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Barium Titanate Based Ceramic Materials for Dielectric Use

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SUMMARY

Modern semiconductor integrated circuits require low-voltage capacitors which can store high electric energy in a minimum volume. Monolithic ceramic multilayer capacitors (CMC) offer the possibilities of high volume capacity at low self-inductance and IC compatibility. The ceramic materials used for the thin dielectric layers (15–30 μm) of CMCs are normally based on ferroelectric $BaTiO_3$*. The ferroelectric and dielectric properties of these materials are largely determined by heterogeneities in the microstructure and chemical composition. The influences of grain size and heterogeneity on the ferroelectric phase transition, domain size, permittivity and temperature characteristics are discussed.*

1 INTRODUCTION

In the production of passive electronic components, ceramic multilayer capacitors (CMC) play a prominent part. Due to their high volume efficiency, their excellent dielectric properties and their rather low self-inductance, these components are compatible with modern IC and hybrid technology. Multilayer chip capacitors have moreover become a dominant component in the surface mounting technology of consumer electronics.

For many years now there has been a continuous increase in the capacitance per volume of CMCs, which is more or less the result of improved materials technology. The increase in the capacitance per volume of monolithic capacitors,[1] as shown in Fig. 1, has mainly been due to reduction of the dielectric layer thickness and enhancement of the dielectric constant. In recent years the thickness of the dielectric layers has been reduced to about 20 μm, and a further reduction is still to be expected.

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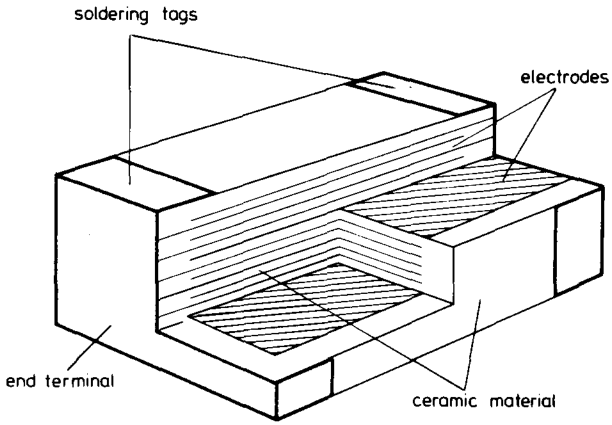

Fig. 1. Cut-away view of a ceramic multilayer chip capacitor.

Although the degree of miniaturization in monolithic capacitors is still rather low compared with that of integrated circuits, dielectric ceramics nowadays have to withstand electric field strengths of 2–3 V μm^{-1} at temperatures of 125°C. The present stringent requirements of dielectric ceramic materials with respect to insulation resistance, lifetime and permittivity can only be met by careful control of the impurity level, the grain size and the distribution of the additives in the material. The high performance of these materials owes much to new chemical preparation techniques such as coprecipitation and sol–gel processing.

Even today most of the dielectric materials in use are based on ferroelectric barium titanate. In the last ten years the permittivity of these materials has been increased to values of $\varepsilon_r \approx 4000$–$4500$ for the temperature-stable materials of specification 'X7R',* and $\varepsilon_r \approx 10\,000$–$14\,000$ for the materials of specification 'Y5V'.*

For the future choice of new dielectric materials for CMCs it is very important to know the maximum permittivities that are feasible in $BaTiO_3$ based materials. Recently a number of new dielectric materials have appeared that show higher permittivities and lower sintering temperatures, as for instance the $Pb(Mg_{1/3}Nb_{2/3})O_3$ relaxors[2] and the PLZT materials.[3]

This paper discusses some of the microstructural aspects and physical properties conditioning and limiting the maximum permittivity of the classical $BaTiO_3$ based materials.

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* EIA specification X7R: ε_r must not change by more than ±15% from ε_r (25°C) in the temperature range −55°C–125°C.

EIA specification Y5V: ε_r must not change by more than +22%– −82% from ε_r(25°C) in the temperature range −30°C–85°C.

EIA: electric industries association.

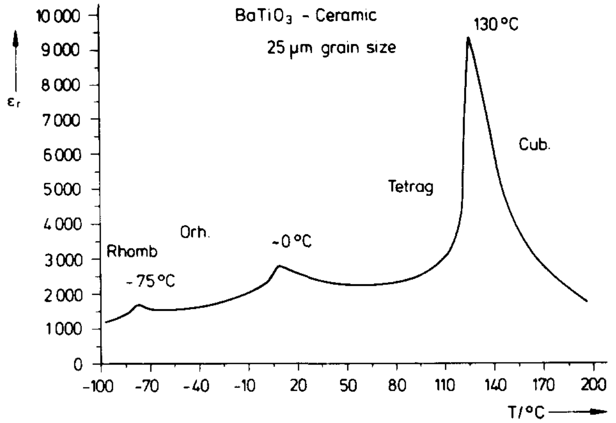


Fig. 2. Dielectric constant versus temperature of coarse-grained $BaTiO_3$.

2 THE PERMITTIVITY OF PURE $BaTiO_3$ CERAMICS

The temperature characteristic of the ceramic $BaTiO_3$ dielectric constant (Fig. 2) displays three relative maxima which can be assigned to the three reversible phase transitions of $BaTiO_3$. At the so-called Curie point (130°C), the ferroelectric tetragonally distorted perovskite unit cell transforms into the cubic paraelectric one. The dielectric constant maximum at the Curie point is often used for materials with very high capacitances ('high-K materials') which, however, show the inferior temperature stability of specification Y5V. The ferroelectric region below the Curie point is used for materials with lower capacitances, which then have the higher temperature-stability of specification X7R.

Pure $BaTiO_3$ ceramics obviously are not qualified for dielectric use. In 'high-K materials' the Curie maximum has to be broadened and shifted to room temperature. In the temperature-stable X7R materials, the permittivity of the ferroelectric region has be be increased, and in particular the temperature characteristic has to be improved at the low temperature end.

