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Permittivity and the Form Factor of $BaTiO_3$ and Related Powders

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Abstract

Capacitance measurements of ferro- and paraelectric oxide powders in the frequency range of 1 kHz–10 MHz have been performed in order to deduce a form factor which is related to the morphology of the particles and their arrangement in the powder. Using a capacitor measuring setup the frequency independent real part of the complex dielectric constant was measured in the range of 1 kHz–2 MHz as a function of the volume fraction. The interpretation follows a model derived for inhomogeneous dielectrics, which makes it possible to calculate a morphology dependent parameter provided that the permittivity of the solid is known. The results are verified for various $BaTiO_3$ *powders and for aggregated and stepwise ground* $Ba_{1-x}Sr_xTiO_3$ *powders and are related to other particle shape parameters derived from SEM studies indicating the suitability of this method to describe the morphology of ferroelectric powders. For comparision the specific surface area BET data and the* d_{50} *values from grain size distribution measurements of the powders are also reported. The applicability of the method for checking the reproducibility of different lots of ferroelectric capacitor raw materials is shown for Z5U and X7R powders.*

Zusammenfassung

Es wird über Kapazitätsmessungen an ferro- und paraelektrischen Oxidpulvern im Frequenzbereich 1 kHz bis 10 MHz und deren Auswertung zwecks Ermittlung eines Formparameters berichtet, der zur Morphologie der Partikel und deren Anordnung im Pulver in Beziehung steht. Mit Hilfe einer Kondensator—Meßanordnung wird für die Pulver im Bereich bis zu 2 MHz der frequenzunabhängige Realteil der komplexen Dielektrizitätskonstante in Abhängigkeit vom Volumenbruch ermittelt. Die Auswertung folgt den für inhomogene Dielektrika abgeleiteten Modellen, die bei Kenntnis der DK des betreffenden Feststoffes einen morphologieabhängigen Formparameter zu berechnen gestatten. Am Beispiel von verschiedenen $BaTiO_3$ *Pulvern und von aggregierten und in mehreren Stufen fein gemahlenen* $Ba_{1-x}Sr_xTiO_3$ *Pulvern wird durch Vergleich mit anderen aus REM-Studien erhaltenen Formparametern gezeigt, daß diese Methode zur Beschreibung der Partikelmorphologie ferroelektrischer Pulver herangezogen werden kann. Zum Vergleich werden jeweils die BET—Werte für die spezifische Oberfläche und der* d_{50} *Wert aus der Korngrößenverteilung angegeben. Die Eignung der Methode zur Kontrolle der Chargenreproduzierbarkeit von ferroelektrischen Kondensatorpulvern wird am Beispiel von Z5U und X7R-Massen aufgezeigt.*

1 Introduction

In a recently published paper,[1] the permittivity measured in the powder state of a solid has been shown to be sensitively dependent on the shape of the particles. Using the models of inhomogeneous dielectrics as developed by Lorentz,[2] Lorenz,[3] Rayleigh,[4] Wiener,[5] Bruggeman[6,7] and other researchers,[8–10] such an interpretation relies on the premise that the dielectric constant of the bulk material is also valid for particles in the powder state. The latter should be sufficiently valid for solids with a linear dependence of polarization on the electric field strength. It has been shown that increasing bulkiness and roundness as defined by Medalia[11] indicating agglomeration or porosity of particles give rise to relatively high values of a new defined form factor β which was deduced from dielectric measurements. On the other hand, powders predominantly consisting of primary or less aggregated grains reveal β to be the more sensitive to particle shape the higher the permittivity of the material. The β values of powders, whose anisometry

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results from the crystal structure, e.g. wurtzite or alumina, have found to be consistent with the results of electronmicroscopic studies.

It is the aim of the present paper to check if the form factor β can be used for characterizing ferroelectric powders. Because of the non-linear polarization of these materials, the field dependence of the permittivity has to be taken into consideration. Furthermore, it seems questionable to use the dielectric constant of ferroelectric bulk ceramics for particles in the powder state. As a cardinal question the well known grain size dependence of the dielectric constant of $BaTiO_3$[12–14] has to be taken into account. Finally, the data obtained with the capacitor arrangement could become falsified due to piezoelectric effects when the volume fraction of the solid is varied by changing the pressure.

2 Ferroelectric Powders and Characterization

The investigated powders are listed in Table 1. $BaTiO_3$ I and $Ba_{1-x}Sr_xTiO_3$ powders ($x = 0{\cdot}295$ and $x = 0{\cdot}593$) have been prepared following the mixed oxide route. Wet grinding of mixtures of $BaCO_3$ and $SrCO_3$ with highly dispersed rutile (8 m^2/g) using agate spheres (10 and 20 mm ∅) in a cylinder mill was followed by calcination at 1150 or 1200°C, respectively. The coarse powders consisting predominantly of highly aggregated particles have been ground in order to study the dielectric properties as a function of the morphological state. Besides different commercial $BaTiO_3$ powders, Z5U and X7R materials have also been studied.

