

Microstructure development and dielectric properties of fast-fired BaTiO₃ ceramics

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The technique of zone sintering was applied to three BaTiO₃ source materials; studies were made in air, oxygen and vacuum. The optimum firing conditions suggested for the zone sintering of these materials were a temperature of 1450°C and a time in the hot zone of 5 min. The temperature dependence of the dielectric constant could be closely related to the firing conditions and material microstructure. Lower room-temperature dielectric constants and lower Curie temperatures were found as the holding time in the hot zone was increased, yielding larger grained structures.

1. Introduction

Since its discovery, BaTiO₃ has been used as a high permittivity capacitor material with relative permittivity value around 1500. However, in 1954 Kniepkamp and Heywang [1] reported that this relative permittivity value can be increased to 3500, if polycrystalline BaTiO₃ of approximately 1 μm grain size is sintered to about 90% of its theoretical density. Jonker and Noorlander [2] prepared a high permittivity BaTiO₃ by a similar process to that followed by Kniepkamp and Heywang, but they did not find any evidence for the separate BaO·2TiO₂ phase initially thought to be responsible for the enhanced permittivity. High relative permittivity (~6000) ceramic BaTiO₃ has also been prepared [3] from chemically pure material, confirming Jonker and Noorlander's observation. Following the early investigations, a significant amount of work has been done in recent years to establish the fact that the dielectric properties of ferroelectrics and piezoelectrics such as BaTiO₃ are strongly dependent on microstructure, in particular on fine grain size. Hot-pressing techniques [4-8], flash-firing methods [9, 10] and varieties of grain growth inhibitors [1, 2, 11-17] have been investigated as means for preparing small-grained BaTiO₃.

A procedure for avoiding the problems created by surface diffusion and grain growth can be the use of high temperatures and short times during firing. In this technique which has primarily been proposed for the fabrication of dense, fine-grained polycrystalline β-alumina [18], the sample is subjected to a nonisothermal treatment by being passed through a short hot zone which is held at high temperature. Under such conditions, densification can be promoted relative to grain growth and other microstructural changes [19]. Such "fast-firing" processes have successfully been used to prepare translucent aluminas [20, 21] with high density and fine grain size. Also, ferrites having identical microstructures to samples that have been conventionally fired have been produced by fast-firing techniques [22]. There are also cases, exemplified by MgO [23], in which the technique has been found to be unsuccessful.

The aim of the present investigation is to study the fast-firing of BaTiO₃ compounds with a view to identifying the conditions under which samples of high density and fine grain size can be obtained. The dielectric constant and loss tangent of selected samples are then measured to determine the effect of the processing variables on the dielectric properties BaTiO₃.

2. Experimental procedure

2.1. Materials

Three grades of BaTiO₃ powder were employed in this investigation: one synthesized grade (>99.4% purity), and two high purity commercial grades (>99.8% purity, National Lead and Anzon high purity BaTiO₃ both supplied by Allen Clark Research Centre, Plessey Co, Caswell, Towcester, UK). The synthesized titanate was prepared by calcining the required proportions of Analar grade BaCO₃ (BDH Chemicals Ltd) and Analar grade TiO₂ (Koch-Light Laboratories Ltd). Different nonstoichiometric mixtures were prepared [24] by varying the proportions of the TiO₂ and BaCO₃ used in the formation of the titanate powder.

Scanning electron microscopy observations of the powders were indicative of different morphologies in the initial powders. The particle size of the BaTiO₃ (National Lead) was the finest of all (<0.5 μm) but the powder was highly agglomerated. The high purity BaTiO₃ (Anzon) consisted of a rather wide spectrum of particle sizes (0.5 to 2.5 μm). Finally, the synthesized powder consisted of uniform particles with size around ~1 μm. These powders will be referred to as fine-agglomerated, wide distribution, and narrow distribution in the following descriptions.