3 DIELECTRIC IMPROVEMENT OF $BaTiO_3$ MATERIALS

For many years the $BaTiO_3$ based dielectrics could only be improved by making simple changes to their chemical composition or by the formation of mixed crystals. By incorporation of so-called 'shifters', like Sn or Zr for Ti, or Sr for Ba, the Curie point of $BaTiO_3$ can be reduced to room temperature. The permittivity maximum then rises by a factor of 3 or more.[4] This observed rise of the permittivity maximum with increasing Zr content was

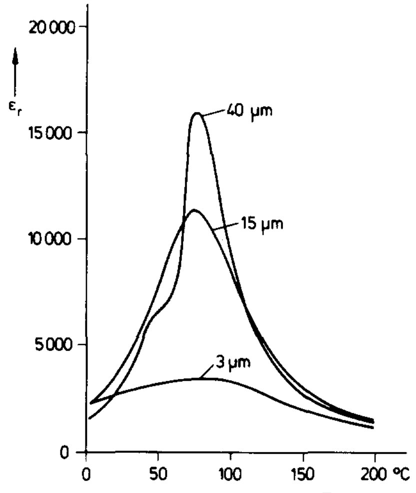


Fig. 3. Maximum permittivity at Curie point of $(Ba_{0\cdot87}Ca_{0\cdot13})(Ti_{0\cdot88}Zr_{0\cdot12})O_3$ ceramics with different grain sizes.

explained in terms of a gradual change of the ferroelectric phase transition from first to second order.[5] Theoretically, the permittivity maximum at a second-order phase transition should be infinitely high. However, due to the more or less pronounced broadening of the peak, the maximum hardly ever exceeds a value of $\varepsilon_{r,\max} \approx 35\,000$. The broadening of the peak is strongly dependent on the microstructure.

3.1 Use of diffused phase transitions

The ferroelectric and dielectric properties of $BaTiO_3$ ceramics generally show a strong dependence on the microstructure. The simplest way to change a microstructure is by varying the grain size and the grain size distribution. The dramatic decrease of the maximum of the permittivity at the Curie point and broadening of the peak of $(Ba, Ca)(Ti, Zr)O_3$ mixed crystal ceramics after the reduction of the average grain size can be seen in Fig. 3. In these materials the character of the ferroelectric phase transition becomes more and more diffuse with decreasing grain size.

Up to Zr contents of $y = 0{\cdot}13$, mixed crystals of $Ba(Ti_{1-y}Zr_y)O_3$ undergo a first order phase transition at the Curie point. The remanent ferroelectric polarization of materials showing an ideal first order phase transition abruptly disappears at the Curie point. In contrast to an ideal first order phase transition, in a diffuse phase transition the remanent polarization gradually disappears near the Curie point. The change from ferroelectric to paraelectric in these materials often extends over several degrees centigrade, as can be seen in Fig. 4.

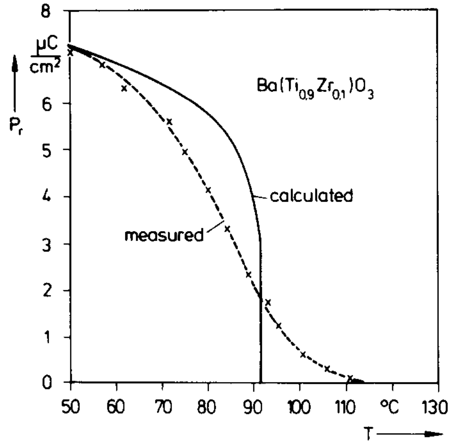


Fig. 4. Temperature dependence (measured and calculated) of remanent ferroelectric polarization of $Ba(Ti_{0.9}Zr_{0.1})O_3$ ceramic.

In the commonly used Y5V material (Ba, Ca)(Ti, Zr)O_3, the diffuse ferroelectric phase transitions can be characterized in terms of a distribution of Curie points. The remanent polarization is then a superposition of the polarization function $P(T, T_c)$ which is calculated by using the Devonshire theory[6] and a distribution function of Curie points $\chi(T_c)$.[5]

$$P(T) = \int_0^\infty P(T, T_c) \times \chi(T_c)\,\mathrm{d}T_c \qquad (1)$$

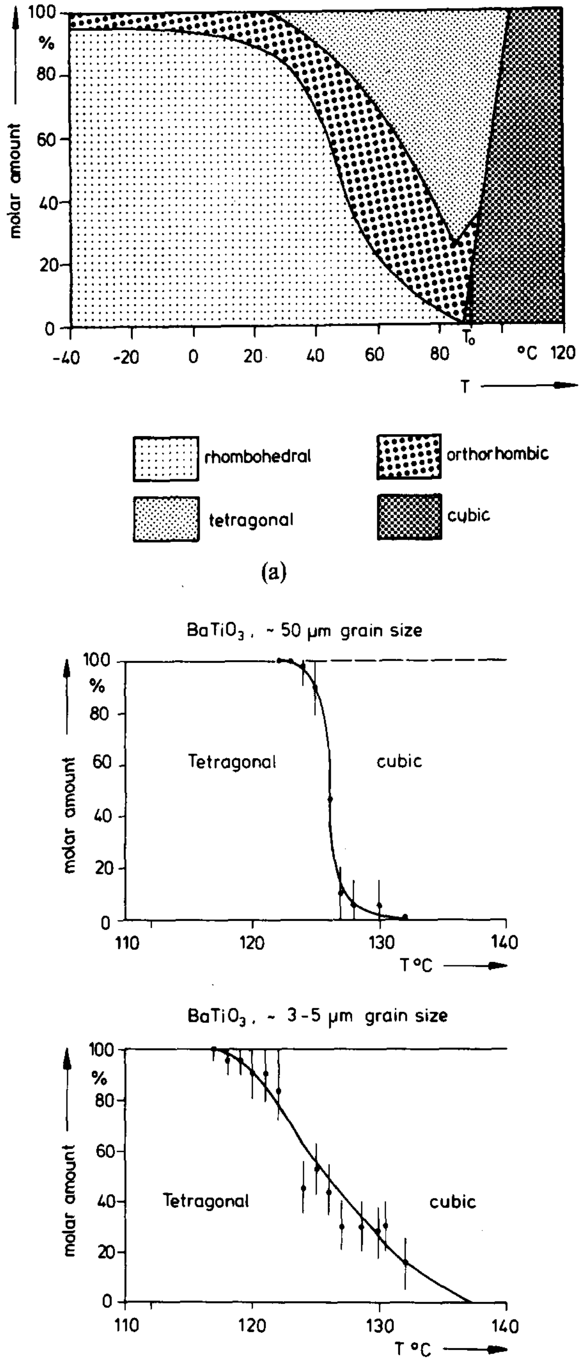
For $X(T_c)$ a normal Gaussian distribution of T_c around a mean value of θ_c showing the width s was chosen:

$$\chi(T_c) = (1/\sqrt{s})\exp - [(T_c - \theta_c)^2/s] \qquad (2)$$

From Fig. 4 it can be seen that $P(T)$ of (Ba, Ca)(Ti, Zr)O_3 ceramics is in fact well described by using a normal distribution of T_c. Depending on the grain size, the width of the distribution can increase up to values of $\sqrt{s} \approx 20$K. From this we concluded that small local regions exist in these materials, all of which have somewhat different Curie points.

By evaluating the X-ray diffraction line profiles in the paraelectric and ferroelectric states we found that internal stress, and not chemical inhomogeneity, seems to be the major reason for the local distribution of Curie points in these materials.