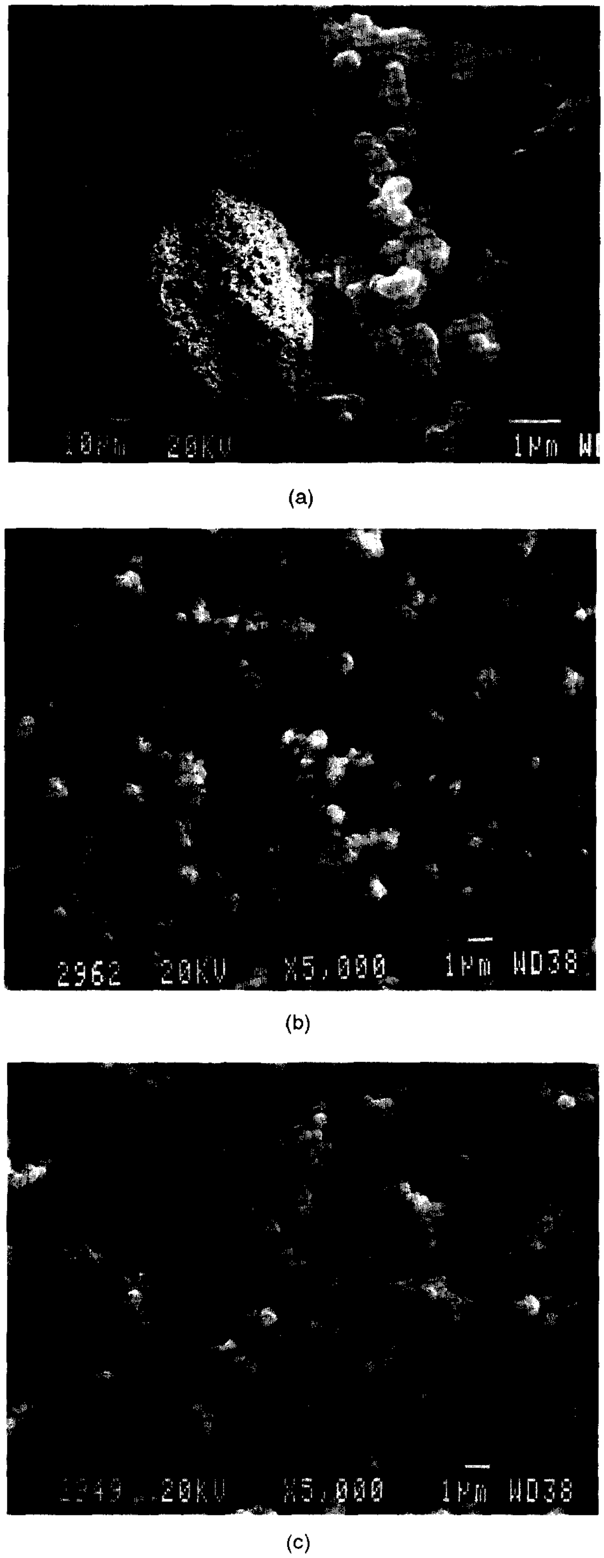
According to $d_s = 6/(\rho S)$ the BET specific surface area S gives an average value for the diameter d_S assuming spherical particles with ρ as the density. Grain size distribution was evaluated by light scattering measurements using the Microtrac apparatus. Particle shape was estimated from SEM studies providing the form parameters anisometry, bulkiness and roundness.[11] Anisometry and bulkiness of particles were calculated from the equivalent ellipse having the same first and second degree moments about its central principal axes. For this purpose the particles were assumed to be planar and of uniform thickness and density. The anisometry was then defined as the ratio of the major axis to the minor axis of the equivalent ellipse and bulkiness as the ratio of the ellipse area to the particle area. The roundness is the square of the ratio of the particle perimeter to the perimeter of a circle having the same area as the particle and is given by (perimeter)^2/(4π area). The three shape parameters are equal to 1 for spheres. The anisometry is high for elongated particles while

Table 1. Composition, preparation and morphological properties of the investigated powders

Compound	*Preparation conditions*	ρ_{th} *g/cm³*	*S (BET) m²/g*	d_S *μm*	*Grain size distribution*			*SEM information*			β
					$d_{10}/\mu m$	$d_{50}/\mu m$	$d_{90}/\mu m$	*Anisom.*	*Bulkin.*	*Roundn.*	
$BaTiO_3$ I coarse	1200°C 10 h	6·040	1·5	0·66	0·45	1·81	12·38	1·35	1·16	52·9	–
ground	Milling 5 h		4·3	0·23	0·29	0·46	0·84	1·67	1·06	1·72	0·385
$BaTiO_3$ II	Commercial Degussa		8·0	0·12	0·23	0·34	0·54	1·47	1·05	1·93	0·45
$BaTiO_3$ III	Commercial Nippon Chem. BT3L		2·3	0·43	0·28	0·41	0·63	1·62	1·05	1·71	0·37
$BaTiO_3$ IV	Commercial Nippon Chem. BL1		1·5	0·66	0·31	0·61	1·69	1·44	1·03	1·43	0·31
$BaTiO_3$ V	Commercial Ferro 6A		2·2	0·45	0·31	0·58	1·49	1·47	1·04	1·51	0·32
$Ba_{1-x}Sr_xTiO_3$ $x = 0{,}295$ coarse	1150°C 10 h	5·783	0·9	1·15	1·46	5·92	42·98	1·40	1·21	28·0	–
ground (a)	Milling 5 h		1·1	0·94	0·56	3·73	17·30	1·44	1·06	2·64	0·48
ground (b)	Milling 27 h		1·2	0·86	0·32	1·74	3·50	1·52	1·04	1·83	0·31
$Ba_{1-x}Sr_xTiO_3$ $x = 0{,}563$ coarse	1150°C 10 h	5·541	0·9	1·20	1·19	4·03	12·59	1·54	1·18	67·6	–
ground (a)	Milling 5 h		1·2	0·90	0·32	2·77	6·87	1·61	1·09	6·67	0·55
ground (b)	Milling 27 h		1·2	0·90	0·32	1·85	3·72	1·60	1·06	1·88	0·39
Z5U ε_{8700} lot 1	Commercial	6·0	3·1	0·32	0·32	0·49	0·82	1·42	1·03	1·68	0·255
Z5U ε_{8700} lot 2	Commercial		2·9	0·34	0·31	0·49	0·82	1·42	1·02	1·37	0·195
X7R ε_{3000} lot 1	Commercial	6·0	5·0	0·20	0·30	0·46	0·76	–	–	–	0·225
X7R ε_{3000} lot 2	Commercial		4·2	0·24	0·31	0·49	0·79	1·33	1·02	1·40	0·205

bulkiness and roundness are high for rugged ones. The roundness is also sensitive to elongation.

SEM photographs indicate that the powders prepared via the mixed oxide route are highly aggregated and rugged. Figure 1(a) shows the coarse grain structure of $BaTiO_3$ I, Fig. 1(b) one of the ground powders consisting predominantly of primary particles and Fig. 1(c) a commercial powder $BaTiO_3$ IV for comparison.



(a)

(b)

(c)

Fig. 1. SEM photographs of coarse [Fig. 1(a)] and ground [Fig. 1(b)] $BaTiO_3$ I powders and of commercial $BaTiO_3$ IV powder [Fig. 1(c)].

3 Dielectric Measurements

The capacitance $C = \varepsilon_0 \varepsilon_r A/L$ of the powders was measured in air at room temperature as a function of frequency using a capacitor arrangement with a guard ring at the displaceable electrode, as described elsewhere.[1] Analysis of the complex dielectric constant $\varepsilon^* = \varepsilon' + i\varepsilon''$ makes it possible to check the frequency independent range of values of the real part $\varepsilon' = \varepsilon_r$. Figures 2(a) and (b) show the data for $BaTiO_3$ and $Ba_{1-x}Sr_xTiO_3$ powders at a given volume fraction v_2. In order to obtain data at several volume fractions in the frequency independent range, different degrees of compression caused by the movable electrode have to be applied. In the case of ferroelectric powders, it is necessary after compression to reduce the pressure to zero, in order to avoid piezoelectric contributions to the measuring signal. The different effect of densification pressure increasing the volume fraction for ferroelectric $Ba_{0.705}Sr_{0.295}TiO_3$ and paraelelectric $Ba_{0.437}Sr_{0.563}TiO_3$ is demonstrated by the data of Fig. 3.