2.2. Specimen preparation and firing schedule

Specimens were made by wet bag isostatic pressing in the form of thin walled tubes (~1 mm wall thickness, 10 mm o.d. and up to 30 mm long); for consistency, all the samples were produced at the same pressure (~140 MN m⁻²). Samples in the form of discs were also made for electrical testing purposes; these were

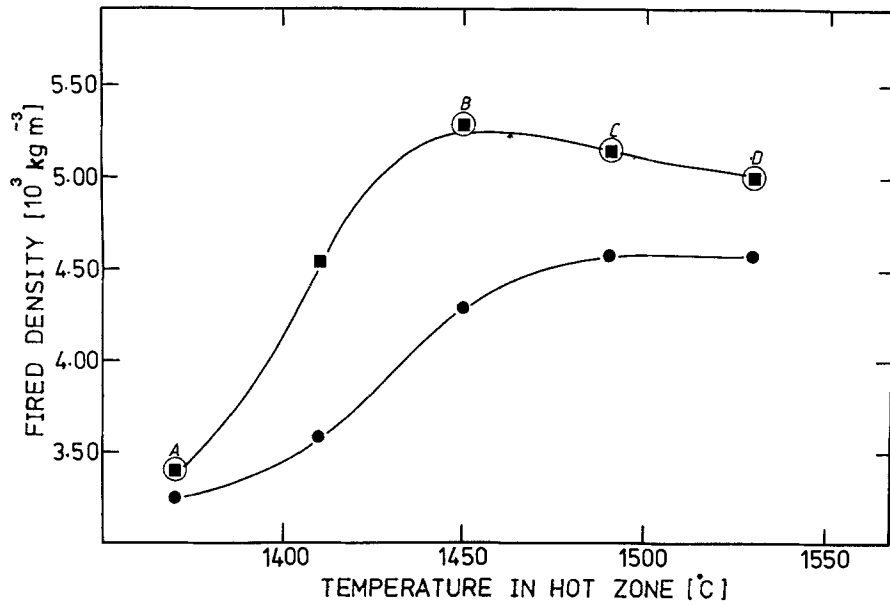


Figure 1 The effect of temperature on the reaction sintering of stoichiometric mixtures of $(\text{BaCO}_3 + \text{TiO}_2)$ powders. Time in hot zone: ●, 1 min; ■, 4 min.

