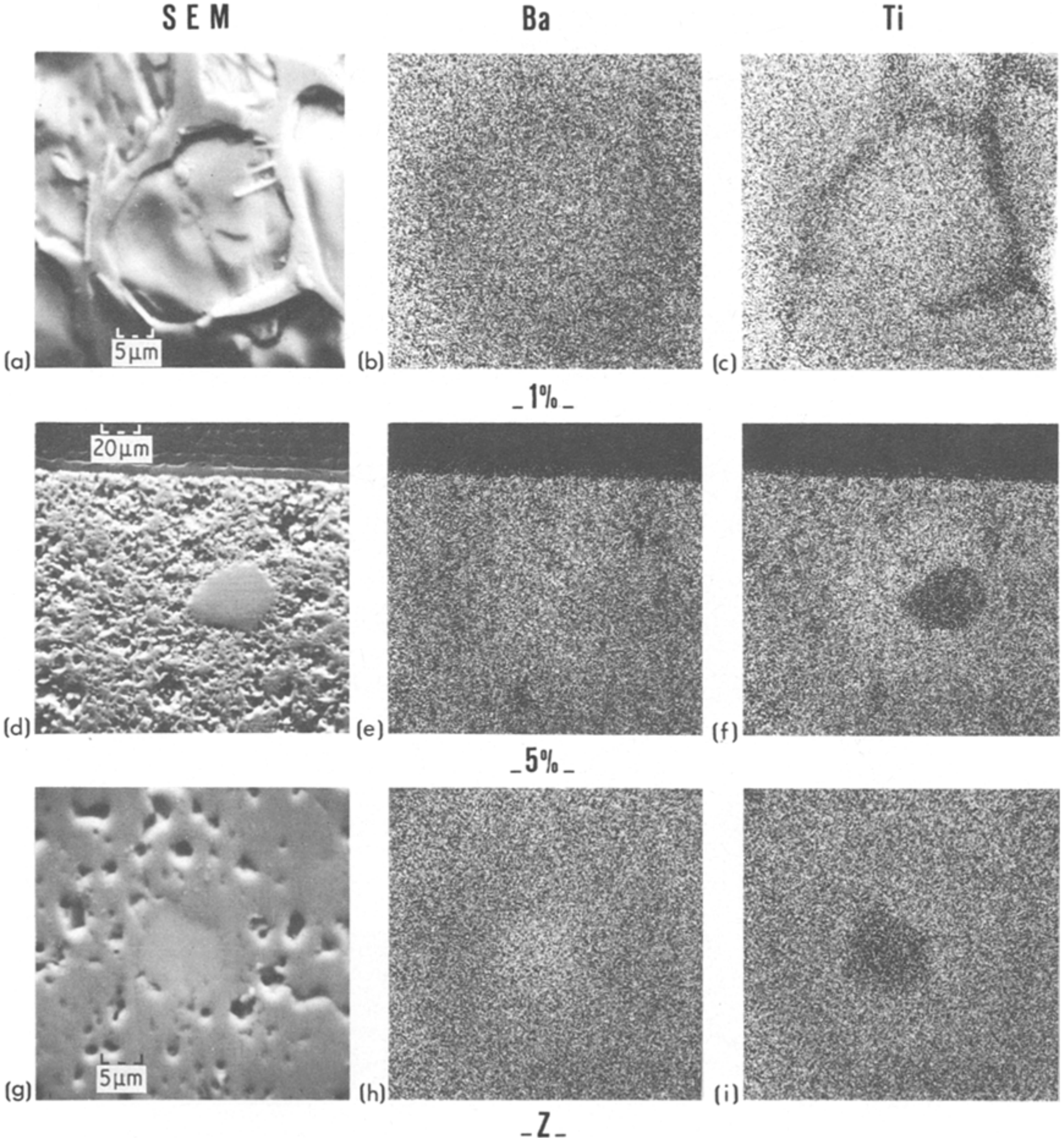


Figure 5 Localization and composition of the degradation product of Ba_2TiO_4 after firing of various ceramics at 1400° C. (a) (b) (c) Ceramic from mixture of calcine $BaTiO_3$ Y and of 1% of $BaTiO_4$. (d) (e) (f) Ceramic from mixture of calcine $BaTiO_3$ Y and of 5% of Ba_2TiO_4. (g) (h) (i) Ceramic from calcine $BaTiO_3$ Z.

5. Conclusions

The above results show that there is a relation between the presence of Ba_2TiO_4 in a calcine of $BaTiO_3$ and some disturbances in the dielectric properties of ceramics prepared from such a powder. The part played by Ba_2TiO_4, even if proved, is not however explained.