During cooling of densely sintered $BaTiO_3$ ceramics strong internal stress arises in the material at the Curie point due to the mechanical deformation of the unit cell from cubic to tetragonal. Although the mechanical deformation is largely equalized by the formation of ferroelectric domains, a residual stress remains in the material. Upon the reduction of the grain size



(a)

(b)

Fig. 5. Coexistence of ferroelectric and paraelectric phases in (a) $Ba(Ti_{0.9}Zr_{0.1})O_3$ and (b) $BaTiO_3$ ceramics.

this residual stress is assumed to increase strongly due to the smaller number of domains per grain.[7,8]

The increasing internal stress gives rise to the coexistence of ferroelectric and paraelectric phases. In ferroelectric mixed crystals of (Ba, Ca)(Ti, Zr)O_3 the coexistence of cubic, tetragonal, orthorhombic and rhombohedral perovskite phases could be observed (Fig. 5).[5] In pure $BaTiO_3$, only cubic and tetragonal phases were found to coexist near the Curie point. The diffuse phase transitions observed in fine-grained $BaTiO_3$ based ceramics can thus be explained in terms of a stress-induced coexistence of different ferroelectric and paraelectric perovskite phases. The smaller the grains, the broader and lower the permittivity maximum becomes at the Curie point. Increasing grain size on the other hand favours the formation of very high but narrow permittivity maxima, which unfortunately do not fit any permittivity/temperature specification. The search for materials showing high permittivities and suitable temperature characteristics is therefore above all a matter of critical grain size control. Nowadays the maximum permittivity which can be achieved at room temperature after careful control of the microstructure in $BaTiO_3$ based Y5V materials is about $\varepsilon_r(25°C) \approx 15\,000$. This maximum value is not likely to be considerably exceeded in the future.

3.2 Grain size effects in ferroelectric $BaTiO_3$ below the Curie point

The ferroelectric properties of $BaTiO_3$ far below the Curie point show a strong dependence on the grain size. Whereas in normal coarse-grained ($\geq 10\,\mu m$) $BaTiO_3$, permittivities of $\varepsilon_r \approx 1500$–$2000$ are found in the temperature range of 20°C–80°C, in fine-grained materials ($< 1\,\mu m$) much higher permittivities of $\varepsilon_r \approx 4000$–$5000$ are observed in the same temperature range. At very small grain sizes ($< 0{\cdot}5\,\mu m$), however, the permittivity is rather low again. The measured permittivities plotted against the average grain size show a pronounced maximum of $\varepsilon_{r,max} \approx 5000$–$6000$ at $0{\cdot}7$–$0{\cdot}8\,\mu m$ (Fig. 6). This maximum value seems to be the highest permittivity attainable in ferroelectric $BaTiO_3$ below the Curie point. The grain size dependence of the permittivity observed in the ferroelectric region of $BaTiO_3$ again illustrates the importance of careful grain size control.

The physical reasons for the permittivity maximum at grain sizes of $0{\cdot}7$–$0{\cdot}8\,\mu m$ are not yet completely understood. From the single crystal properties, the high permittivity values of the fine-grained $BaTiO_3$ cannot be deduced. The dielectric constant of single-crystal $BaTiO_3$ is strongly anisotropic for the different crystallographic axes. In the direction of the tetragonal c-axis the permittivity of a $BaTiO_3$ single crystal is only $\varepsilon_c \approx 400$, whereas in the two perpendicular directions it is $\varepsilon_a = \varepsilon_b \approx 4000$.[9] In sintered polycrystalline $BaTiO_3$ a more or less statistical distribution of the three

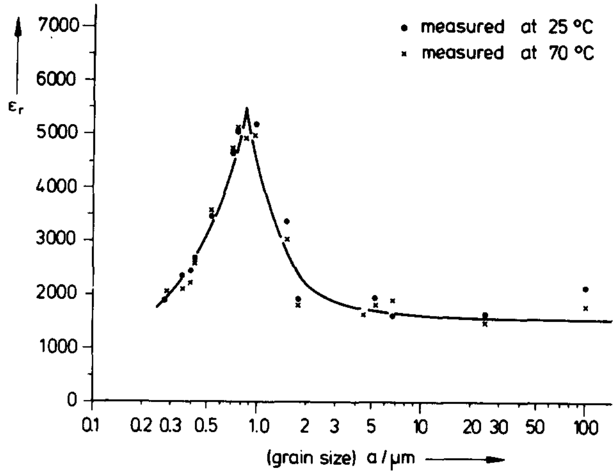


Fig. 6. Grain size dependence of the permittivity of $BaTiO_3$ ceramics at 25°C and 70°C.

axes and a resulting average value $\varepsilon_{r,av}$ are expected. The average permittivity of polycrystalline $BaTiO_3$ was calculated by several authors[10,11] from the single crystal data. The values of $\varepsilon_{r,av} \approx 800\text{–}1000$ calculated by these authors are surprisingly low compared with those of $\varepsilon_r \approx 1500\text{–}2000$ measured in normal coarse-grained $BaTiO_3$.

The much higher permittivity values found in the experiment obviously are a peculiarity of ceramic $BaTiO_3$. Arlt and Sasko[11] interpreted the much higher permittivities of ceramic $BaTiO_3$ in terms of domain wall contributions to ε_r. The permittivity of $BaTiO_3$ ceramics can then be regarded as the sum of a volume contribution, $\varepsilon_{r,vol}$, which is based on the single-crystal dielectric constants, and a contribution from the ferroelectric domain walls moving in the electric field, $\varepsilon_{r,dom}$:

$$\varepsilon_r(T) = \varepsilon_{r,vol}(T) + \varepsilon_{r,dom}(T) \qquad (3)$$

In a first approximation, the contribution of the ferroelectric domain walls can be assumed to be proportional to the total area of the 90°-walls per volume, A_{dom}:

$$\varepsilon_{r,dom} \approx k \times A_{dom} \qquad (4)$$

Whereas the mobility of the walls is considered to be largely independent of the grain size, this is not the case for the number of domain walls per volume. A study of the number and size of ferroelectric domains in $BaTiO_3$ carried out by several authors[7,8,12–14] came to a somewhat confusing conclusion. Jonker and Noorlander[12] and Buessem *et al.*[7,8] found constant widths of the ferroelectric domains in $BaTiO_3$ of about 0·8 μm. These authors therefore concluded that ferroelectric domains must be absent in $BaTiO_3$ ceramics of ~1 μm grain size. Yamaji *et al.*[13] and Enomoto and Yamaji[14] confirmed that only rather few ferroelectric domains exist in fine-grained Dy-doped

$BaTiO_3$. In contrast to these results, Arlt *et al.*[15] found, even at 0·5 μm grain size, very small ferroelectric domains in pure $BaTiO_3$ by means of SEM in surface-etched ceramics as well as TEM of ion-beam-etched hot pressed ceramics. Moreover, they observed a monotonic reduction of the domain width with decreasing grain size. Thus, at $a = 0{\cdot}5$ μm average grain size, a domain width of about $d \approx 0{\cdot}1$ μm was found. In the electron micrograph (TEM) (Fig. 7(b)), these very small domains can be seen. However, at grain sizes below 0·5 μm, more and more of the grains no longer show ferroelectric domains.