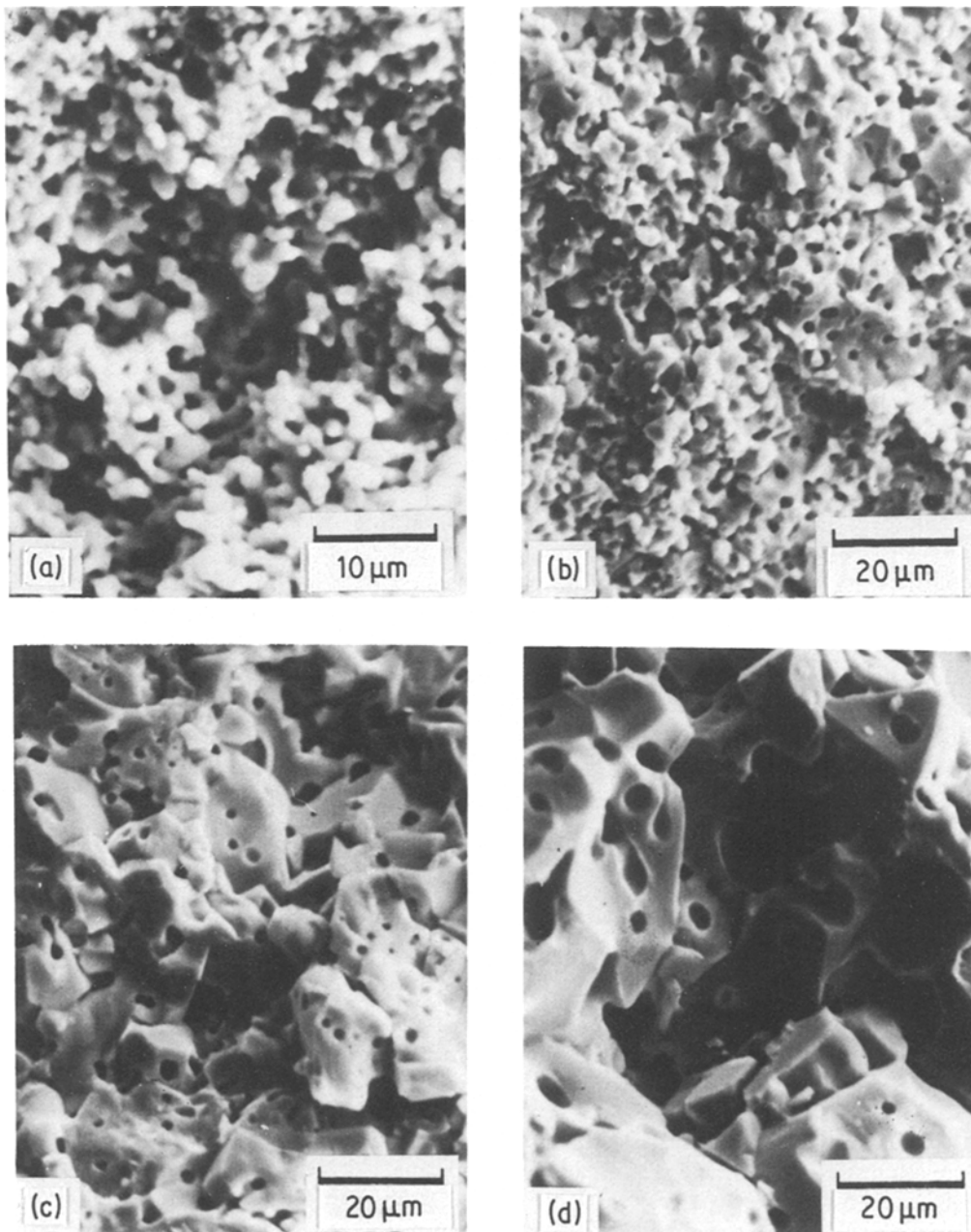


Figure 2 Microstructure development in the zone sintered stoichiometric mixtures of $(\text{BaCO}_3 + \text{TiO}_2)$ powders relative to T : (a) A, 1370°C; (b) B, 1450°C; (c) C, 1490°C; (d) D, 1530°C (letters correspond to points marked in Fig. 1).

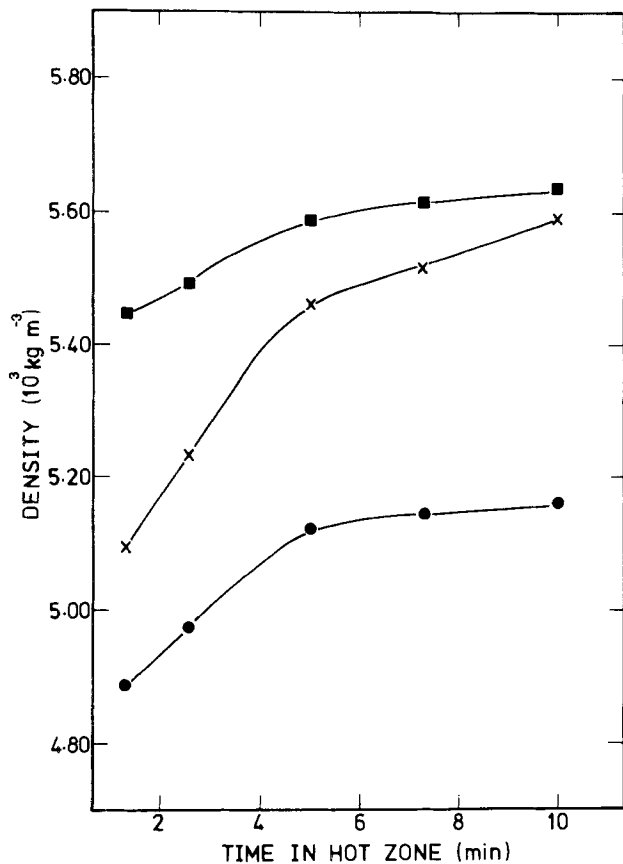
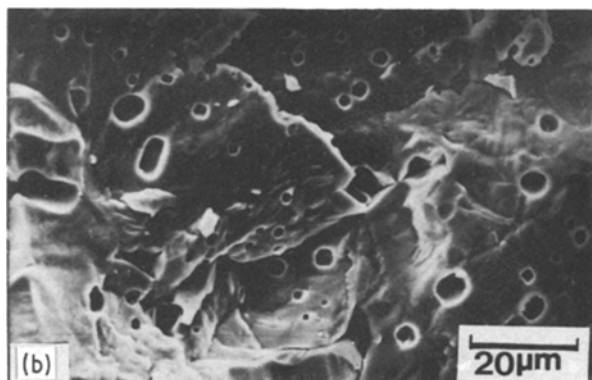
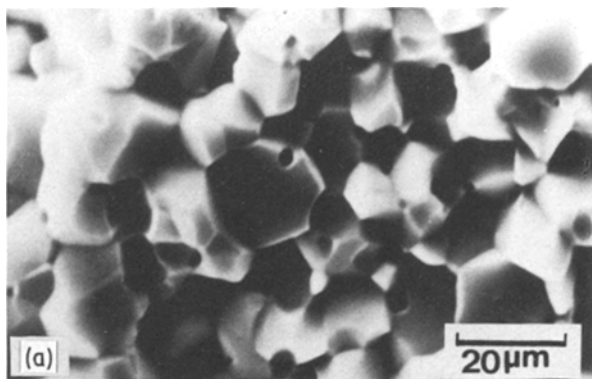