The results reported show that orthotitanate inhibits the growth of $BaTiO_3$ grains; this role has been confirmed by tests on samples of powder Z with prior removal of Ba_2TiO_4 by washing in acetic acid. The tests have shown that with the disappearance of orthotitanate the grain growth during sintering becomes normal. However, the inhibiting factor of sintering is not clear. Indeed, how can one explain that the growth of $BaTiO_3$ grains is limited whereas the phase formed by the transformation of Ba_2TiO_4 during curing is assembled as blocks that are far away from one another in the ceramic although this is not the case when this phase is at the periphery of $BaTiO_3$ grains?

In addition, the identity of transformation

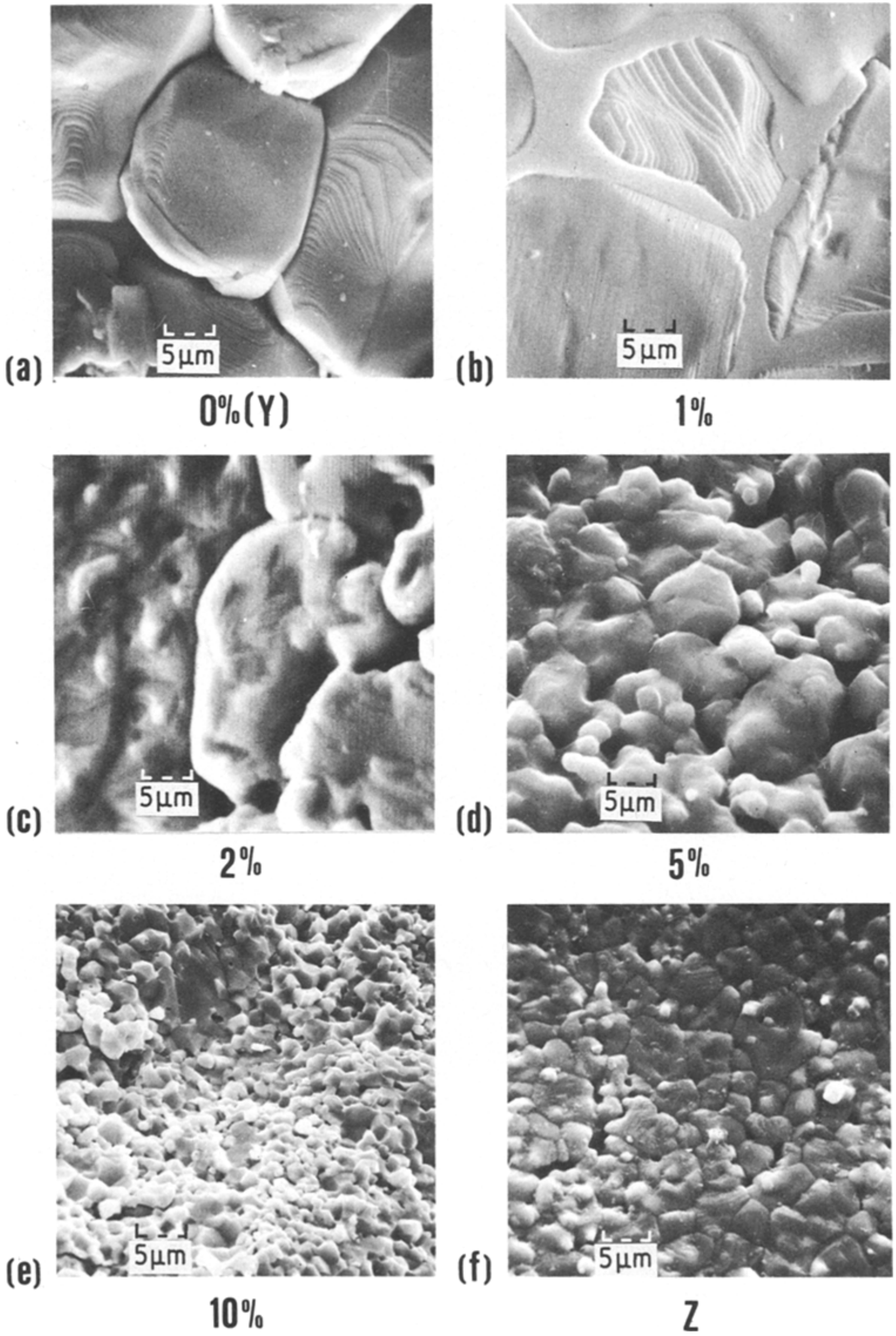


Figure 6 SEM study of $BaTiO_3$ grains in various ceramics after firing at 1400° C.

observed for ceramics containing initially a large amount of Ba_2TiO_4 and for ceramics resulting from calcine Z, shows that the part played by Ba_2TiO_4 during curing does not seem to depend on its location in the initial powder.

These results are to be related to those obtained by Murray [3] and to those of Goswami [4] who showed the close dependence of dielectric properties against particle size and the sintering state of barium titanate; two features, as we have shown, that depend on the amount of Ba_2TiO_4 remaining in the metatitanate.

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