4 The Frequency Independent Real Part of the Permittivity of the Powders

The analysis follows the model which has been proposed in the preceding paper.[1] Starting from the equations of Bruggeman[6] with $\varepsilon'_{\mathrm{sph}}$ for spheres with permittivity ε_2 and volume fraction v_2 randomly embedded in a continuous medium with ε_1 (e.g. air) given by:

$$1 - v_2 = \frac{\varepsilon_2 - \varepsilon'_{\mathrm{sph}}}{\varepsilon_2 - \varepsilon_1} \sqrt[3]{\frac{\varepsilon_1}{\varepsilon'_{\mathrm{sph}}}} \tag{1}$$

and with $\varepsilon'_{\mathrm{lam}}$ for lamella-like particles also randomly distributed in a continuous medium given by:

$$\varepsilon'_{\mathrm{lam}} = \varepsilon_2 \frac{3\varepsilon_2 + 2v_2(\varepsilon_2 - \varepsilon_1)}{3\varepsilon_2 - v_2(\varepsilon_2 - \varepsilon_1)} \tag{2}$$

The form parameter u as defined by Wiener[5] according to

$$\frac{1}{\varepsilon' + u} = \frac{v_1}{\varepsilon_1 + u} + \frac{v_2}{\varepsilon_2 + u}$$
$$\text{and } \frac{\varepsilon'}{\varepsilon' + u} = \frac{v_1 \varepsilon_1}{\varepsilon_1 + u} + \frac{v_2 \varepsilon_2}{\varepsilon_2 + u} \tag{3}$$
with $0 < u < \infty$

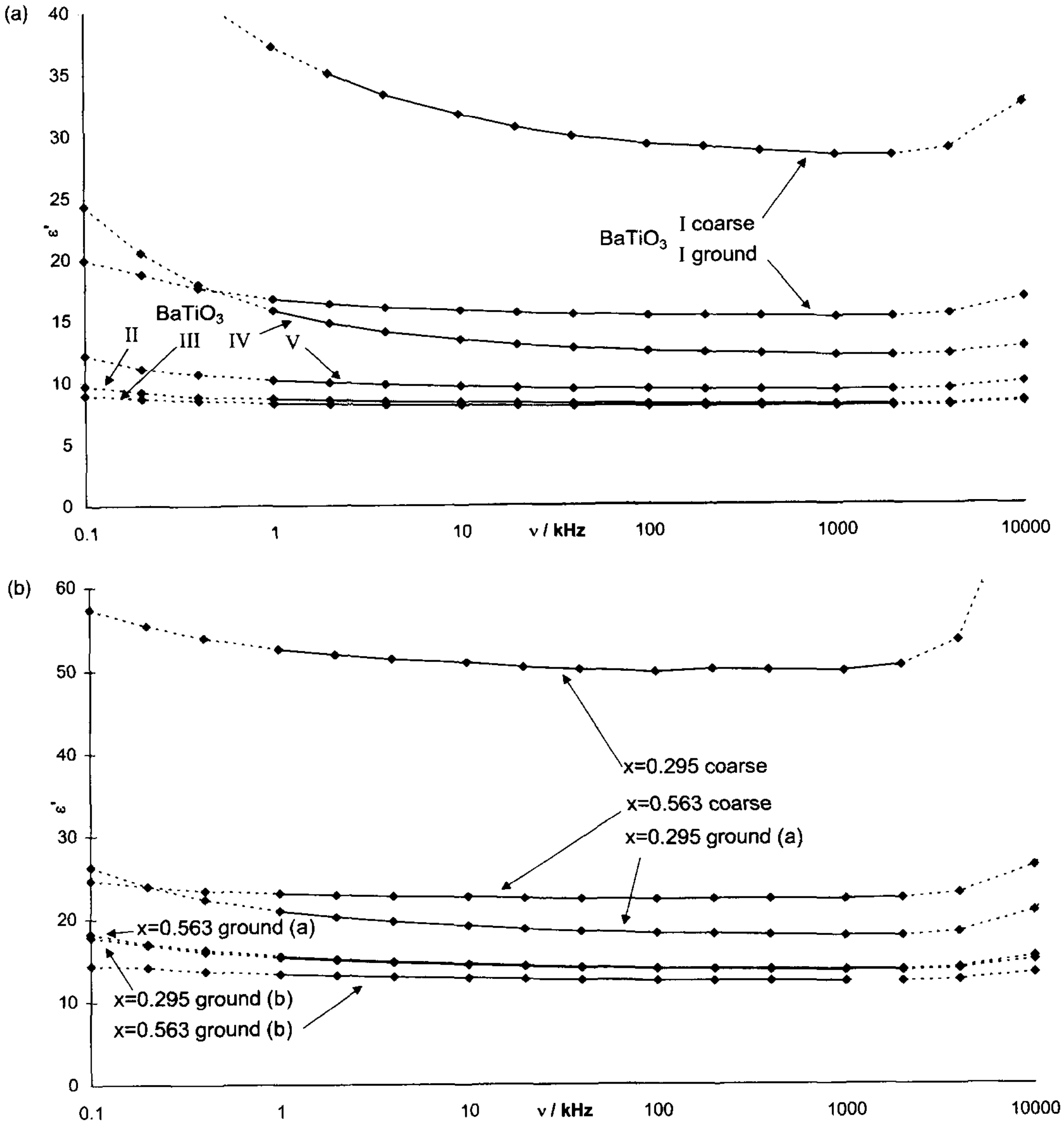


Fig. 2. Measured powder dielectric constant ε' for BaTiO$_3$ [Fig. 2(a)] powders (I) coarse ($v_2 = 0{\cdot}196$), ground ($v_2 = 0{\cdot}421$), and the commercial powders (II) ($v_2 = 0{\cdot}280$), (III) ($v_2 = 0{\cdot}312$), (IV) ($v_2 = 0{\cdot}409$) and (*V*) ($v_2 = 0{\cdot}359$) and for Ba$_{1-x}$Sr$_x$TiO$_3$ [Fig. 2(b)] powders with $x = 0{\cdot}295$ coarse ($v_2 = 0{\cdot}266$), ground (a) ($v_2 = 0{\cdot}356$), ground (b) ($v_2 = 0{\cdot}414$) and $x = 0{\cdot}563$ coarse ($v_2 = 0{\cdot}282$), ground (a) ($v_2 = 0{\cdot}371$) and ground (b) ($v_2 = 0{\cdot}381$).