Figure 3 The zone sintering behaviour of different BaTiO₃ ceramics in air. Temperature in hot zone: 1460° C; firing atmosphere: air; ■, narrow distribution; ×, wide distribution; ●, fine-agglomerated.

uniaxially cold-pressed in a steel die at $\sim 75 \text{ MN m}^{-2}$ (no binder was used). About 1 g powder was used for producing each disc with dimensions of 12.7 mm diameter and 2.5 mm thickness before firing.

For firing, the samples were first pushed up to a



predetermined position (temperature range 700 to 800° C in the zone-sintering apparatus [25]); the automatic driving equipment was then started and the samples were moved through the furnace at a constant speed.

2.3. Dielectric property measurements

Samples were first cleaned in carbon tetrachloride; silver paint (Electrodag 915, Acheson Colloids Ltd, UK) was then brushed on both parallel surfaces of each pellet. The samples were then heated to 60° C for 2 h to remove all traces of the solvent. Capacitance and loss measurements on the samples were carried out using a digital LCR meter (Hewlett Packard 4274 multi frequency LCR meter) at 1 kHz.

The relative permittivity of selected samples was also measured at 1 kHz as a function of temperature on an auto-balance Wayne-Kerr bridge (model B642) using an X-Y plotter (Bryans 2600) for continuous recording of the variation of capacitance with temperature. The capacitance of the discs was measured over the temperature range 0 to 160° C.

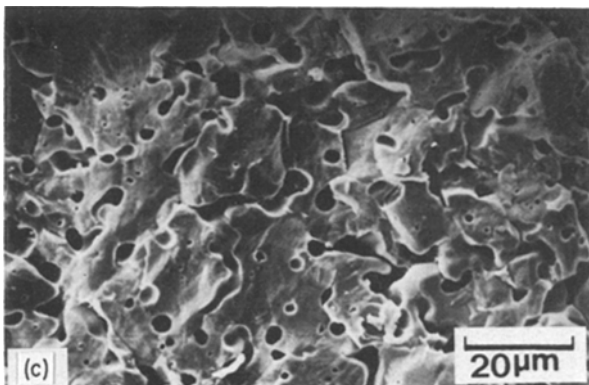
3. Results

3.1. Fast-firing of BaTiO₃ compositions

The effect of firing temperature was initially studied by using an uncalcined unreacted powder (BaCO₃ + TiO₂). For this purpose, the samples, in the form of thin-walled tubes or pellets, were fired at various temperatures and for fixed times of 1 and 4 min. The results are shown in Fig. 1. The occurrence of a density maximum at 1450° C was encountered at all firing times above 4 min for all powders. The effect of the temperature in the hot zone on the microstructural development in the samples can be seen in Fig. 2. The features in these figures (notably the rapid structural coarsening at temperatures above 1450° C) are consistent with the findings in Fig. 1.

The differences between the various source powders in terms of sinterability were substantial as can be seen in Fig. 3. The microstructures of samples made from the three powders by fast-firing for 10 min at 1450° C in air are compared in Fig. 4. The microstructure of the technical grade material consists of a relatively uniform grain matrix with pores remaining mainly at

Figure 4 Scanning electron micrographs of fracture surfaces of the samples prepared from various stoichiometric BaTiO₃ powders fired at 1450° C for 10 min: (a) BaTiO₃ (narrow distribution); (b) BaTiO₃ (wide distribution); (c) BaTiO₃ (fine-agglomerated).