Arlt *et al.*[15] therefore concluded that the strong increase of the permittivity at grain sizes of 0·7–1 μm results from the large number of domains per volume, or from the corresponding large area of the domain walls. Buessem *et al.*[7,8] explained the high permittivity of fine-grained $BaTiO_3$ in terms of increased values of $\varepsilon_{r,vol}$ due to internal stress in the material. Using the Devonshire theory[6] they calculated strongly increasing volume dielectric constants $\varepsilon_{r,vol}$ in the case of internal tensile stress applied to $BaTiO_3$.

3.3 Reduction of the domain widths in fine-grained $BaTiO_3$

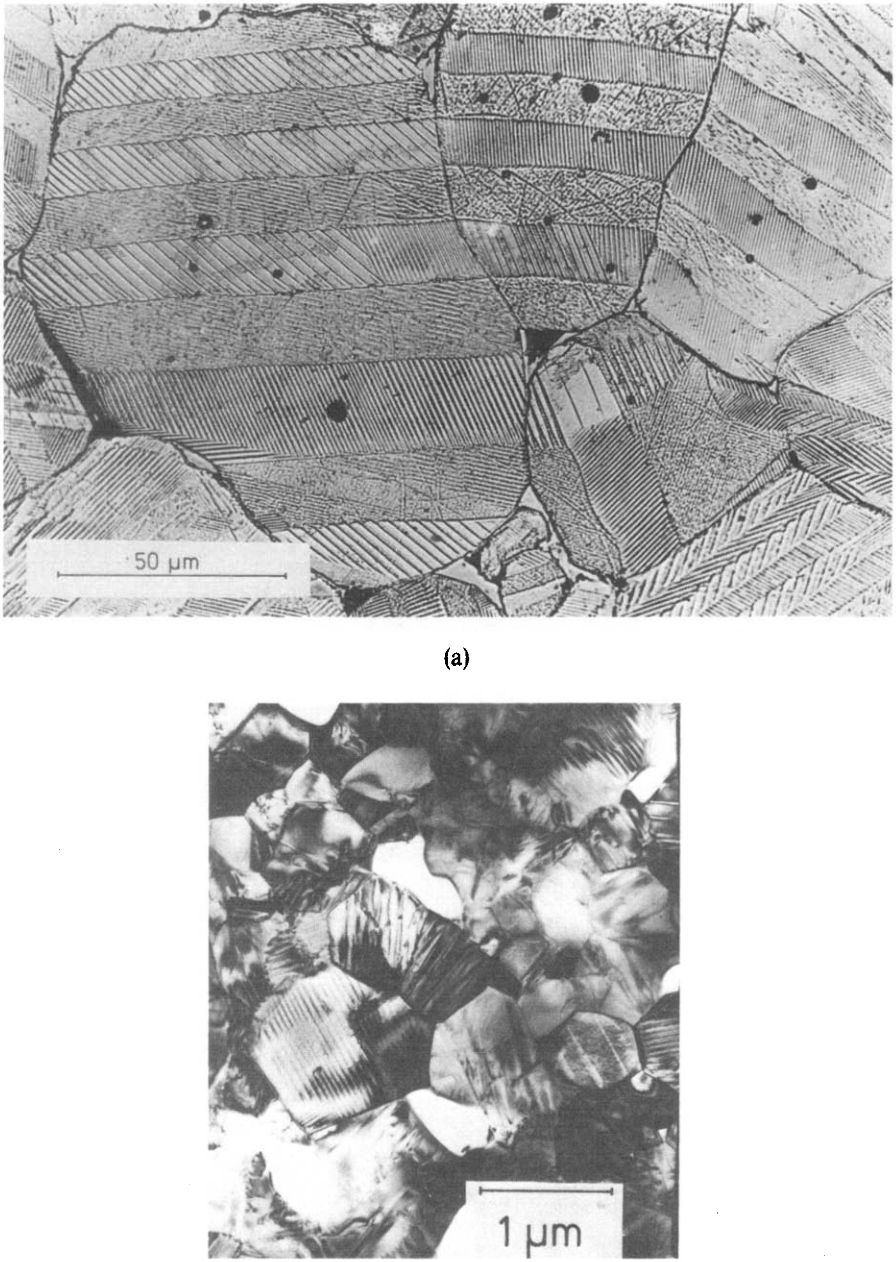
The decreasing width of the ferroelectric domains in fine-grained $BaTiO_3$ can again be explained in terms of internal stress. From a simple model of stacked 90° domains,[15] one can easily derive that in each domain certain regions exist that show either compressive or tensile stress. In these regions the perovskite is elastically deformed and as a result the mechanical energy has increased. On reduction of the grain size the stress strongly increases. It was further shown that the elastic deformation, and thus the increase of elastic energy as well, is reduced as the width of the 90° domains becomes smaller. It is suggested that the internal mechanical deformation energy is reduced by the formation of the maximum possible number of ferroelectric domains per unit volume. However, each domain wall gives a certain contribution of domain wall energy to the total free energy of the ceramic. Thus the increase of mechanical energy in fine-grained $BaTiO_3$ is only partly compensated by the formation of additional domains.

The total increase of the free energy is the sum of elastic and domain wall energy which, under equilibrium conditions, is a minimum:

$$w_{tot} = w_{mech} + w_{dom} = \text{Minimum} \tag{5}$$

The mechanical energy of the 90° domains per unit volume was calculated from[15]

$$w_{mech} = \frac{d^2 \times c_{11} \times S_s^2}{128 \times \pi \times a} \tag{6}$$



(a)

(b)

Fig. 7. Ferroelectric domain pattern in $BaTiO_3$ ceramics. (a) Light micrograph of chemically etched $BaTiO_3$, (b) TEM of ion-beam-etched hot-pressed $BaTiO_3$.

In this formula, a is the average grain size, d the domain width, $c_{11} = 1{\cdot}7 \times 10^{11}\,\mathrm{N\,m^{-2}}$ (the average longitudinal elastic constant) and $S_s = 10^{-2}$ (the spontaneous tetragonal deformation $(c/a - 1)$ of the perovskite unit cell.