together with the fundamental relations for parallel and series interconnection in the Effective Medium Theory (EMT)

$$\varepsilon_p = v_1\varepsilon_1 + v_2\varepsilon_2 \tag{4a}$$

and

$$\varepsilon_s = \frac{1}{\frac{v_1}{\varepsilon_1} + \frac{v_2}{\varepsilon_2}} \tag{4b}$$

lead to the equation

$$\varepsilon' = \frac{\varepsilon_s\left(\varepsilon_p u + \varepsilon_1\varepsilon_2\right)}{\varepsilon_1\varepsilon_2 + u\varepsilon_s} \tag{5}$$

The combination of (5) with (1) or (2) expresses $\varepsilon'_{\mathrm{sph}}$ and $\varepsilon'_{\mathrm{lam}}$ as a function of the parameter u_{sph} or u_{lam}, respectively. For modelling a real powder consisting of polyhedral particles of varying shape, geometric averaging of u_{sph} and u_{lam} can be justified; the mixing parameter β for continuous adaption has accordingly been defined,

$$u_{\mathrm{pol}} = 2\sqrt{u_{\mathrm{lam}}^{\beta} u_{\mathrm{sph}}^{2-\beta}} \quad \text{with } 0 \le \beta \le 2 \tag{6}$$

thus leading to

$$\varepsilon'_{\mathrm{pol}} = \frac{\varepsilon_S\left(\varepsilon_p u_{\mathrm{pol}} + \varepsilon_1\varepsilon_2\right)}{\varepsilon_1\varepsilon_2 + u_{\mathrm{pol}}\varepsilon_S} \tag{7}$$

Knowing ε_1 of air to be approximately 1·00, the measuring data $\varepsilon'_{\mathrm{pol}}$ are only determined for pairs of ε_2 and β, i.e. it is necessary to fix ε_2 in order to

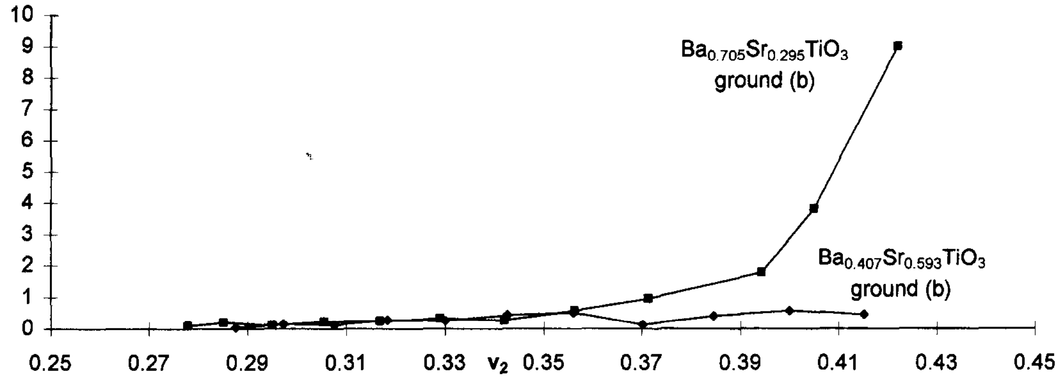


Fig. 3. Effect of densification pressure on the relative enhancement of the dielectric constant ε' of Ba,$SrTiO_3$ powders.

determine the form factor β or inversely. However, theoretical reasons suggest limits for the validity of EMT.[15] Particles of inhomogeneous dielectrics must have sizes, which lie between certain limits if the EMT's are to be applicable.

4.1 Dielectric constant of $BaTiO_3$ in the powder state and the form factor β

At 2 MHz the dielectric constant of ferroelectric $BaTiO_3$ results from electronic polarization and phonon lattice dynamics (ionic polarization) and domain wall motion. In bulk $BaTiO_3$ ceramics, the grain size has a strong effect on the permittivity at room temperature for grain sizes below about 10 μm.[12–16] The permittivity rises as the grain size decreases down to about 0·7 μm, which has been explained by the increasing contributions of domain wall motion. The domain thickness becomes diminished and subsequently the domain wall density is growing per unit of volume.[12] Below the maximum shown in Fig. 4, the permittivity sharply drops and at the same time the tetragonality and remanent polarization are reduced.[12–14,17] Below about 0·8 μm single domain particles prevail.[12] Obviously, the missing contributions from domain wall motion act as one of the reasons for the decrease in the permittivity in this lower range of the grain size. Other arguments are based on thermodynamics,[13] space charge layers,[18] and the transition to a superparaelectric state.[14]

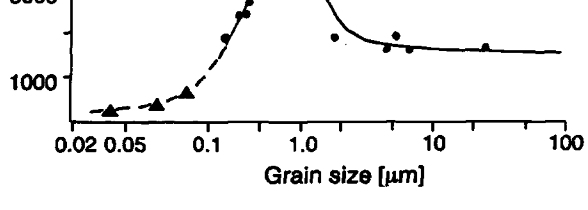


Fig. 4. Grain size dependence of the relative dielectric permittivity of $BaTiO_3$ ceramics according to Waser.[14]

The $BaTiO_3$ powders of Table 1 have grain sizes between 0.3 and 0.6 μm; therefore domain wall contributions are suggested to be negligible. Assuming that in this range of small grain sizes the permittivity of the powder is predominantly determined by electronic and ionic polarization as in the bulk ceramic state, the values of the dielectric constant have been taken for this band of grain sizes from the falling branch of the curve of Fig. 4 in order to calculate the form factor β.

Figure 5 shows data for ε' as a function of the volume fraction v_2 for the ground powder $BaTiO_3$I together with the fitting curves obtained by varying the permittivity ε_2 in relation with the form factor β. Extrapolation to $v_2 = 1$ provides $\varepsilon' = \varepsilon_2$. When ε_2 is increased in the range of 2000–4000 according to the grain size 0.3–0.6 μm, β is found to have values between 0·38 and 0·41. Of course, β is more sensitive to shape than to size. Furthermore, it is clearly indicated that at high particle dielectric constants, β is relatively less dependent on ε_2. This means that the grain size dependence of the dielectric constant has only a secondary effect on the derived form factor β.