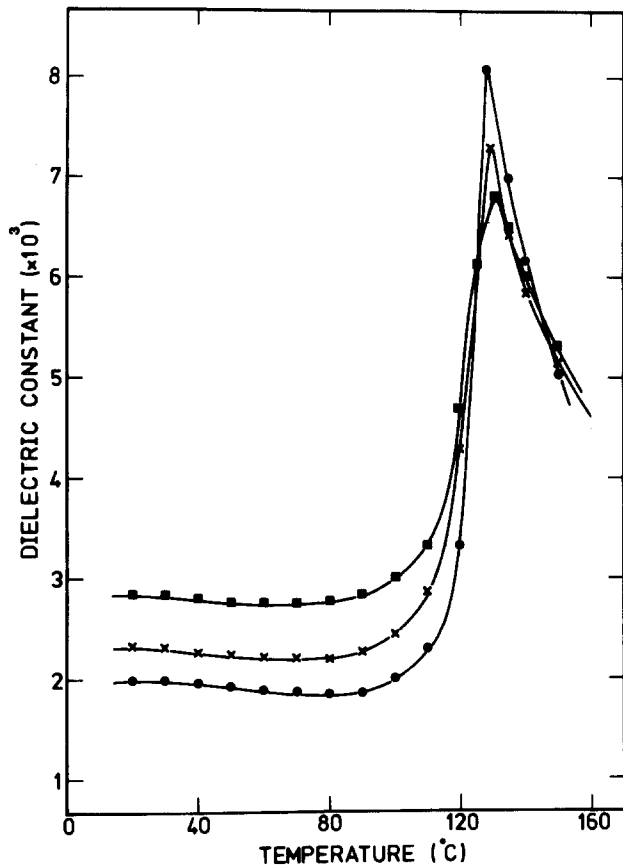


Figure 5 Temperature dependence of the dielectric constant for fast-fired BaTiO₃ ceramics in vacuum. BaTiO₃ (narrow distribution); temperature in hot zone, 1460°C. Time in hot zone: ■, 2 min; ×, 5 min; ●, 10 min.

the grain edges and corners, a structure consistent with the initial narrow size distribution in the powder. The microstructure development in the sample made from the "wide-distribution" powder is indicative of rapid grain and pore growth even after a short time at temperature. The specimens made from the "fine-agglomerated" powder show poor sinterability in accord with the degree of agglomeration found.

All materials showed similar behaviour in having small but significantly higher bulk densities when fired in vacuum. It was also found that oxygen firings produced higher densities than air firings.

3.2. Dielectric property measurements on the various fast-fired BaTiO₃ compositions

The dependence of the dielectric constant and the Curie temperature on the fast-firing parameters has been examined for the samples made from the three different BaTiO₃ powders. In Fig. 5, the dielectric constant is plotted against temperature from room temperature to 150°C for specimens made from the "narrow distribution" powder for vacuum firings over the firing range studied. The general trend is toward lower room temperature dielectric constants and lower Curie temperature as the holding time in the hot zone is increased. Higher firing temperatures and/or longer holding times in the hot zone result both in a decrease in the dielectric constant (Fig. 6) and in a reduction in the density (firing temperatures above 1450°C). It is therefore possible to make a link between these results and conclude that the reduction in dielectric constant is a consequence of structural coarsening of the type seen in Fig. 2. The presence of the hexagonal phase of BaTiO₃ at temperatures higher than 1450°C provides an additional reason for the considerable decrease in dielectric constant.

To obtain a broader view of the variation of dielectric properties with grain size, measurement of the dielectric constant was carried out on a full range of fast-fired samples. The densities together with values for the grain size and dielectric constant of the materials studied are shown in Table I. Results from the samples having densities of $5.4 \times 10^3 \text{ Mg m}^{-3}$ or higher can be used to plot dielectric constants at room temperature (K'_{25}) and at the Curie point (K'_C), as functions of the grain size (Fig. 7).

Finally, measurements of the temperature dependence of the dielectric constant were made on identical compositions processed either by conventional sintering or by fast-firing. As can be seen in Fig. 8, the benefits that are expected from the finer grain size are, in fact, realized, the room temperature dielectric constant having a substantially higher value in the fast-fired sample.