The domain wall energy per unit volume is given by the formula[15]

$$w_{\mathrm{dom}} = \sigma/d \tag{7}$$

where $\sigma = 3 \times 10^3\,\mathrm{J\ m^{-2}}$ is the wall energy of 90° domains as given by Zhirnov.[16]

In the grain size range of 1–10 μm the calculated values of the equilibrium width of the ferroelectric domains are in good agreement with the experimental widths determined from electron micrographs. The equilibrium width can also be calculated directly from the energy minimum condition:

$$d = \sqrt{\frac{128 \times \pi \times \sigma \times a}{c_{11} \times S_s^2}} \approx \sqrt{a} \tag{8}$$

The equilibrium width of the ferroelectric domains is thus proportional to the square root of the grain size. From Fig. 8 it can be seen that this dependence is well confirmed by the experiments for grain sizes in the range 1–10 μm. Above 10 μm so-called 'mixed walls' appear in the microstructures, acting as artificial grain boundaries.[11] Thus nearly constant domain widths of $d \approx 0{\cdot}8\ \mu$m are observed in $BaTiO_3$ ceramics with grain sizes > 10 μm. For grain sizes < 1 μm the differences between calculated and measured domain widths become more and more conspicuous. At the average grain size of 0·3 μm in many of the grains, the ferroelectric domains have disappeared.

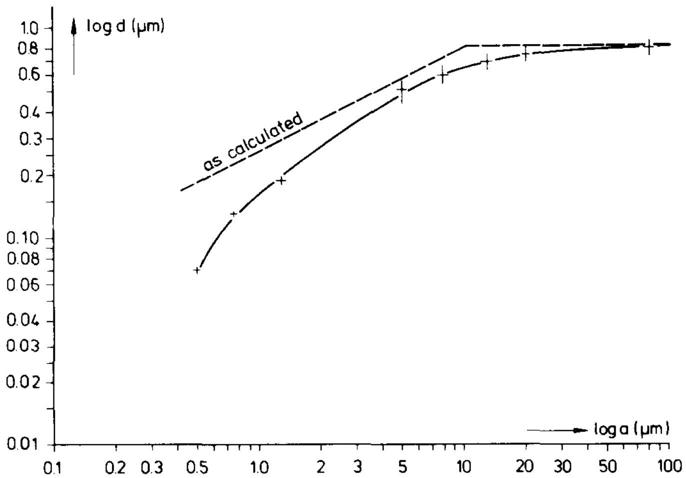


Fig. 8. Measured and calculated widths of 90° domains, d, as a function of the average grain size, a, in $BaTiO_3$ ceramics.

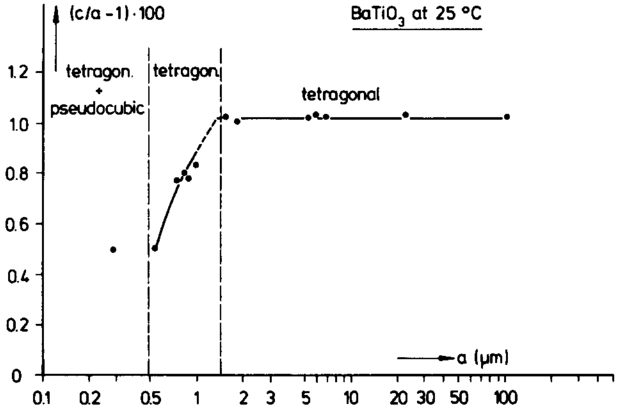


Fig. 9. Tetragonal deformation of the perovskite unit cell of $BaTiO_3$ ceramics as a function of the average grain size.

At such small grain sizes the internal stress and the mechanical energy obviously have so strongly increased that the tetragonal deformation of the unit cells is widely reduced to the pseudocubic or even cubic state. Figure 9 shows the tetragonal deformation ($c/a - 1$) of the $BaTiO_3$ unit cell, plotted against the average grain size. At about 1 µm grain size the c/a ratio drastically decreases. Additionally, some new reflections appear in the X-ray diffraction diagrams which cannot unambiguously be attributed to any of the known perovskite phases of $BaTiO_3$. As in the (Ba, Ca)(Ti, Zr)O_3, there are some indications that several ferroelectric phases coexist here too.

3.4 Discussion of the models

Full agreement exists between all investigators of fine-grained $BaTiO_3$ that internal stress is responsible for the enhanced permittivity. Whether the internal stress gives rise to increased values of $\varepsilon_{r,vol}$, as proposed by Buessem *et al.*,[7,8] or $\varepsilon_{r,dom}$ as proposed by Arlt *et al.*,[15] is still under discussion. However, the large numbers of very small domains recently observed in the fine-grained $BaTiO_3$ strongly suggest that the domain wall contribution plays an important role.

At grain sizes of 0·7–1 µm the $BaTiO_3$ obviously has achieved the maximum density of 90° domains. At even smaller grain sizes the tetragonal deformation of the perovskite unit cell is reduced to a pseudocubic state and as a result the ferroelectric domains disappear. The domain wall contribution $\varepsilon_{r,dom}$ can then be neglected so that the permittivity ε_r is determined by the volume contribution $\varepsilon_{r,vol} = 800\text{–}1000$, which is the average of the single crystal dielectric constants (see Section 3.2 and eqn (3)).

4 TAILORING OF $BaTiO_3$ DIELECTRICS

The practical consequences of this study are quite obvious. In $BaTiO_3$ based materials, maximum permittivities can only be achieved if the microstructure is carefully controlled. For high-K materials of specification Y5V, the optimum grain sizes were found to lie in the range of 5–10 μm. Temperature-stable materials of specification X7R should have much smaller grain sizes of about 0·7–1 μm.

4.1 High-K materials

The relatively coarse-grained microstructures typical of the $BaTiO_3$ based high-K materials are usually formed during secondary recrystallization of the matrix.[17] In most cases secondary recrystallization of the matrix is caused by sintering aids added to the ceramic powders which not only strongly promote the densification but also give rise to exaggerated grain growth. In exaggerated grain growth, or secondary recrystallization, small numbers of grains start to grow very rapidly at the expense of the other grains, which are then completely consumed.[18]

Secondary recrystallization of $BaTiO_3$ normally takes place in the presence of small amounts of liquid phase formed by the additives or certain impurities. For instance TiO_2, the most commonly used sintering aid, forms the eutectic $Ba_6Ti_{17}O_{40}$–$BaTiO_3$, melting at about 1315°C.[19] Nowadays a number of lower melting additives are known which can reduce the sintering temperatures of $BaTiO_3$ dielectrics from 1350°C to about 1050°C.[20,21]

Extensive studies of the recrystallization process of $BaTiO_3$[18] have led to the conclusion that the number of 'nuclei' (i.e. the grains taking an active part in the exaggerated grain growth) increases exponentially with time. The growth of the nuclei was found to be simply proportional with time. Thus in the early stage of secondary recrystallization only very few nuclei occur which are able to grow without hindrance to very big grains. However in the final stage large numbers of nuclei are formed which cannot grow so much. The microstructures of liquid-phase sintered $BaTiO_3$ therefore always exhibit rather broad distributions of grain sizes which are hard to control.