Figure 6 shows the experimental data for the powder permittivity ε' as a function of v_2 for the five different $BaTiO_3$ samples together with the curves which result from model calculation using the grain size dependent ε_2 values according to the correlation of Fig. 4. The d_{50} values of Table 1 have been applied for estimating ε_2. In accordance with electronmicroscopic investigations, there is only a small variation in the shape of the commercially available $BaTiO_3$ samples and therefore the form factors β agree within small limits. The ground state of the $BaTiO_3$ I closely relates to the other highly dispersed powders which are commercially available. On the other hand, presumably because of the high degree of roundness (Table 1), the coarse state of powder I consisting of relatively large rugged particles [Fig. 1(a)] formed as a result

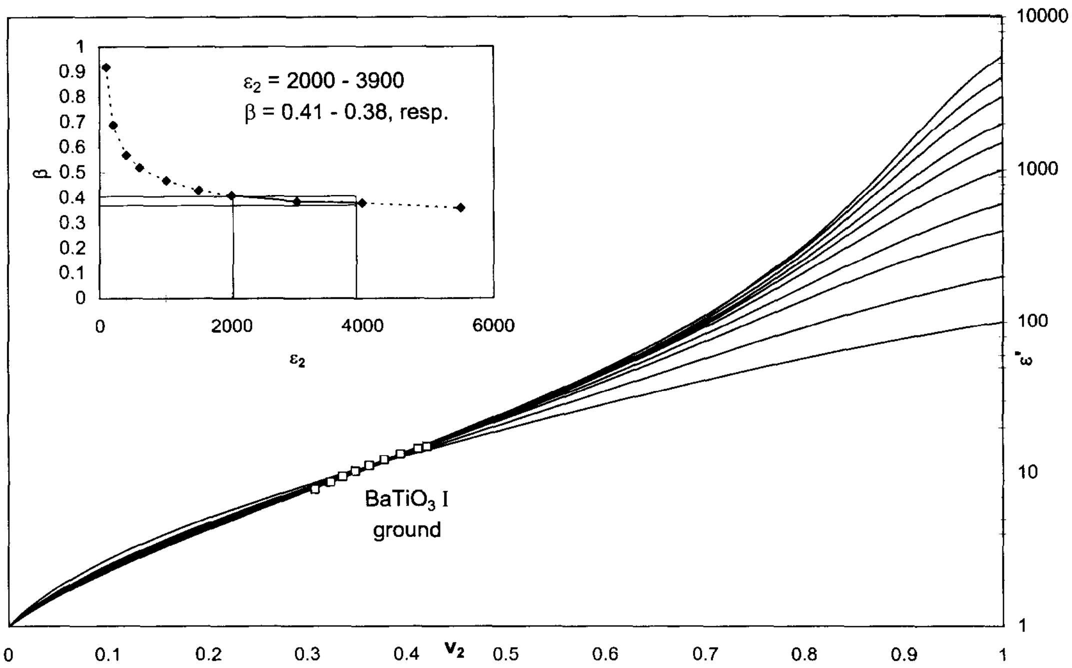


Fig. 5. Powder dielectric constant ε' of $BaTiO_3$ (I) measured at 2 MHz and 1 V/cm in dependence on the volume fraction v_2. The dependence of β upon variation of ε_2 is shown in the insert.

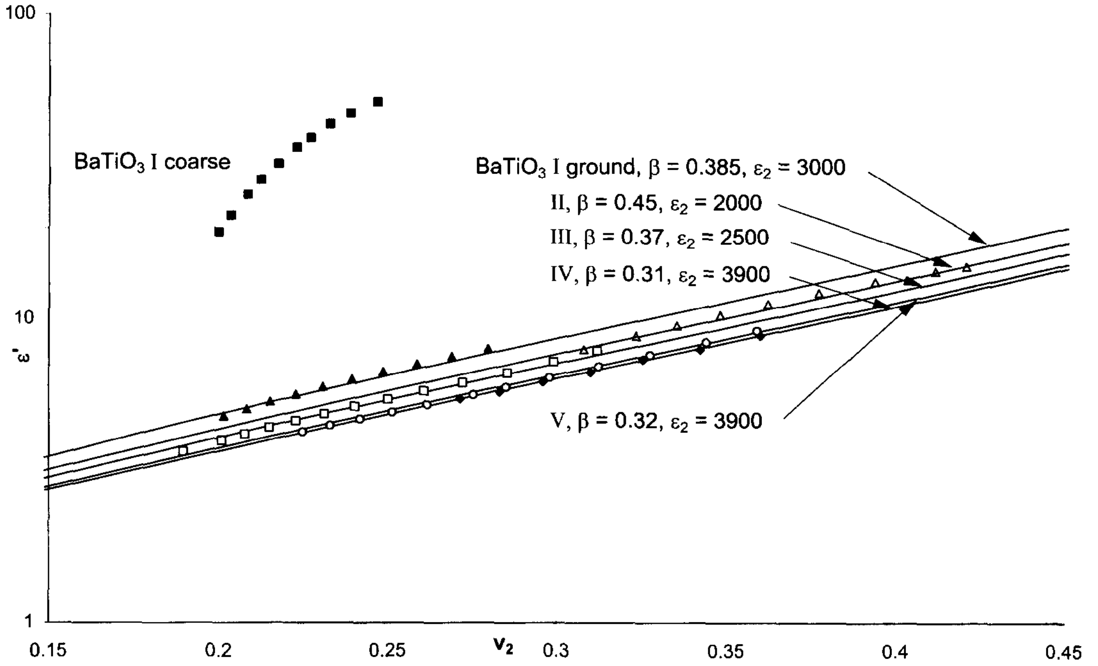


Fig. 6. Permittivity ε' in dependence on the volume fraction v_2 for $BaTiO_3$ I (coarse, ■) and (ground, △), II (▲), III (□), IV (◆) and V (○) powders according to Table 1. Solid lines are calculated ε'_{pol} according to (7).

of mixed oxide preparation could not be included in the modelling. Indeed, the particles are extraordinary large and therefore out of the limits of validity of the theoretical prerequisites.