4. Conclusions

1. Differences among the powders drawn from different sources particularly in respect to degree of agglomeration, size distribution and size, exert a

TABLE I The dependence of the relative dielectric constant at room and Curie temperature on the holding time in the hot zone for stoichiometric BaTiO₃ ceramics, zone sintered at 1450°C

Feeding rate (mm min ⁻¹)	Approx. time in hot zone (min)	Fired density (Mg m ⁻³)	Average grain size (μm)	Relative dielectric constant		K'_C/K'_{25}
				At room temp. (K'_{25})	At Curie temp. (K'_C)	
3	16	5.69	14.2	2276	8784	3.86
4.8	10	5.65	12.4	2355	7995	3.39
6.1	7.9	5.59	9.8	2234	6836	3.06
6.6	7.25	5.60	8.6	2397	5993	2.50
9.6	5	5.57	7.1	2470	6126	2.48
14.5	3.3	5.44	6.8	2495	5778	2.32
19.3	2.5	5.39	5.6	2449	5290	2.16
38.6	1.25	5.32	4.9	2605	5054	1.94
60.5	0.8	5.05	3.8	1738	3580	2.06
76.9	0.6	4.96	2.6	1376	2463	1.79

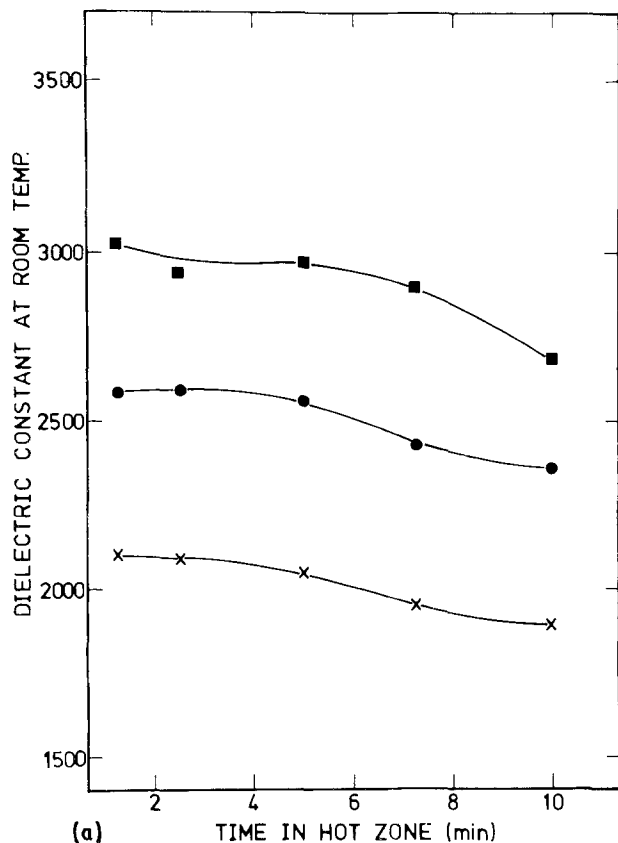
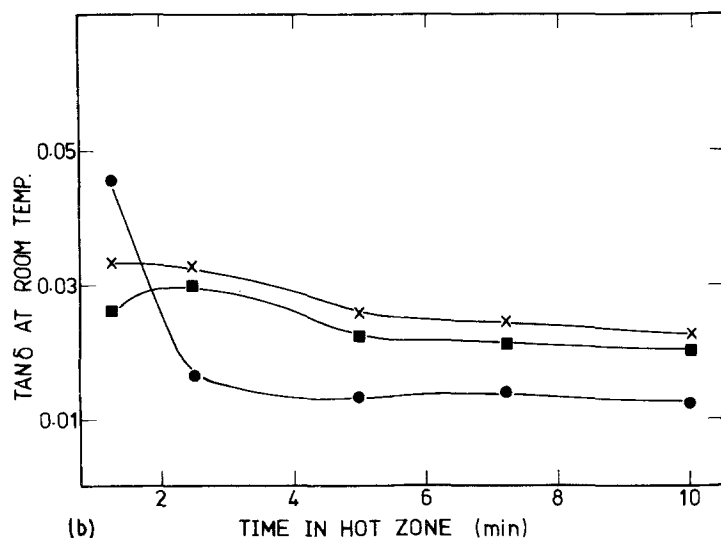


Figure 6 The influence of time in hot zone (1460°C) on (a) the relative dielectric constant, and (b) loss tangent of vacuum-fired ceramics made from three different BaTiO₃ powders. Firing atmosphere: vacuum. BaTiO₃: ■, narrow distribution; ●, wide distribution; ×, fine-agglomerated.



significant influence on the zone-sintering behaviour of BaTiO₃. The best results were obtained with a powder of relatively narrow size distribution and of fine size. The disparity of conclusions in the literature, where different raw materials and means of fabricating and firing have been used, may well stem from such differences and from variations in the resulting microstructures.