A successful means of controlling the grain size as well as the grain size distribution of discontinuously growing $BaTiO_3$ is the addition of 'seed grains' to the $BaTiO_3$ powders before sintering.[18] Seed grains are powder particles that have the same chemical composition as the powder to be sintered but considerably larger particle diameters. The addition of quite small amounts of seed grains (2–3 wt%) can substantially modify the microstructure of the $BaTiO_3$. The more seed grains that are added, the

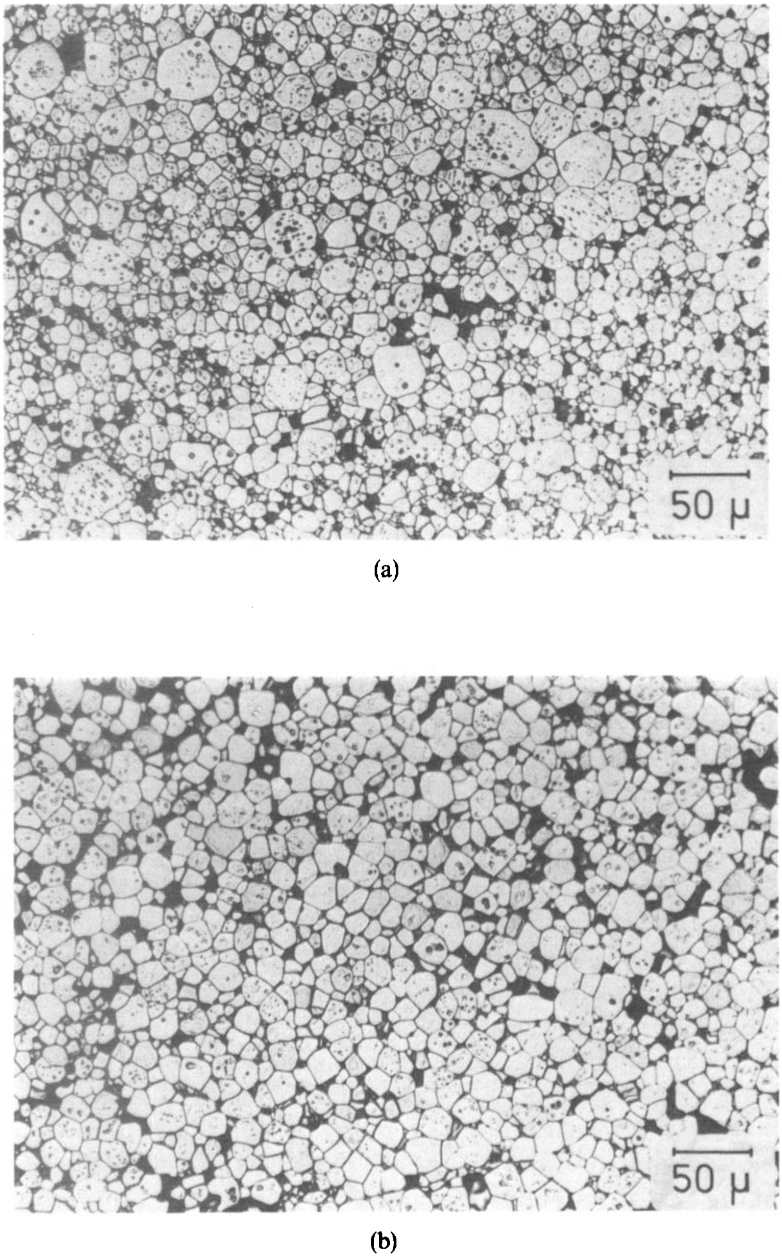
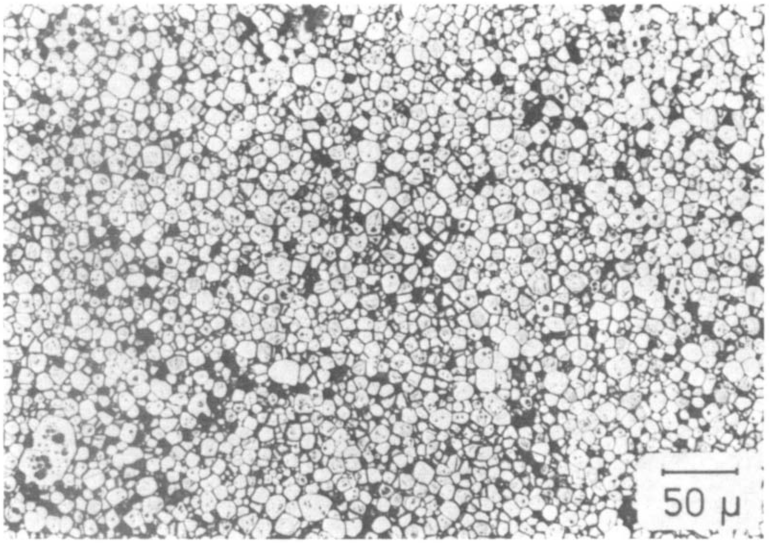


Fig. 10. Microstructure of $BaTiO_3$ ceramics sintered for 5 min with x% seed grains at 1350°C. (a) $x = 0\%$, (b) $x = 3\%$, (c) $x = 5\%$.



(c)

Fig. 10.—*contd.*

smaller are the grains and the narrower the grain size distribution, as can be seen in Fig. 10. Thus, by adding adequate numbers of seed grains, the microstructures of high-K materials can be tailored to the optimum grain size distribution.

4.2 Temperature-stable materials

High quality temperature-stable materials must have not only a small temperature dependence but also a very high dielectric constant of $\varepsilon_r \approx 3000$–$4000$ at room temperature. The temperature characteristic of the permittivity is normally determined by the degree of chemical heterogeneity in these materials, whereas the value of the permittivity largely depends on the grain size. Thus, in temperature-stable materials, both the grain size and the distribution of the additives have to be controlled.