4.2 Dielectric constant of $Ba_{1-x}Sr_xTiO_3$ powders with $x = 0{\cdot}295$ and $0{\cdot}563$

The formation of single phase solid solutions for $Ba_{1-x}Sr_xTiO_3$ is quite well documented[19] resulting in a shift of the ferroelectric Curie temperature T_C to lower temperatures.[20] Figure 7 shows the temperature dependence of ε_2 for the two ceramic samples $Ba_{0{\cdot}705}Sr_{0{\cdot}295}TiO_3$ and $Ba_{0{\cdot}437}Sr_{0{\cdot}563}TiO_3$. Curie Weiss Law analysis provides the values $T_C = 36°C$ ($\theta = 37°C$) and $T_C < -55°C$ ($\theta = -48°C$), respectively. They are in satisfactory accordance with data from the literature.[20] However, the grain size dependence of ε_2 in the ferroelectric state of this solid solution series seems to be unknown up to now.

Neglecting this aspect and relying on the conclusions deduced for $BaTiO_3$ powders, the room

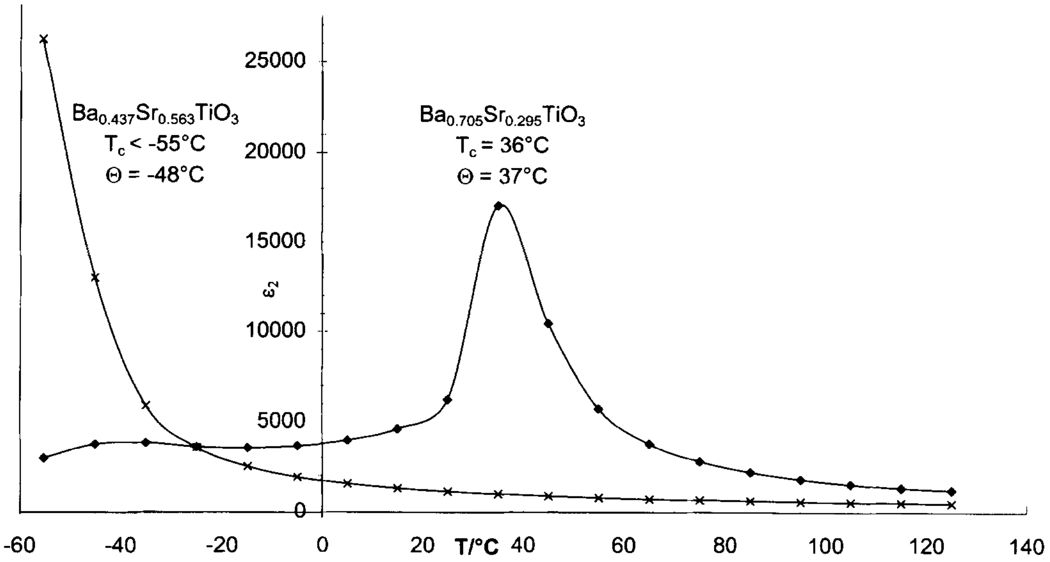


Fig. 7. Temperature dependence of the dielectric constant of $Ba_{0.705}Sr_{0.295}TiO_3$ and $Ba_{0.437}Sr_{0.563}TiO_3$ ceramics.

temperature dielectric constant $\varepsilon_2 = 5560$ of the ferroelectric ceramic sample $Ba_{0.705}Sr_{0.295}TiO_3$ was applied as a trial value for calculating the form factor β of the powder. As an example, for the ground state (b) mentioned in Table 1, $\beta = 0{\cdot}31$ is found. Such a proceeding appears justified, because if ε_2 were to change in the range 5560 ± 3000, β would only vary between 0·29 and 0·34.

The results shown in Fig. 8 clearly indicate the effect of grinding. Again the coarse powder from the mixed oxide preparation route cannot be interpreted. On the other hand, continuous grinding leading to the powder states (a) with $d_{50} = 3{\cdot}7$ and (b) with $d_{50} = 1{\cdot}7\,\mu m$ is characterized by decreasing β values 0·48 and 0·31, respectively. Of course, as a result of grinding, the spherical contribution to the polyhedral powder state is expected to increase. Similar results were obtained for the $Ba_{0.437}Sr_{0.563}TiO_3$ powders. Because of the paraelectric state of $Ba_{0.437}Sr_{0.563}TiO_3$, the interpretation is less questionable. Taking $\varepsilon_2 = 1170$ from the diagram of Fig. 7, the β values 0·55 and 0·39 were found corresponding to $2{\cdot}8\,\mu m$ and $1.9\,\mu m$ for the two ground powders (a) and (b).

It has to be noticed, in spite of the essential difference in the permittivity of ferroelectric $Ba_{0.705}Sr_{0.295}TiO_3$ and paraelectric $Ba_{0.437}Sr_{0.563}$ TiO_3 that the ground powder states (b) showing

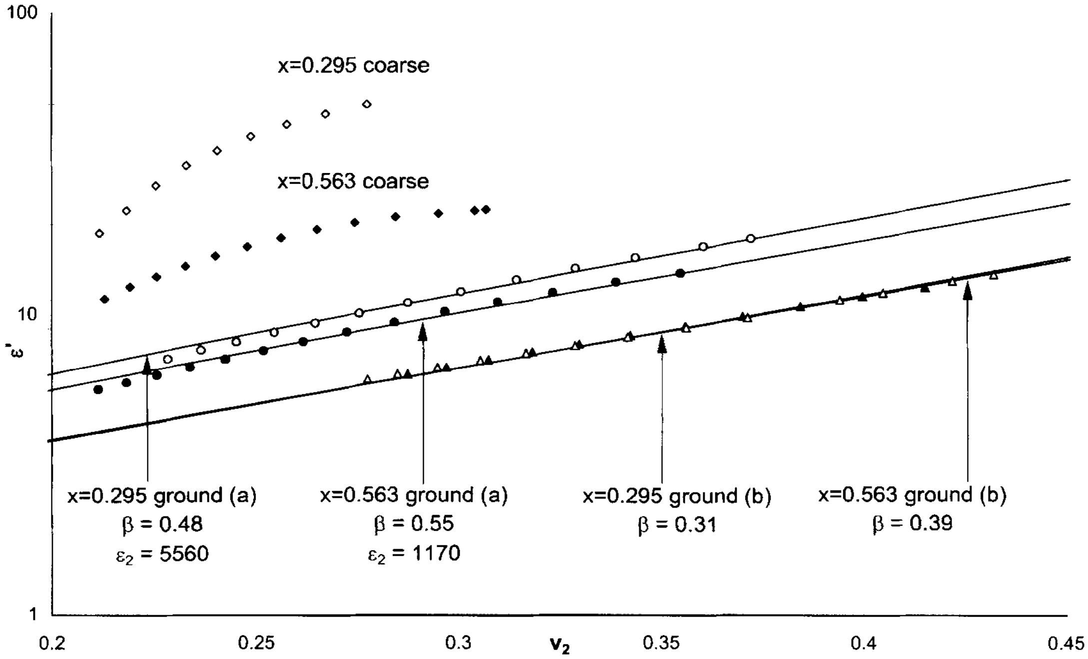


Fig. 8. Permittivity ε' in dependence on the volume fraction v_2 for powders $Ba_{1-x}Sr_xTiO_3$ in the coarse state and after grinding according to Table 1 with $x = 0{\cdot}295$ (coarse, ◇), (a, ○) and (b, △) and $x = 0{\cdot}563$ (coarse, ◆), (a, ●) and (b, ▲). Solid lines are calculated ε'_{pol} according to (7).