2. The use of vacuum for the sintering of BaTiO₃ shows modest benefits in microstructure and in dielectric properties.

3. The room-temperature relative dielectric constant increases as the grain size of the fast-fired BaTiO₃ ceramic is decreased. Since fast firing is a suitable route to the preparation of the fine grain sized materials, it therefore offers promise as a firing procedure for BaTiO₃ ceramics, the optimum condition being 1450°C with a firing time of 5 min.

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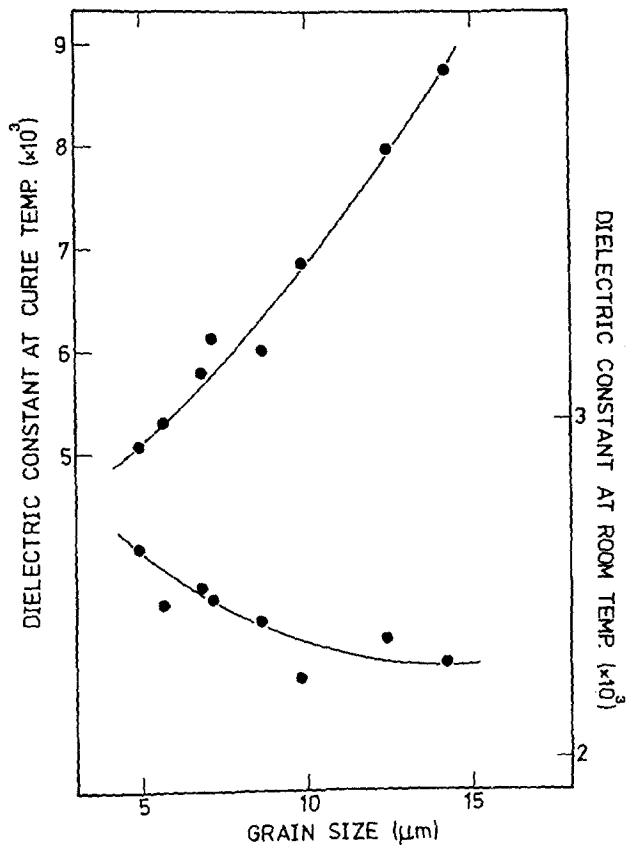


Figure 7 The variation of relative dielectric constant of the fast-fired BaTiO₃ ceramics (fired in air at 1450° C for various lengths of time) at room temperature and Curie temperature, as a function of grain size.

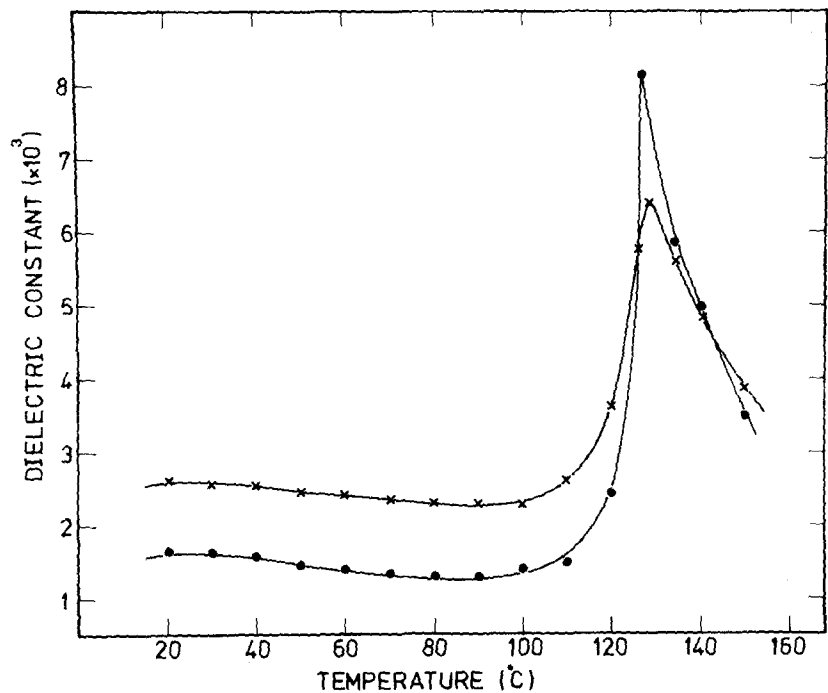


Figure 8 The temperature dependence of relative dielectric constant for the (x) fast-fired and (●) conventionally-fired BaTiO₃ ceramics (narrow distribution).

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