In a first approximation, one can interpret the dielectric properties of these chemically heterogeneous materials as a combination of pure fine-grained $BaTiO_3$ and a second dielectric material showing a dielectric Curie maximum at a lower temperature. The most obvious idea would be to combine different dielectric materials in the dielectric sheets of a multilayer capacitor. Due to the numerous problems arising from different thermal expansion coefficients and shrinkage behaviour of the dissimilar materials, in practice capacitors are preferred which consist of only one heterogeneous material. The dielectric behaviour of two-phase materials can be well characterized by using the 'Lichtenecker formula':[22]

$$\log \varepsilon_r = X_1 \times \log \varepsilon_{r,1} + X_2 \times \log \varepsilon_{r,2} \qquad (9)$$

In this formula, X_1 and X_2 are, respectively, the mole and volume fractions of the two dielectric components. Earlier experiments[23] have shown that this formula can be successfully applied for combinations of dielectric phases if the dielectric constants $\varepsilon_{r,1}$ and $\varepsilon_{r,2}$ do not differ from one another by more than a factor of 10.

In a simple model calculation using the Lichtenecker formula one can show that 20 vol% of a dielectric phase with the Curie point at −70°C in combination with fine-grained $BaTiO_3$ will be enough to produce temperature-stable dielectrics showing very high permittivities of ε_r (25°C) ≈ 4000–4500 (Fig. 11). This model suggests that the $BaTiO_3$ component largely determines the permittivity of the X7R materials. The second dielectric component should therefore be added in amounts as small

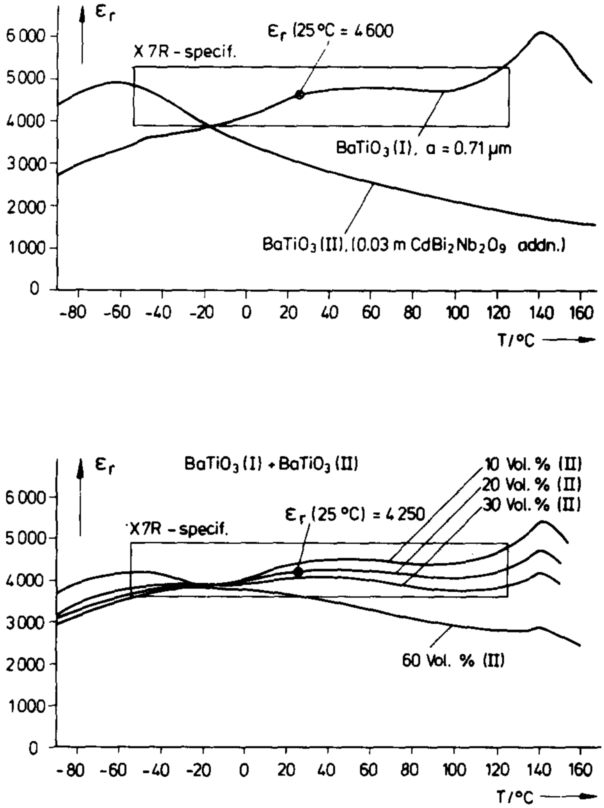


Fig. 11. Calculation of the dielectric constant of various combinations of pure fine-grained $BaTiO_3$ and Cd, Bi-doped $BaTiO_3$ (Curie point at −70°C).

as possible for correcting the temperature characteristic at the low-temperature end.

4.3 Control of chemical heterogeneity

Controlled heterogeneity is generally not easy to produce in perovskite materials. Since most of the perovskites are completely miscible, any kind of thermal treatment gives rise to interdiffusion and improved distribution of the constituents. The distribution of the additives normally takes place in

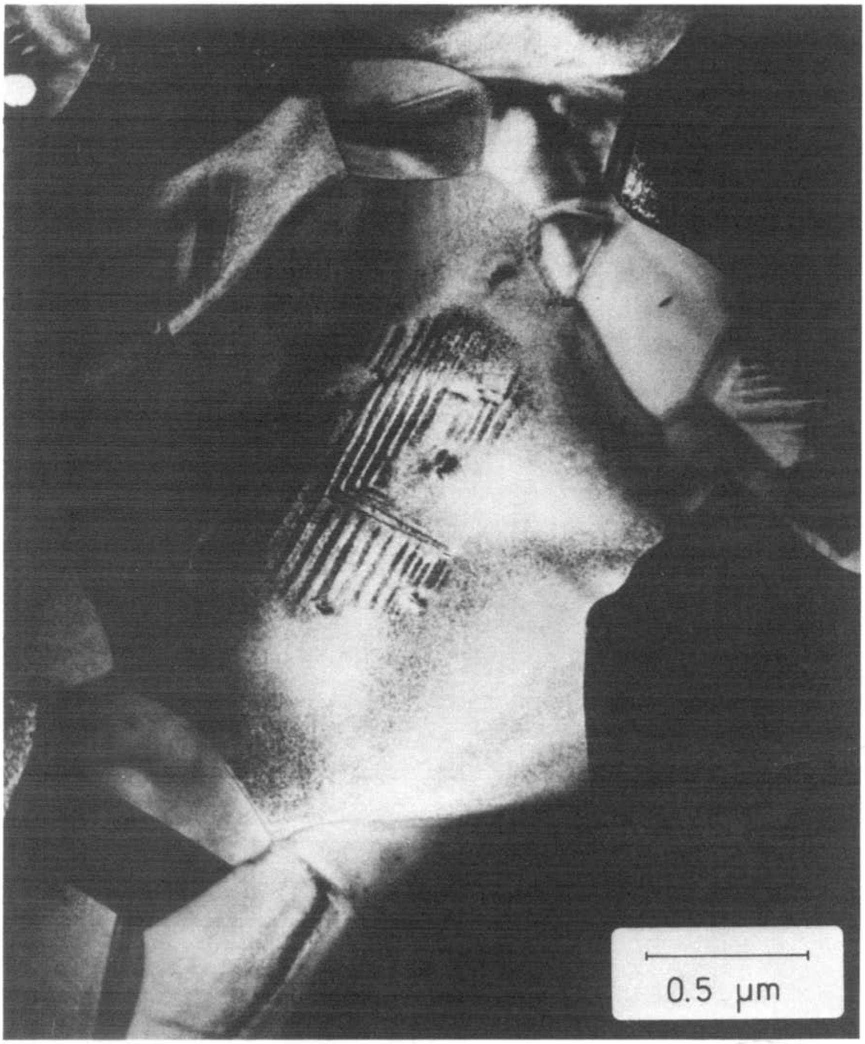


Fig. 12. TEM showing core-shell structures in $BaTiO_3$ doped with CdO, Bi_2O_3 and Nb_2O_5, and sintered for 3 h at 1200°C.

$BaTiO_3$ materials during sintering and grain growth. Non-uniform distributions of additives are therefore preferentially observed in the case of inhibited grain growth. The following three examples may briefly demonstrate the methods by which chemical heterogeneity can be realized in the materials.