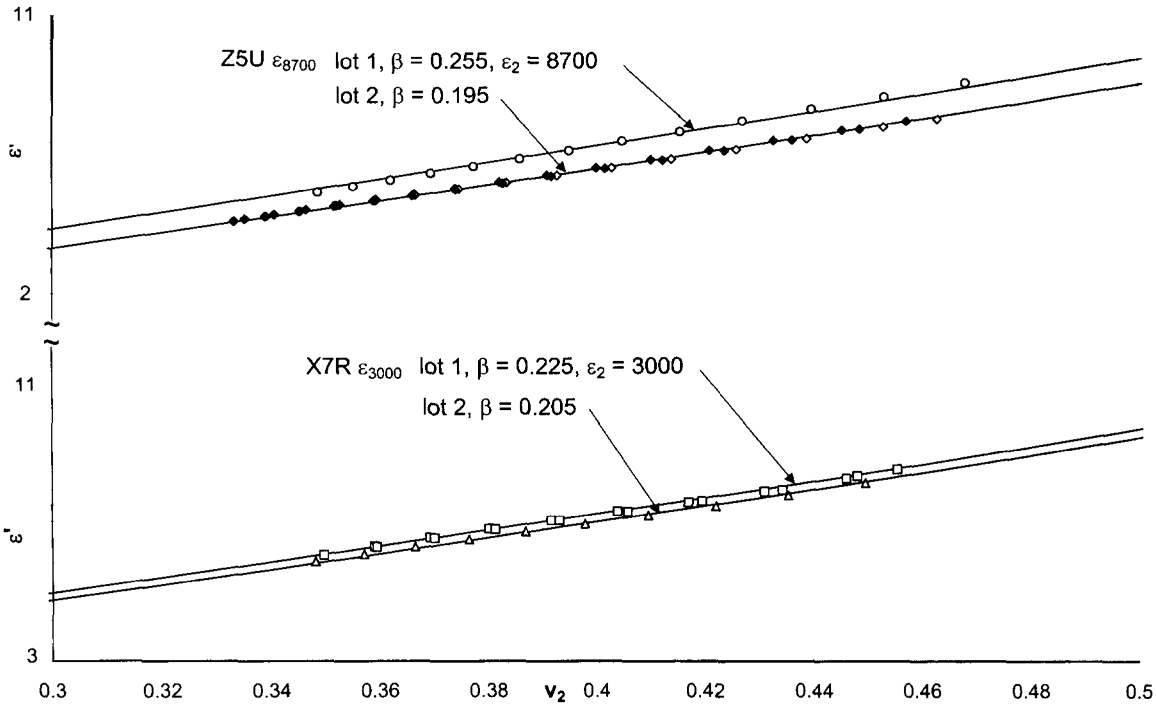


Fig. 9. Permittivity ε' in dependence on the volume fraction v_2 for different lots of Z5U (○,◇,◆) and X7R (□,△) capacitor mass powders according to Table 1. Solid lines are calculated $\varepsilon'_{\text{pol}}$ according to (7).

comparable average grain sizes (Table 1) tend to provide less different values β = 0·31 or 0·39, respectively.

4.3 Ferroelectric capacitor raw materials

Figure 9 shows the experimental results for two lots of commercial Z5U and X7R powder materials leading in the ceramic state at room temperature to the permittivity of $\varepsilon_2 = 8700$ and $\varepsilon_2 = 3000$, respectively. Fitting of the experimental data of ε' is possible with these values, although because of the complex composition of the raw materials the application of the ceramic permittivity to powder particles is to be seen as questionable. On the other hand, the resolution to detect small differences between lots is found to be relatively high. Therefore β is more an empirical factor suitable for controlling the constancy of the morphological state of charges. The two lots of the X7R raw material indicate the reproducibility that has been achieved. The measurement of the Z5U powder lot 2 has been carried out three times in order to check the reproducibility. The difference between lot 1 and lot 2 results in part from the type of the vitreous sintering aid in the powder. It is interesting to note that this small difference may be detected by the difference of the β value of 0·195 (lot 2) or 0·255 (lot 1), respectively.

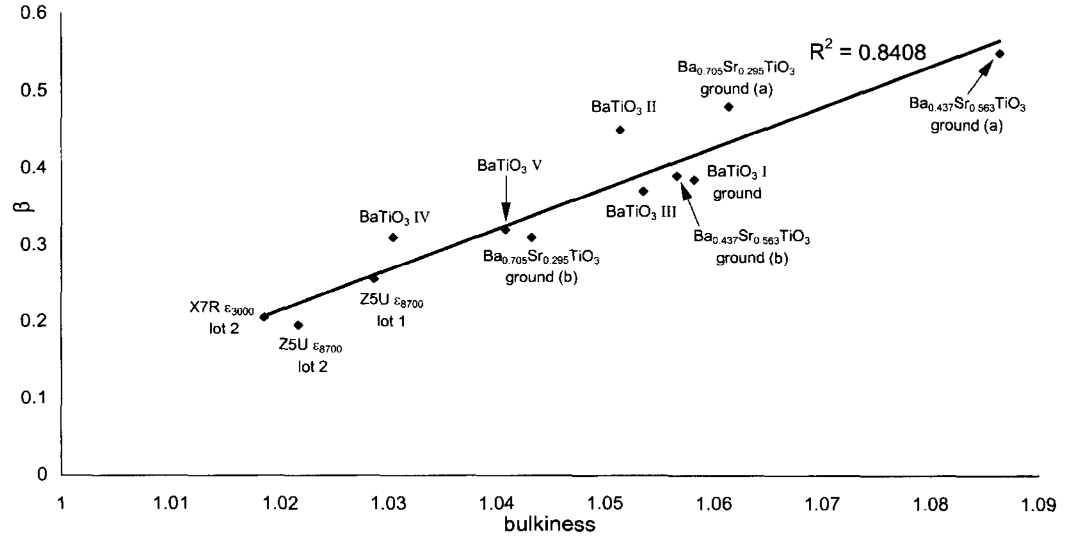


Fig. 10. Correlation of the form factor β to the particle bulkiness. Pearson's correlation coefficient R is given.