In a number of temperature-stable dielectric materials, so-called 'core-shell' structures have been found.[24,25] These materials exhibit chemically heterogeneous grains consisting of two phases at room temperature (Fig. 12). The core phase, which is usually located in the centre of the grains, consists of more or less pure $BaTiO_3$ showing the typical ferroelectric domain pattern. The shell phase, on the other hand, is paraelectric at room temperature, containing all the dopes. In the liquid phase, which contains Bi_2O_3 and Nb_2O_5,[25] the smaller $BaTiO_3$ grains are dissolved. After saturation with $BaTiO_3$, a Bi, Nb-doped perovskite phase then separates (from the liquid) on the larger undissolved grains. Due to the rather low diffusion coefficients in the solid state, most of the grains remain two-phase after sintering. Such core-shell materials fit rather well with the simple Lichtenecker model and are thus best suited for model calculations.

Another way of producing controlled heterogeneity is to form certain types of lattice defects that act as strong grain-growth inhibitors. Especially if the donor character of the additive prevails, grain growth and diffusion of additives are drastically reduced.[26,27] After addition of combined Co_3O_4 and Nb_2O_5 dopes, strongly heterogeneous materials are observed,[27]

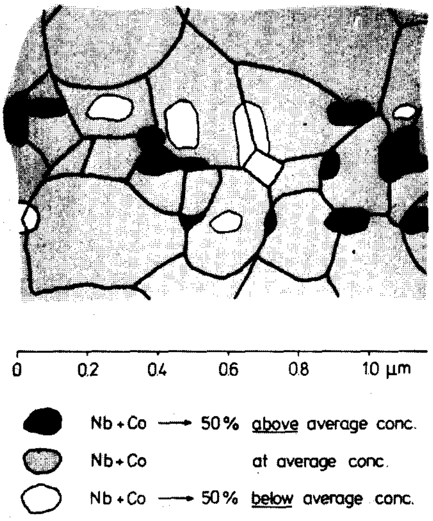


Fig. 13. Microdistribution of Nb and Co in $BaTiO_3$ sintered for 2 h with Nb_2O_5 and Co_3O_4 additions at 1300°C.

showing small local regions of high Nb and Co concentration as well as practically pure $BaTiO_3$ in the microstructure (Fig. 13).

In both the Bi, Nb- and the Co, Nb-doped materials, a pronounced cosolubility of the dopants was observed by means of electron microbeam analysis, suggesting the formation of complex perovskites such as $Ba(Bi_{0.5}Nb_{0.5})O_3$ and $Ba(Co_{0.33}Nb_{0.67})O_3$. Such complex perovskites are most probably responsible for the drastic depression of the Curie point in the shell phase.

Heterogeneous materials can be formed by hot-pressing two perovskites

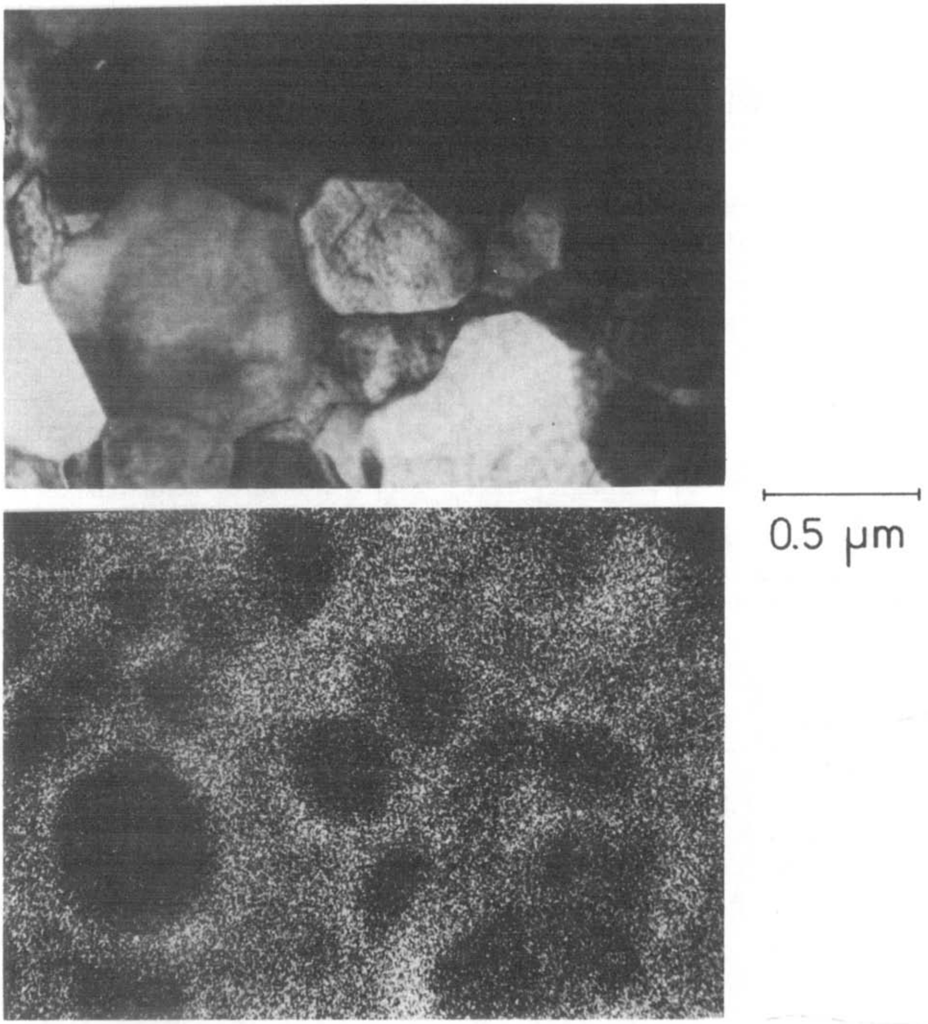


Fig. 14. Sr–K_α map showing microdistribution of Sr in hot-pressed mixtures of $BaTiO_3$ and $SrTiO_3$ (10:1). Hot-pressed 1150°C for 15 min at 6×10^7 N/m^2.

with different Curie points.[28] During hot-pressing at 1100°C, the densification of $SrTiO_3$ and $BaTiO_3$ is obviously largely accomplished by surface diffusion of the $SrTiO_3$ (Fig. 14). Volume diffusion seems to play a less important role here. Thus, the microstructure of mixed hot-pressed powders of $BaTiO_3$ and $SrTiO_3$ exhibits typical core-shell structures with $BaTiO_3$ in the centre of the grains.

5 CONCLUSIONS

The study of grain size effects in $BaTiO_3$ based materials has revealed strong correlations between the dielectric and ferroelectric properties of these materials and their microstructural characteristics. In the light of these correlations, the possible physical limits for further dielectric improvements in this family of dielectric ceramics have been discussed. Considering the present high dielectric standard achieved in the $BaTiO_3$ based materials, no further dramatic improvement of their dielectric properties is to be expected.

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