5 Comparision of the Form Factor β with Anisometry, Bulkiness and Roundness

The morphological significance of the form factor β is demonstrated in Fig. 10 showing the dependence of β on the bulkiness of the investigated powders. In accordance with previous studies on dielectric powders,[1] a good correlation between the bulkiness of the grains and the observed β value is found also for ferroelectric particles. However, a high bulkiness of the grains, together with the high roundness listed in Table 1 seems to lead to a dielectric behaviour of the powders that cannot be interpreted in the frame of dielectric models based on the assumptions of the EMT's. Therefore the form factors β for the coarse $BaTiO_3$ I and the coarse $Ba_{0\cdot437}Sr_{0\cdot563}TiO_3$ and $Ba_{0\cdot705}Sr_{0\cdot295}TiO_3$ powders have not been used for calculation of linear regression. Moreover, β shows a weak increasing correlation with anisometry which may be due to a dominating influence of bulkiness. Consequently for ferroelectric particles with a low bulkiness the β value seems to be a very sensitive measure of particle shape.

6 Summary and Conclusions

Ferroelectric powders can be described in terms of a particle shape dependent form factor β deduced from dielectric measurements using models of the EMT which have been developed for inhomogeneous dielectrics. The permittivity of the solid particles ε_2 and of the continuous medium ε_1 have to be known, while the volume fraction v_2 and the dielectric constant ε' of the mixture are measured. At high values of the permittivity of the ferroelectric particles, the form factor β is found to be independent of ε_2. On the other hand, β becomes the more sensitive to shape as the permittivity rises. Below about $0\cdot7\,\mu m$, i.e. in the range of single domain grains, the dielectric constants ε_2 of the ferroelectric ceramics and their dependence on temperature and grain size are assumed to be also valid for powders. A comparision of the form factor β with the shape parameters (anisometry, bulkiness and roundness) shows a dominating influence of bulkiness. β increases with increasing anisometry, bulkiness and roundness. However, the method seems to be unsuitable for powders, whose grains sizes lie outside the theoretical validity of EMT's. The possibility of using these methods to monitor the morphologies of X7R and Z5U powders is elucidated. They show low roundness and good approximation to spheres embedded in air. Relatively small differences in the morphological state of ferroelectric capacitor raw materials have been successfully detected.

References

1. Ragossnig, H. and Feltz, A., Characterization of dielectric powders by a new defined form factor. *Journal of Europ. Ceram. Soc.*, 1998, **58**, to be published.
2. Lorentz, H. A., Ueber die Beziehung zwischen der Fortpflanzungsgeschwindigkeit des Lichtes und der Körperdichte. *Wied. Ann.*, 1880, **9**, 641–665.
3. Lorenz, L., Ueber die Refractionsconstante. *Wied. Ann.*, 1880, **11**, 70–103.
4. Rayleigh, J. W., On the influence of obstacles arranged in rectangular order upon the properties of a medium. *Phil. Mag.*, 1892, **34**, 481–502.
5. Wiener, O. *Abh. Sächs. Ges. Wiss. Math. Phys. Kl.*, 1912, **32**, 509, refereed after Bruggeman.
6. Bruggeman, D. A. G., Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen I. *Ann. Phys. Lpz.*, 1935, **24**, 636–664.
7. Bruggeman, D. A. G., Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen I. *Ann. Phys. Lpz.*, 1935, **24**, 665–679.
8. Bragg, W. L. and Pippard, A. B., The form birefringence of macromolecules. *Acta Crystallogr.*, 1953, **6**, 865–867.
9. Bernasconi, J., Brüesch, P., Kuse, D. and Zeller, H. R., Ultraviolet to far infrared optical properties of the onedimensional conductor $K_2Pt(CN)_4Br_{0,3}$. *Journal of Phys. Chem. Solids*, 1974, **35**, 145–157.
10. Stümpler, R., Rhyner, J. and Greuter, F., Nonlinear dielectric composites. In *Proceedings of SPIE—Int. Soc. Opt. Eng. (USA) Smart structures and materials*, 1995, **2441**, 256–266.
11. Medalia, A. I., Dynamic shape factors of particles. *Powder Tech.*, 1970, **4**, 117–138.
12. Hennings, D., Arlt, G. and deWith, G., Dielectric properties of fine grained barium titanate ceramics. *Journal of Appl. Phys.*, 1985, **58**(4), 1619–1625.
13. Niepce, J. C., Permittivity of fine grained $BaTiO_3$. In *Proc. Electroceramics IV Conf.*, 1994, **1**, 29–39.
14. Waser, R., Dielectric analysis of integrated ceramic thin film capacitors. *Integrated Ferroelectrics*, 1997, **15**, 39–51.
15. Niklasson, G. A. and Granqvist, C. G., Optical properties and solar selectivity of coevaporated Co-Al_2O_3 composite films. *Journal of Appl. Phys.*, 1984, **55**(9), 3382–3410.
16. Bernaben, N., Leriche, A., Thierry, B., Niepce, J. C. and Waser, R., Pure barium titanate ceramics: crystalline structure and dielectric properties as a function of grain size. In *Proc. Electroceramics IV Conf.*, 1994, **1**, 105–109.
17. Uchino, K., Sadanaga, E. and Hirose, T., Dependence of the crystal structure on particle size in barium titanate. *Journal of Amer. Ceram. Soc.*, 1989, **72**, 1555–1558.
18. Shih, W. Y., Shih, W. H. and Aksay, I. A., Size dependence of the ferroelectric transition of small $BaTiO_3$ particles: effect of depolarization. *Phys. Rev. B*, 1994, **50**(21), 575–585.
19. Levin, E. M., Robbins, C. R. and McMurdie, H. F., *Phase Diagrams for Ceramists.* American Ceramic Society, Columbus, Ohio, 1964, Vol. 1, p. 195.
20. Hilton, A. D. and Ricketts, B. W., Dielectric properties of $Ba_{1-x}Sr_xTiO_3$ ceramics. *Journal of Phys. D: Appl. Phys.*, 1996, **29**, 1321–1325.